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TESIS DOCTORAL

**Nanocatalizadores para procesos medioambientales:
obtención de energía y eliminación de contaminantes**

Doctorado en Química y Tecnologías Químicas, Materiales y Nanotecnología.

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UNIVERSIDAD DE MÁLAGA

Facultad de Ciencias

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Mineralogía**

*“Nanocatalizadores para procesos medioambientales:
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Isabel Barroso Martín

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**NANOCATALIZADORES PARA PROCESOS
MEDIOAMBIENTALES: OBTENCIÓN DE ENERGÍA Y
ELIMINACIÓN DE CONTAMINANTES**

MEMORIA presentada por la Ingeniera Química y Máster en Química
D^a Isabel Barroso Martín para aspirar al grado de Doctora en Ciencias,
sección de Químicas, con la mención de “**Doctorado Internacional**”

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de subidas y bajadas
en las que todo cambia, todo pasa,
y nada permanece,
incluso tú.
Recuérdalo cuando estés arriba.*

Recuérdalo cuando estés abajo.”

Laura Chica

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RESUMEN

Resumen

En la presente tesis doctoral se han abordado dos temáticas de gran interés para la sociedad: la obtención de energía a través de procesos medioambientalmente sostenibles y la eliminación de contaminantes.

El uso de fuentes de energías no renovables para la obtención de energía ha sido uno de los pilares fundamentales en el desarrollo de países que hoy día se postulan como potencias mundiales con un sector industrial consolidado y un fuerte desarrollo socioeconómico gracias a las actividades derivadas de su industria. El consumo masivo e incontrolado que se ha realizado de estos recursos no renovables durante décadas, junto con el crecimiento exponencial de la población y la consecuente creciente demanda energética, han derivado en dos graves consecuencias que ponen en jaque el desarrollo económico de la sociedad tal y como se conoce hoy día: por un lado, el agotamiento a corto plazo de estos recursos; por otro, las graves consecuencias medioambientales derivadas de su uso. Con una contribución de más del 80 % al consumo mundial de energía primaria, la quema de combustibles fósiles (carbón, el petróleo y gas natural) es la principal responsable de las emisiones de gases de efecto invernadero (GEI), principalmente de CO₂.

Con objeto de mitigar las consecuencias del uso de los combustibles fósiles, la Agencia Internacional de la Energía ha desplegado un modelo retrospectivo y dinámico llamado Escenario de Desarrollo Sostenible (EDS), en el que se han desarrollado distintas estrategias para lograr el cumplimiento de los objetivos de la Agenda 2030 de las Naciones Unidas garantizando el bienestar social y el mantenimiento del desarrollo económico actual. Atendiendo a este modelo, se hace patente la necesidad de desarrollar procesos más limpios y menos contaminantes para la obtención de energía que hagan uso de las infraestructuras ya existentes para el procesamiento de combustibles fósiles.

La comunidad científica ha dedicado numerosos esfuerzos a la búsqueda de alternativas eficientes y medioambientalmente sostenibles con emisiones mínimas de gases de efecto invernadero que sean competitivas con los procesos convencionales de obtención de energía y recursos para los principales sectores de consumo a nivel mundial.

Teniendo en cuenta que casi el 25 % de este consumo se dedica al sector del transporte, el desarrollo de la obtención de combustibles a partir de procesos inocuos para el medioambiente que puedan utilizarse en vehículos convencionales ha ganado gran interés en las últimas décadas. De entre todas las fuentes de energía renovables, la biomasa se postula como una alternativa bastante prometedora, ya que es una materia prima abundante y bien distribuida y no depende de fenómenos ambientales como lo hace la energía solar o la eólica. Además, su utilización trae intrínsecas otras ventajas como la reforestación de tierras baldías y consecuente aumento de la biodiversidad de zonas vulnerables, el aumento del empleo en zonas rurales gracias al tratamiento de la biomasa o el gran aporte a la economía circular que supone la revalorización de un recurso considerado la única fuente de carbono renovable.

Según la Directiva 2009/28/CE del Parlamento Europeo y del Consejo, de 23 de abril de 2009, relativa al fomento del uso de energía procedente de fuentes renovables y por la que se modifican y se derogan las Directivas 2001/77/CE y 2003/30/CE, se considera biomasa la fracción biodegradable de productos y residuos provenientes de actividades como la agricultura, la silvicultura y sus industrias relacionadas, así como la fracción biodegradable de los residuos industriales y municipales. De entre todas las fuentes de biomasa, la biomasa lignocelulósica es la más abundante y accesible. Su compleja estructura espacial está formada por tres unidades principales: celulosa, hemicelulosa y lignina, con una gran diversidad de grupos funcionales con un alto potencial para ser transformados en productos de alto valor añadido.

Existen multitud de procesos de conversión de biomasa que dan lugar a un amplio abanico de productos. Por ejemplo, la hidrólisis de la fracción celulósica de la biomasa permite la obtención de bioetanol, mientras que la de lignina ofrece una gran variedad de moléculas plataforma que se pueden utilizar en la industria de la química fina. Mediante gasificación se puede obtener gas de síntesis que puede ser empleado en procesos de gran interés industrial como la síntesis de dimetil éter o para la obtención de hidrocarburos mediante Fischer-Tropsch. Por último, cabe destacar la conversión de la biomasa mediante pirólisis que, en función de las condiciones en las que se realice, dará lugar a una amplia distribución de productos.

En función a la fuente de biomasa empleada, los biocombustibles pueden clasificarse en cuatro generaciones:

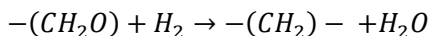
La primera generación comprende biocombustibles obtenidos a partir de cultivos comestibles como la soja o la palma. El bioetanol obtenido por fermentación de los azúcares presentes en estos cultivos y el biodiesel obtenido por transesterificación de estos aceites vegetales entran dentro de esta clasificación. El principal inconveniente del consumo de estos biocombustibles es que interfieren en la cadena alimentaria, ocupan grandes extensiones de terreno y consumen una gran cantidad de agua, lo que hace cuestionarse su sostenibilidad.

Los biocombustibles de **segunda generación** son aquellos obtenidos a partir de residuos agrícolas, forestales e industriales y cultivos energéticos no comestibles abundantes y económicos cuyo tratamiento permite la obtención de bioetanol, biodiesel o biogás. Aunque aún hay importantes barreras tecnológicas al correcto desarrollo a escala industrial de los procesos asociados a la transformación de biomasa lignocelulósica, hoy día más del 90 % de la producción comercial de biocombustibles es de segunda generación.

En la **tercera y cuarta generación** de biocombustibles se consideran cultivos altamente energéticos como microalgas y bacterias y cultivos modificados genéticamente, respectivamente. Aunque estas generaciones son muy prometedoras, su desarrollo se ve aún impedido por el alto coste asociado a la implementación a gran escala de los procesos asociados al tratamiento de esta biomasa.

Teniendo en cuenta la viabilidad asociada a los biocombustibles de segunda generación, uno de los procesos más consolidados para el tratamiento de esta biomasa es la pirólisis rápida. Este proceso termoquímico da lugar a una fracción sólida conocida como alquitrán y una fracción gaseosa que, a su vez, puede dar lugar a productos no condensables conocida como “fuel gas” y una fracción condensable llamada “bio-oil” o bio-aceite, de la que se pueden obtener biocombustibles y productos de alto valor añadido. Este bio-oil presenta interesantes propiedades para ser utilizado en motores de combustión interna en vehículos convencionales, sin embargo, el alto contenido en agua y compuestos orgánicos oxigenados le confiere una acidez elevada, corrosividad, inestabilidad y bajo poder calorífico que impiden su uso directo como biocombustible en motores de combustión interna. Por lo tanto, se hace necesaria la mejora de este bio-oil a través de la disminución de su contenido en oxígeno. En este contexto, la reacción de hidrodesoxigenación (HDO) se postula como la alternativa más eficiente para obtener un bio-oil de calidad que sea competitivo con los combustibles líquidos tradicionales.

La reacción de HDO se da a temperaturas moderadas (120-400 °C) y presiones altas (10-50 bar) en presencia de un catalizador:



Aunque idealmente la reacción se da sin pérdida de átomos de carbono y con agua como único subproducto, en la práctica multitud de reacciones secundarias pueden tener lugar debido a la compleja composición del bio-oil derivado de biomasa lignocelulósica. Por ello, el estudio de esta

reacción se realiza principalmente haciendo uso de moléculas modelo representativas del bio-oil, con objeto de entender los procesos implicados en todo el transcurso de la reacción: limitaciones difusionales, mecanismos de reacción, etc. La elección de la molécula modelo a estudiar debe considerar una baja reactividad, así como una estructura molecular sencilla que permita el estudio del mecanismo de reacción de la misma. Por ello, en la presente tesis se ha estudiado la reacción de HDO de anisol debido a su pequeño tamaño, baja reactividad y presencia de un único grupo funcional.

Con respecto a los catalizadores empleados en HDO, hoy día hay una extensa bibliografía que considera una amplia variedad de fases activas, todas con un nexo común: la bifuncionalidad del catalizador, de manera que tanto la activación de la molécula de hidrógeno por los sitios activos del metal como la activación del oxígeno en los grupos ácidos se vean favorecidas.

Los primeros catalizadores empleados en esta reacción fueron los sulfuros de metales de transición que se usaban ya en reacciones de hidrotratamiento de biocombustibles derivados del petróleo. Sin embargo, la necesidad de reactivación de la fase activa mediante adición de H_2S y la subsecuente formación de SO_2 ha promovido la búsqueda de otras fases activas. Otras diversas fases se han estudiado en la reacción de HDO, como los fosfuros, carburos y nitruros de metales de transición, debido a su alta estabilidad y resistencia a la oxidación. De entre todos los metales de transición, cabe destacar el papel del níquel en la reacción de HDO, ya que es un metal no noble, abundante, con alta capacidad hidrogenante, baja acidez y alta resistencia a la formación de coque. Es por ello que, en esta tesis doctoral, se han estudiado distintas fases activas conteniendo níquel en la reacción de hidrodesoxigenación de anisol llevada a cabo en un reactor de alta presión de lecho fijo.

Por otro lado, debido a su gran capacidad hidrogenante, los metales nobles han resultado excelentes fases activas en la reacción de HDO

promoviendo la saturación de enlaces C=C y C=O. Además, la adición de un segundo metal no noble confiere a estos catalizadores la bifuncionalidad necesaria para HDO. Así, metales de transición como el molibdeno, el cobalto, el hierro, o los óxidos reducibles como los de cerio o niobio, han demostrado gran capacidad para activar los grupos oxy de los compuestos oxigenados, facilitando así la ruptura del enlace C-O. Debido a su abundancia y bajo coste, en esta tesis se ha evaluado la actividad catalítica de catalizadores de platino y hierro en la reacción de HDO de anisol.

En los capítulos 4 y 5 de la presente tesis doctoral, se recoge el estudio catalítico de catalizadores basados en níquel en la reacción de HDO de anisol. La actividad catalítica de los catalizadores ha sido justificada mediante una extensa caracterización de sus propiedades texturales, cristalinas, morfológicas, ácidas y superficiales mediante isothermas de adsorción-desorción de nitrógeno a -196 °C, difracción de rayos-X (XRD), microscopía electrónica de transmisión de alta resolución (HR-TEM), desorción termoprogramada de amoníaco (NH₃-TPD) y espectroscopía fotoelectrónica de rayos-X (XPS), respectivamente. Las principales conclusiones obtenidas de estos capítulos son las siguientes:

- El capítulo 4 aborda el estudio de catalizadores basados en niobio soportado sobre SBA-15 en los que se ha incorporado un segundo metal, níquel, cobalto o hierro, en la reacción de HDO de anisol a 15 bar y 275 °C. La actividad catalítica siguió la tendencia NiNb > CoNb > FeNb, obteniéndose ciclohexano como principal producto desoxigenado. Los difractogramas de XRD mostraron que la estructura de la SBA-15 se mantuvo tras la incorporación de ambos metales, aunque se observó un mayor desorden de la estructura con la adición de Co y Fe, debido al mayor radio iónico de estos metales. La caracterización superficial y morfológica mostró una alta dispersión de las fases activas en la superficie micro- y mesoporosa del soporte,

especialmente en el catalizador con níquel como mostraron los resultados de quimisorción de hidrógeno, evidenciándose así una mayor interacción Ni-Nb. Con respecto a la caracterización superficial, mediante XPS se confirmó la coexistencia de los óxidos de niobio (IV) y (V), responsables de la acidez de los catalizadores. De hecho, la NH_3 -TPD mostró que los catalizadores con una acidez moderada de naturaleza débil eran aquellos con una mayor proporción de NbO_2 , especialmente notable en el catalizador de NiNb, en el que las especies de niobio se encontraban más superficialmente expuestas y, por lo tanto, interaccionando con las pequeñas partículas de níquel en superficie.

- El capítulo 5 se centra en el estudio de la reacción de HDO de anisol a 15 bar y 275 °C utilizando como catalizadores óxidos mixtos de níquel, aluminio y cerio obtenidos a partir de hidróxidos dobles laminares (LDHs) sintetizados con distintas cargas de Ce y a partir de precursores de Ce^{3+} y/o Ce^{4+} . La caracterización de los precursores LDHs mediante XRD, análisis termogravimétrico (TGA) y microscopía de barrido (SEM) mostraron que la estructura de los LDHs se distorsiona a altas cargas de cerio, lo que sugiere que existe una cantidad limitante de cerio que puede añadirse a la formulación de la hidrotalcita sin perder la estructura de la misma y evitando la formación de fases segregadas. Además, dicha cantidad depende del precursor de cerio utilizado, debido al mayor radio iónico del Ce^{3+} en comparación con el Ce^{4+} . La caracterización mediante XRD de los óxidos mixtos y sus fases reducidas reveló la presencia de NiO, CeO_2 y de la fase espinela NiAl_2O_4 en los óxidos, mientras que en las reducidas se observó también la presencia de Ni metálico, quedando el resto de los metales en su estado oxidado debido a la moderada temperatura de reducción, insuficiente

para reducir el cerio o el aluminio. Los óxidos derivados de LDHs mostraron una superficie de naturaleza meso- y macroporosa, con superficies específicas entre 265 y $115 \text{ m}^2 \cdot \text{g}^{-1}$, con valores decrecientes al aumentar el contenido en cerio debido al bloqueo de los poros por la especie no porosa CeO_2 . La caracterización superficial mostró una alta exposición superficial del níquel. Además, en las muestras más activas, que fueron aquellas conteniendo Ce^{4+} , presentaron una mayor presencia de grupos hidroxilo en superficie. La mayor actividad catalítica y selectividad hacia productos desoxigenados (ciclohexano y benceno) en estas muestras se asoció a la mayor estabilidad térmica del precursor LDH, acidez moderada de naturaleza débil, alta superficie específica y presencia del par redox $\text{Ce}^{3+}/\text{Ce}^{4+}$ junto con una buena dispersión de la fase activa NiO .

Por último, en relación con la temática de HDO, en el capítulo 6 se estudió la reacción de HDO de anisol utilizando catalizadores soportados basados en platino y hierro. Las principales observaciones derivadas de este capítulo son las siguientes:

- Mediante DRX se observó la presencia de óxido de hierro en sus fases hematita y magnetita, además de la presencia de Pt altamente disperso. A pesar de las altas cargas de Fe (5, 15 y 30 % en peso) incorporadas por el método de impregnación a humedad incipiente, el mantenimiento de la estructura mesoporosa de la SBA se confirmó mediante isothermas de adsorción-desorción de nitrógeno, obteniéndose valores de superficie específica por encima de los $175 \text{ m}^2 \cdot \text{g}^{-1}$ en todos los casos. La caracterización superficial por XPS mostró una mayor contribución de grupos hidroxilo y agua adsorbida en superficie en las muestras con mayor contenido en óxido de hierro, demostrando así el carácter oxofílico de este compuesto. Con

respecto a la actividad catalítica en la reacción de HDO de anisol a 30 bar y 275 °C, el catalizador con una carga media de 15 % Fe resultó el más activo, teniendo en cuenta no solo la actividad si no también la selectividad y estabilidad del catalizador. El estudio de las condiciones de reacción óptimas para la reacción de HDO de anisol en un reactor de lecho fijo a alta presión realizado utilizando este catalizador demostró que el empleo de altas presiones (30 bar *vs.* 15 bar) favorecía la conversión a productos desoxigenados, mientras que el aumento de la temperatura (275 °C *vs.* 300 °C) aumentaba la selectividad a compuestos oxigenados hidrogenados como el ciclohexil metil éter.

Junto con la biomasa lignocelulósica, el hidrógeno se presenta como una valiosa alternativa para su uso como combustible, ya que presenta una alta densidad energética y un bajo peso que le confieren un gran potencial como vector energético para aplicaciones portátiles. De hecho, una de las aplicaciones más exploradas del uso del hidrógeno como transportador de energía es como combustible en celdas de combustible de membranas de intercambio protónico (PEMFC, su acrónimo en lengua inglesa) debido a que estas celdas de combustible funcionan a temperaturas bajas, son muy eficientes e involucran reacciones medioambientalmente sostenibles, ya que en ella se producen la oxidación del hidrógeno y la reducción del oxígeno del aire, obteniéndose como subproducto agua. Sin embargo, las PEMFCs se enfrentan a una limitación importante: el hidrógeno empleado como combustible debe ser de alta pureza ya que, compuestos como el monóxido de carbono, el azufre o el amoníaco, incluso en concentraciones traza, envenenan el catalizador de platino utilizado en los electrodos de la celda de combustible.

En la actualidad, el hidrógeno se produce principalmente por reformado con vapor de metano, del que se obtiene una mezcla de hidrógeno

y monóxido de carbono. Aunque la concentración de CO se puede disminuir hasta el 1 % mediante la reacción de desplazamiento de agua (WGS por sus siglas en inglés), que además aumenta el rendimiento a hidrógeno, este debe ser aún más purificado para su uso en PEMFCs, con concentraciones menores a 10 ppm. En bibliografía se han reportado diversos métodos para disminuir la concentración de CO, como la difusión selectiva, la metanación selectiva de CO o la oxidación preferencial de CO (CO-PROX); siendo esta última la alternativa más interesante debido a que la reacción tiene lugar en condiciones ambientales de operación, por lo que podría acoplarse antes de la celda de combustible PEM.

La oxidación preferencial de CO en corrientes ricas en hidrógeno puede llevar intrínsecas reacciones secundarias como la metanación de CO o la reacción inversa de desplazamiento de agua (RWGS, en inglés) que disminuyen el rendimiento de la misma, además de consumir hidrógeno. Es por ello por lo que el desarrollo de catalizadores que sean activos y selectivos a la obtención de CO₂ es uno de los principales desafíos en CO-PROX.

Óxidos de metales de transición como CuO, ZnO o CeO₂ han demostrado una actividad considerable en la reacción. Además, su combinación con metales nobles como el platino o el rutenio presenta un efecto sinérgico que mejora la actividad catalítica. Por otro lado, los catalizadores basados en nanopartículas de oro han demostrado una excelente actividad en esta reacción, especialmente cuando estas se encuentran soportadas en óxidos reducibles como la titania (TiO₂), debido a que esta combinación favorece la movilidad de especies de oxígeno a la vez que aumenta la densidad electrónica en la superficie de los sitios activos de oro. Teniendo en cuenta que la titania es el fotocatalizador por excelencia, el rendimiento de la reacción de CO-PROX puede mejorarse notablemente si se utiliza una fuente de irradiación electromagnética, denotándose entonces como photo-PROX. No obstante, este rendimiento puede

maximizarse mediante la optimización de la formulación del catalizador, de manera que sea altamente fotoactivo y selectivo a la formación de CO₂.

Siguiendo la línea fotocatalítica de esta tesis, cabe destacar el papel de la fotocatálisis en los procesos de oxidación avanzada (AOPs, por sus siglas en inglés) en otro de los grandes problemas a los que se enfrenta la sociedad: la severa contaminación de las aguas debido al fuerte desarrollo de industrias con grandes volúmenes de producción como la industria textil o la papelera, que descargan enormes cantidades de aguas cargadas de compuestos recalcitrantes como colorantes a los recursos hídricos. De entre todos los contaminantes, cabe destacar el papel de los colorantes, ya que son compuestos con alta pigmentación que, incluso en baja concentración, pueden impedir el paso de la luz solar al agua, interfiriendo así en los procesos biológicos y fotosintéticos que permiten el desarrollo normal de los ecosistemas acuáticos y poniendo en riesgo no solo la biodiversidad y el suministro de agua, sino también la salud humana, ya que estos efluentes contienen una amplia gama de productos tanto orgánicos como inorgánicos con estructuras químicas diversas que, si se degradan o combinan, pueden desarrollar un alto potencial mutagénico y/o carcinogénico. Aunque las técnicas de adsorción de estos contaminantes resultan efectivas y actualmente están en aplicación en multitud de industrias, la fotodegradación de colorantes se postula como una alternativa más limpia y eficiente, ya que permite operar en condiciones ambientales y consigue la completa mineralización de estos a moléculas inocuas.

Aunque la titania, especialmente en su fase cristalina anatasa, presenta excelentes propiedades para ser utilizada como fotocatalizador como su baja toxicidad, su gran estabilidad térmica y química y su alto poder oxidante, presenta dos desventajas que limitan su aplicación: por un lado, la rápida recombinación de los pares electrón-hueco que actúan como portadores de carga en los procesos de oxidación y, por otro, su amplio *band gap* o brecha energética (que oscila entre los 3.0 y 3.2 eV según la fase

cristalina) que limita su operatividad a la región ultravioleta del espectro solar. Teniendo en cuenta que esta región representa solo alrededor de un 5 % del espectro solar incidente, uno de los mayores desafíos en el campo de la fotocatalisis es extender la operatividad de la titania al rango del visible, que supone aproximadamente un 43 % del espectro solar. Para mitigar las mencionadas desventajas se han estudiado diferentes estrategias, como la adición de dopantes que disminuyan esta brecha energética. o la modificación de la morfología de nanoestructuras de titania. Metales de transición como el molibdeno o el hierro y no metales como el nitrógeno o el carbono se han utilizado como dopantes en estructuras de titania debido a que por su similar tamaño al oxígeno pueden incorporarse fácilmente a la red de la titania o colocarse en posiciones intersticiales, disminuyendo así la brecha energética y desplazando la absorción de estos compuestos a mayores longitudes de onda. De entre todos los metales utilizados, los metales nobles nanoparticulados, especialmente el oro, adquieren especial protagonismo debido a sus excelentes propiedades ópticas. La fotoactividad de las nanopartículas de oro está fuertemente relacionada con el tamaño de estas y con el método de síntesis empleado para su obtención, ya que de ello depende la aparición de fenómenos ópticos y superficiales que mitigan limitaciones de la titania pura en fotocatalisis: la creación de una barrera de Schottky en la interfase metal-semiconductor y la resonancia de plasmones superficiales localizados (LSPR, por su acrónimo en inglés), que permiten que, además de reducir la brecha energética de la titania, las nanopartículas de oro actúen como reservorio de electrones y promuevan la inyección de estos en la banda de conducción de la titania, favoreciendo así la activación de los reactantes. Además, el oro presenta una gran capacidad de aleación con otros metales de menor coste que pueden favorecer aún más el proceso fotocatalítico, como es el caso de la aleación AuCu, que mejora tanto la fotorespuesta como la resistencia a la oxidación de estos materiales. Por último, los metales de tierras raras como el cerio también han sido estudiados como dopantes de la titania debido a su alta capacidad de

almacenaje de oxígeno y al par redox $\text{Ce}^{3+}/\text{Ce}^{4+}$, que favorecen la movilidad de especies de oxígeno. Además, se ha demostrado que la incorporación de ceria a estructuras de titania reduce la brecha energética de la titania, extendiendo la operatividad de estos compuestos al visible.

Dada la importancia de la fotocatalisis en procesos medioambientales y en la producción de energía, en la presente tesis se han estudiado dos familias de catalizadores teniendo como nexo común el uso del fotocatalizador óxido de titanio. En primer lugar, se han sintetizado y caracterizado catalizadores basados en nanopartículas de oro y cobre soportadas sobre un sólido mesoporoso con titania en las reacciones de photo-PROX y fotodegradación del colorante azo azul de metileno, ambas reacciones llevadas a cabo en condiciones ambientales (presión atmosférica y temperatura ambiente) bajo luz solar simulada y bajo irradiación UV, respectivamente, cuyos resultados se encuentran en el capítulo 7. En segundo lugar, en el capítulo 8 se ha estudiado la importancia de la morfología en nanocomposites de ceria-titania testados en la reacción de fotodegradación de azul de metileno en condiciones ambientales de operación y tanto bajo irradiación UV como bajo luz solar simulada. Las principales conclusiones obtenidas de estos estudios se detallan a continuación:

- Respecto a los fotocatalizadores basados en AuCu, estos resultaron altamente activos en ambas reacciones a pesar de la baja carga metálica añadida (2 % en peso en total), especialmente los catalizadores conteniendo tanto titania como nanopartículas de oro y cobre sujetas a tratamiento con hidrógeno para formar la aleación AuCu. Mediante DRX se comprobó que la anatasa era la principal fase cristalina presente, con un tamaño medio de cristal de 24 nm, que favorece los procesos fotocatalíticos. La incorporación de la titania no solo en los poros sino también en la matriz del sólido mesoporoso

SBA-15 se confirmó por resonancia magnética nuclear de sólidos (ss-NMR) mediante la presencia de enlaces covalentes entre el silicio y el titanio. Los materiales preparados presentaron una superficie específica considerable, aunque menor que la del soporte puro, indicando que parte de la titania bloqueaba canales porosos de la SBA. Mediante HR-TEM se comprobó que la fase activa se encontraba altamente dispersa sobre el soporte y que, además, la presencia de un segundo metal inducía la disminución del tamaño de nanopartículas obtenidas. El análisis de XPS sugirió que la interacción Ti-Au favorecía la dispersión de las fases activas Au y Cu en la superficie del catalizador, así como la obtención de oro en su estado metálico debido a la transferencia electrónica entre estos metales. Por último, se comprobó por espectroscopía DRUV-Vis que la adición de oro y cobre y posterior tratamiento con hidrógeno redujo la brecha energética de la titania hasta en un 25 %.

- En el último capítulo de esta tesis, se han estudiado dos familias de catalizadores basados en ceria-titania con morfología nanotubular y nanoparticulada y diferente carga de ceria. Los ensayos catalíticos mostraron que una morfología más desordenada con mayor superficie específica como es el caso de las nanopartículas mejoraba el rendimiento fotocatalítico tanto bajo irradiación UV como bajo luz solar simulada. Además, mediante HR-TEM se comprobó que, en el caso de los nanotubos, cargas de cerio mayores al 2.5 % en peso derivaban en la formación de aglomerados. No obstante, en el caso de las nanopartículas, se observó una buena distribución de ambas fases en todo el rango de cargas de Ce estudiadas. Con respecto a la influencia de la carga de cerio, se observó que las bajas cargas favorecen la fotodegradación de azul de metileno usando luz UV, debido al papel del cerio como productor de electrones

que se transfieren a la titania y a la gran accesibilidad de los sitios activos de la titania. Sin embargo, cuando los experimentos se realizaron bajo luz solar simulada, los mejores resultados se obtuvieron para cargas altas de cerio (2.5 y 5 % en peso), debido principalmente a la disminución de la brecha energética de la titania en estas muestras, como se comprobó mediante espectroscopía DRUV-Vis.

1. INTRODUCTION

1.1. Energy outlook

Fossil fuels have been responsible for the great industrialisation modern society has experienced worldwide, and nowadays they are still one of main pillars on which the world economy is based. It is globally acknowledged that the overall tendency is towards an ever-increasing energy demand that, whilst it is true that the percentage of fossil fuels is decreasing thanks to sustainability policies in favour of renewables, it is also a fact that, generally, every year the energy demand increases, hence so does the fossil fuel consumption, as observed in **Figure 1.1**, since energy requirements are still mostly supplied by coal, natural gas and crude oil. With a current total share of ca. 84% in 2021 (see **Figure 1.2**), their massive burning to obtain energy is the main cause for greenhouse gases emissions (GHG), mainly CO_2 . Apart from their obvious negative contribution to global warming, these energy sources are non-renewable, and their ongoing depletion is also a concerning issue that jeopardizes the stability of economy worldwide.

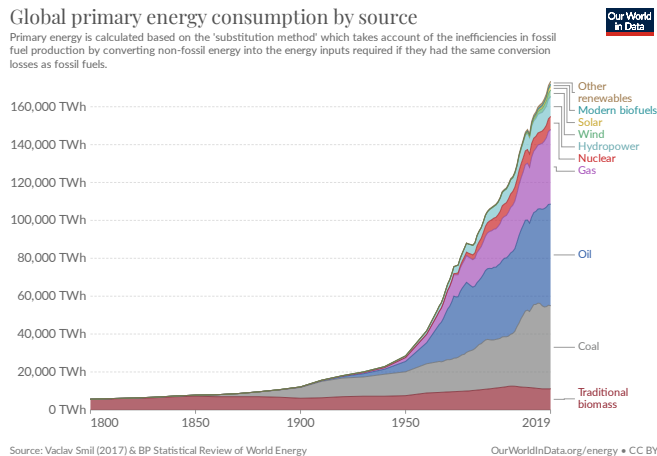


Figure 1.1: Global primary energy consumption by source [1]

To limit global warming imminent consequences, the International Energy Agency sets out the Sustainable Development Scenario (SDS) that, aligned with the Paris Agreement, outlines how the global energy system

could effectively evolve so as to achieve the outcomes of the United Nations 2030 Agenda for Sustainable Development in terms of universal energy access, energy-related CO₂ emissions and climate and air quality goals [2]. Built with retrospective, the SDS firstly establishes the desired outcomes and, after thoroughly studying what is needed to achieve these former goals, it provides marks to measure the progress attained so far [3]. Thus, the SDS is dynamic, and in fact it has changed in 2020 due to the global coronavirus pandemic, that has turned this year into an atypical year with a decrease in global energy demand estimated at 4.5% and 6.3% fall in energy-related CO₂ emissions due to lockdown and restrictive policies [4]. The International Energy Agency estimates that, even if the pandemic had been controlled in 2021, the energy demand would only achieve pre-crisis levels by early 2023. Moreover, a longer pandemic period of more than a year would usher in the slowest decade of energy demand growth in a century [5].

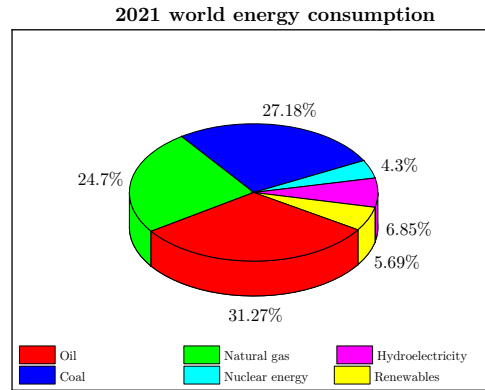


Figure 1.2: Energy consumption by source in 2021 [4]

As stated by Dr. Faith Birol, chief executive officer of the IEA, although the economic recession because of the coronavirus pandemic has temporarily suppressed emissions, this strategy is not an appropriate to accomplish the SDS, as it impoverishes the most vulnerable populations around the world. Instead, change should be focused on the way modern

society produces and consumes energy to attain a resilient, feasible energy system with dwindling emissions that could meet climatic goals.

Pandemic issues aside, the climatic challenge of achieving the sustainable development scenario is compounded by two main factors. On the one hand, it must be considered that the world population is continuously increasing, and so does its energy demand. It is estimated that the number of inhabitants on Earth will increase to 9.6 billion by 2050 (see **Figure 1.3**), an increase of ca. 23% of the current world population.

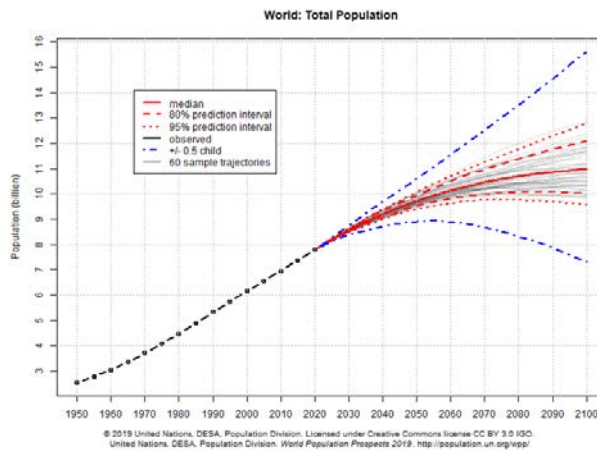


Figure 1.3: Population growth prospect for next 80 years [6]

On the other hand, there is a considerable number of developing countries with expanding economies whose energy demand will increase exponentially in the next decade, like China or India. This, in turn, brings to the fore two concerning issues: the fossil fuels depletion and the exacerbated GHG emissions. Considering the former, estimating a global economic growth of just 1.5%, if the world's energy demand solely relies on fossil fuels, even taking into account the proven, probable and ultimately recoverable fossil fuels reserves, these will be exhausted in less than 100 years from now on [7]. Therefore, it is essential that a significant transition to renewable energies takes place in the coming decades.

Regarding emissions, although the allowable emissions of gases classified as greenhouse effect gases such as CO_2 , SO_x or NO_x are continuously decreasing thanks to governmental regulations, the overriding factor of global warming continues to be CO_2 emissions as a consequence of fossil fuels burning. It seems clear that without changes in the way existing fossil fuels energy transformation infrastructures operate, reducing CO_2 emissions up to 25 Gt by 2030 as established by the sustainable development goal will not be possible and, eventually, it would lead to a long-term rise in global temperature of 1.65 °C, even if no new conventional fossil fuels facilities are built. Therefore, not only is the objective to achieve the SDS with new, zero-emissions, renewable energy technology, but also to meet sustainable goals using the existing energy infrastructures operating in a different, more efficient and environmentally friendly way.

Driven by the awareness of a much-needed change in the energy paradigm, the scientific community has thrown a great effort in the quest for efficient, environment-friendly energetic alternatives with minimal GHG emissions that can compete with non-renewable energy sources, such as hydrothermal, eolic or solar energy, but it is also interesting that they could make use of existing fossil fuels infrastructures. Taking into consideration this last point, it seems reasonable that a great deal of this research focuses on obtaining new efficient and innocuous fuels that can be used in current internal combustion engines, as almost 25% of primary energy consumption is related to the transport sector, of which three-quarters of transport emissions are related to road vehicles functioning with products derived from crude oil refinery and processing [8].

Among all the alternative renewable energy sources, biomass emerges as the one with best future perspectives as an energy feedstock, since it is widely abundant, with non-intermittent power generation and it is the only renewable carbon source [9]. Together with the above-mentioned advantages, it has recently regained interest for several reasons such as (1)

the development of novel physicochemical processes that contribute to circular economy, as they allow the revalorization of biomass through its selective and sustainable transformation into high value-added products and biofuels; (2) the restoration of unforested lands, that brings with it a potential increase of biodiversity; (3) employment generation and rural development related to biomass production [10]; and (4) biomass offers off-grid power generation, which could assure energy access to all segments of society.

1.2. Biomass as an energy source. Composition, feedstocks and uses.

According to the Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, biomass is defined as “the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste” [11].

When these products and residues are transformed through digestion, combustion or decomposition, the energy previously stored in their chemical bonds via photosynthesis, is released as chemical energy [12]. Therefore, the energetic value of different types of biomasses is a function of the physicochemical properties of the biomolecules it consists of.

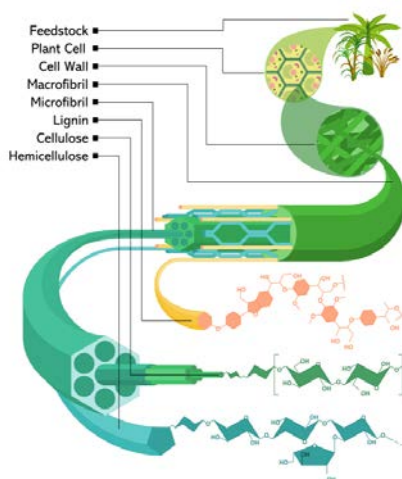


Figure 1.4: Lignocellulosic biomass composition and structure [13]

Among all biomass sources included in the European Commission definition, lignocellulosic biomass is the most abundant and easily available one. It is composed of an elaborated matrix with three dominant biopolymers: cellulose, hemicellulose and lignin, where cellulose microfibrils are enclosed in the lignin and hemicellulose matrix, forming the complex spatial structure represented in

Figure 1.4.

Cellulose (**Figure 1.5 A**) makes up approximately half of the mass of wood [14], being the main component of plant cell structure. It is a high molecular weight homopolymer consisting of D-glucose units bonded by β -1,4-glycosidic linkages forming long linear chains linked together that, in conjunction with hydrogen bonds and van der Waals forces, form the crystalline hydrolysis-resistant microfibrils that provide stiffness and stability to the cell wall [15], [16].

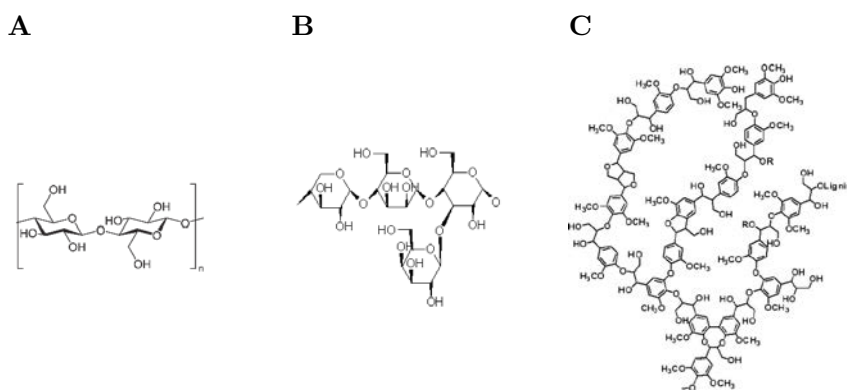


Figure 1.5: (A) Cellulose, (B) Hemicellulose and (C) Lignin

Unlike cellulose, hemicellulose (**Figure 1.5 B**) has an easily hydrolysed amorphous structure consisting of monosaccharides subunits such as D-xylose, mannose, L-arabinose or glucuronic acid mainly linked by β -1,4-glycosidic bonds, although β -1,2-; β -1,3- and β -1,6-glycosidic bonds may be also present. There are three main polysaccharides in hemicellulose: xylan, xyloglucan and mannans, of which xylan is the most abundant one,

consisting of xylose residues connected via β -1,4-glycosidic bonds with different side chains of glucuronic acid and L-arabinose [17].

Lignin (**Figure 1.5 C**) also has an amorphous structure that gives lignin interesting functions in plants such as structural support, impermeability and stiffness, which makes it strongly resistant to chemical and biological degradation [18]. It is built up of phenylpropane units linked by alkyl-alkyl, alkyl-aryl and aryl-aryl groups linkages. Natural lignin presents different ratios of lignin precursors such as p-coumaryl, coniferyl and synapyl alcohols that are irregularly coupled forming three-dimensional phenolic heteropolymers. In fact, the chemical structure of lignin is unresolved, therefore lignin extraction and processing is still a challenge in the field of natural polymers [19] since it contains many functional groups including alcohol, phenolic, carbonyl, carboxyl and methoxyl groups that determine lignin's reactivity, chemical stability and optical properties.

The chemical composition of lignocellulosic biomass varies significantly according to its origin, as collected in **Table 1.1**. On dry basis, it is built up of 40-50% cellulose, 25-35% hemicellulose and 16-33% lignin [20]. Together with these three main components, lignocellulosic biomass, especially herbaceous biomass, may also contain inorganic compounds such as alkali metals, chlorine or silica that could promote slagging, corrosion and gas emissions during biomass processing, as well as reducing the biomass conversion. Thus, prior pre-treatment is crucial in biomass conversion to avoid undesired side reactions. The water leaching method is a simple and common pre-treatment that improves the quality biomass feedstock, by allowing the removal of water-soluble compounds such as potassium, sodium and chlorine. For water-insoluble counterparts, such as magnesium or calcium, bioleaching using microorganisms to extract these metals is an excellent, greener alternative to water leaching, since no large amounts of water is needed [21].

Table 1.1: Cellulose, hemicellulose and lignin contribution in wt.% for different biomass feedstocks [22]

Biomass	Cellulose	Hemicellulose	Lignin	Others
<i>Pine</i>	49.6	20.3	27.3	2.8
<i>Rice straw</i>	37.0	16.5	13.6	32.9
<i>Corn straw</i>	42.7	23.2	17.5	16.6
<i>Bamboo</i>	39.8	19.5	20.8	19.9

1.2.1. Biomass feedstocks

Before the Industrial Revolution, lignocellulosic biomass was the most important energy source for humanity, which was inefficiently used to produce fire and heat. Nonetheless, when energy demand increased as a result of this historical event, lignocellulosic biomass was relegated to the background to give way to the massive use of fossil fuels.

Although biofuel derived from vegetable oils was used for the first time by Rudolph Diesel in 1900 in his state-of-the-art ignition-compression engine [23], it was not until 1970 in the wake of the first energy crisis and the abusive crude oil prices, that biofuels development was significant. Despite the first trials with pure vegetable oils were not successful, the promising results of the Rapeseed-oil-Methyl-Esther (RME) process promoted the construction of the first two biodiesel pilot plants in 1987, located in Silberberg and Wieselburg, Austria. In the following years, industrial-scale biodiesel plants were built, with annual productions of more than 10000 tons [24].

According to the natural sources they are derived from, biofuels can be roughly classified into four generations:

First generation biofuels

Biofuels derived from edible agricultural crops like soybean, palm, sugar cane, sugar beet or sunflower from which biogas, bioethanol (sugar, starch) and biodiesel (vegetable oils) are considered First Generation (1G) Biofuels. The principal crops for biofuels production are oil palm, soybean and rapeseed [25].

Nearly all bioethanol is produced via fermentation of sugars in starch and sugar-based feedstocks, mainly corn, meeting the renewable fuel category of the Renewable Fuel Standard (RFS), i.e., limited to 57 billion L to ensure livestock feed, human food and export markets [26]. Bioethanol can be blended with gasoline up to 15 vol.% for car engines built after 2000, according to the EN 15376:2014 European standard [20], and it can also be used as a feedstock for gasoline oxygenates like ethyl tert-butyl ether (ETBE). According to data from the Renewable Fuels Association (RFA), the leadership of bioethanol production belongs to the United States (55%), followed by Brazil (27%) and the European Union (5%) with more than 90 million m³ produced in 2021 [27].

Regarding first generation biodiesel, it is mainly produced through transesterification of vegetable oils such as rapeseed oil or palm oil. In the European Union, biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable feedstocks, for its use in diesel engines, according to ASTM D6751 standard specification [28]. The mandatory standards for its production inside the European Union, the world's largest biodiesel producer, are collected in the technical regulation EN 14214, which includes specifications not only about the raw material used, but also the catalyst and operating conditions and cleansing procedures employed.

The principal drawback of 1G biofuels is that, if large-scale produced, they compete with global food supply, which calls their sustainability and renewability into question. In fact, it has been reported

that a large use of edible crops to produce biofuels may rise food prices by more than 50%, which could derive in severe inequality between import and export countries. Besides, huge land extensions, agrochemicals and massive water consumption used in crops growth may jeopardize biodiversity and soil quality [29].

Second generation biofuels

Second Generation (2G) Biofuels arose as an alternative to overcome 1G biofuels disadvantages as far as land usage, food competition and sustainability are concerned. 2G biofuels are those produced from cheap, widely abundant non-edible feedstocks like high-yielding biomass crops, agroindustry and municipal wastes or used cooking oil (UCO). Lignocellulosic bioethanol, bio-oil, biodiesel and Fischer-Tropsch oil obtained from processes like biomass pyrolysis are considered in this category [30]. Currently, the production of 2G biofuels is not yet feasible from an economic point of view, since several technical barriers must be overcome, such as the excessive energy required needed or the use of dangerous chemicals to release sugars from the complex aromatic structure of the lignocellulosic biomass, as listed in **Table 1.2**.

Table 1.2: Disadvantages of some processing technologies (adapted from [31])

Pre-treatment	Reaction temperature (°C)	Disadvantages
Acid hydrolysis	200-300	Energy intensive Loss of C5 sugars
Wet oxidation	170-210	Oxygen addition required Loss of C5 sugars
Alkaline	Low temperature	High costs for ammonia recycling

Despite the disadvantages mentioned above, 2G biofuels sowed the seed of what is now known as biorefinery, a term that was defined in 1990 by NREL as “a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass” [32]. In

fact, some industries are switching their production to this kind of facility. For example, in Nevada, Iowa, DuPont's cellulose biorefinery produced 136 million litres a year of ethanol from cellulosic sugars through 2018, switching to renewable natural gas production from corn stalks, husks and cobs when was acquired by the German company Verbio [33].

Although more than 90% of commercially produced biofuels belongs to 2G category (see **Figure 1.6**), much of the research in the field of biorefinery is focused on the quest of catalysts and processes that could reduce mechanical and chemical pre-treatment costs in terms of energy and hazardous chemicals uses. When achieved, it will be a turning point for biorefineries' profitability as they will be able to compete with traditional crude oil facilities making the vision of a bio-based global economy a matter of fact.

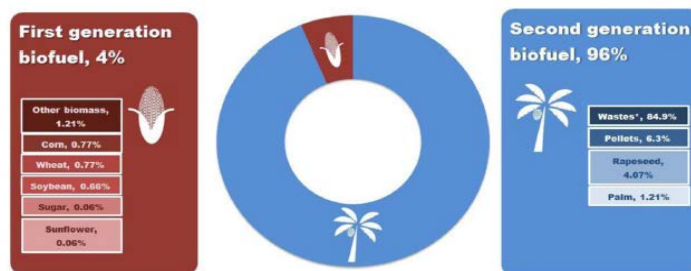


Figure 1.6: Commercial production of biofuel based on generation [34]

Third generation biofuels

Third generation (3G) Biofuels are obtained from the exploitation of oleaginous microorganisms such as microalgae, bacteria, yeast and fungi. Among them, algal biomass arises as the most promising one since it possesses higher growth rates and it is also able to accumulate large cell lipid contents (20-77%) [35]. Moreover, algal biomass does not require an extensive growing area and can produce, not only good quality bio-oil with high heating value and low viscosity, but also high value-added chemical and nutritional products [36].

However, 3G biofuels profitability is hampered by the huge set-up costs for large scale production as well as insufficient biomass production for commercialization [37].

Fourth generation biofuels

Fourth Generation (4G) Biofuels comprises genetically modified organisms like macro- and microalgae or cyanobacteria to boost biofuels production up to 100 times making use of strategies like increasing light penetration and photosynthetic efficient in CO₂ fixation, reducing photoinhibition or applying metabolic engineering to maximize lipid or carbohydrates contents [34]. These microorganisms are capable of survive in extremely hostile environments, but the initial high-cost investment for large-scale cultivation together with the great concern about the potential environmental and health-related risks associated with their use make the competitiveness of 4G biofuels still unfeasible.

1.3. Biomass conversion

Biomass conversion involves a wide range of complex processes governed by the origin-derived properties of the biomass used, comprising physical, chemical, biological and thermochemical processes, as summarized in **Figure 1.7**. In respect to biomass conversion to biofuels, the optimization of conversion processes is still far from achievement due to the wide variety of composition (and therefore properties) and final products. Thus, much research has been dedicated to the development and improvement of biomass to biofuels technologies that can be broadly categorized into three main routes: hydrolysis, gasification and pyrolysis. Among all the processes, the thermochemical biomass conversion is the most promising one, as with it a bio-oil with interesting properties can be obtained to be used as fuel for conventional combustion engines [38].

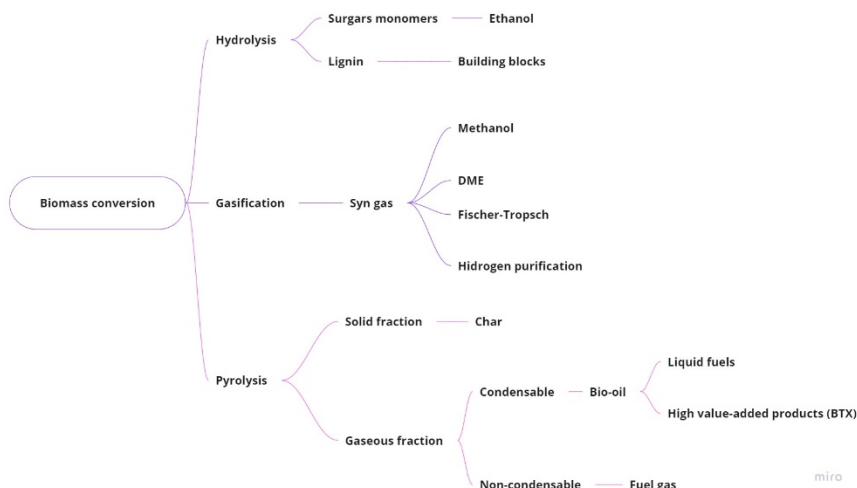


Figure 1.7: Biomass conversion processes

Hydrolysis route comprises all physical, chemical and enzymatic processes required to break lignocellulosic bonds to obtain sugars monomers that can undergo fermentation to produce bioethanol. This reaction is usually carried out using enzymes as catalysts [39], since it has been reported that bases and acids like H_2SO_4 catalysts also promote secondary decomposition reactions in which by-products like furans can be obtained, decreasing the hydrolysis yield (see **Figure 1.8**).

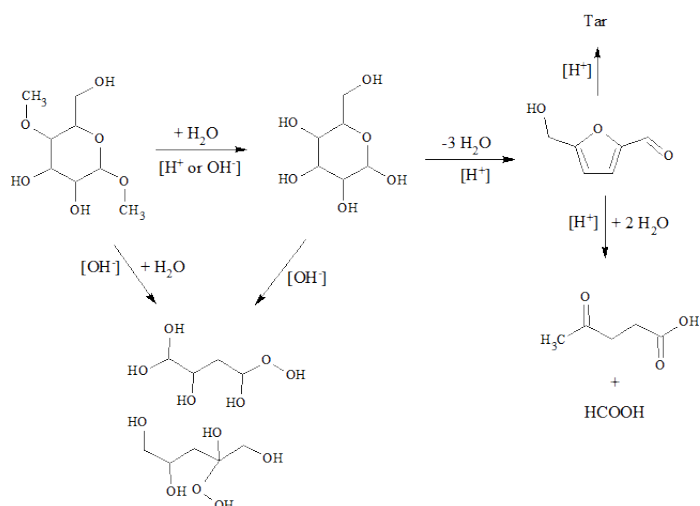


Figure 1.8: Hydrolysis of cellulose

Gasification processes are mainly used to produce syngas that can be further employed to obtain high value-added products, i.e.: hydrogen that can be used in water gas shift reaction; methanol and dimethyl ether using conventional CuO based catalysts and clays or zeolites [40]–[42]; or as reagent in Fischer-Tropsch synthesis [43].

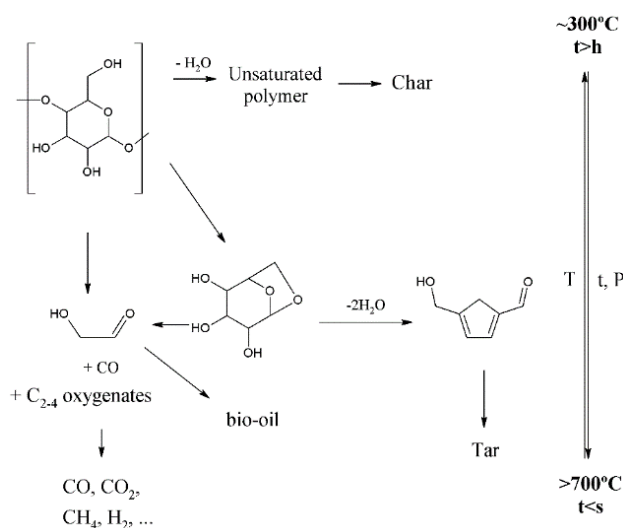


Figure 1.9: Biomass pyrolysis scheme

Pyrolysis consists in the thermochemical decomposition of biomass in the absence of any oxidizing agent like oxygen. It involves cellulose, hemicellulose and lignin depolymerization and fragmentation reactions in which separation, reagents identification and characterization are challenging tasks. Pyrolysis leaves behind a residue consisting in solid products named char, and gaseous products that can be either condensed to give rise to bio-oil or tar liquid fraction or remain non-condensed thus it can be used as fuel gas [44], [45]. Pyrolysis general scheme is depicted in **Figure 1.9**. The depolymerization of hemicellulose occurs at temperatures ranging between 220–315 °C while that of cellulose at 314–400 °C [10]. Over 700 °C, lignin depolymerization takes place, C–C bonds are broken and oxygenated compounds are formed together with lighter ones like CO, CO₂ or methane [39]. The main objective in biomass pyrolysis is to obtain the

highest liquid yield possible, since it presents numerous advantages, not only over its gaseous counterpart like storage or transportation, but also over traditional liquid fuels thanks to renewability, portability, ready availability, higher combustion efficiency and lower sulphur contents [37].

The distribution of the pyrolysis products depends both on the biomass composition and on the operating conditions like temperature, pressure, residence time, heating rate, type of reactor or catalysts employed. Considering these operating variables, pyrolysis processes can be classified as slow, intermediate or fast pyrolysis, whose main differences of which are listed in **Table 1.3**.

Table 1.3: Fast, intermediate and slow pyrolysis comparison [10]

Parameters	Fast pyrolysis	Intermediate pyrolysis	Slow pyrolysis
<i>Heating rate</i>	$>100\text{ }^{\circ}\text{C} \cdot \text{s}^{-1}$	$>10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ and $<100\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$	$<10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$
<i>Temperature</i>	500 $^{\circ}\text{C}$	500 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$
<i>Residence time</i>	1-2 s	10-20 s	Hours to days
<i>Bio-oil</i>	75 %	50 %	30 %
<i>Bio char</i>	12 %	20 %	35 %
<i>Fuel gas</i>	13 %	30 %	35 %

Fast pyrolysis has been widely accepted as the most efficient advanced process for obtaining an energy-dense ($820\text{ GJ} \cdot \text{m}^{-3}$) liquid bio-oil from lignocellulosic biomass [46]. The reaction is carried out at high heating and heat transfer rates as well as controlled moderate temperature ($\sim 500\text{ }^{\circ}\text{C}$), low residence time (0.5-2 s) and it also requires rapid cooling of pyrolysis vapor to maximize bio-oil production [47]. Currently, the leader country in bio-oil derived from fast pyrolysis of lignocellulosic biomass is Canada, with a global production of 40 million litres per year in two plants

located at Ontario and Quebec, both property of Ensyn technologies [46], [48]. The benchmark reactor for fast pyrolysis of lignocellulosic biomass is the circulating fluidized bed reactor (CFB) as this offers numerous advantages such as good thermal control, reliable and proven technology and high-quality bio-oil as final product plant [49]. **Figure 1.10** shows a scheme of a scale fast pyrolysis. Apart from the CFB reactor, several additional components should be added to the pyrolytic system to ensure an optimal utilisation of the facility and bio-oil yields over 70%. First, the raw feedstock needs to be conditioned prior to pyrolysis. To this end, it is dried and treated in a biomass feeder that helps to smooth the raw feedstock and is able to sieve it up to a particle size of 2 mm, achieving optimal heat and mass transfer properties. The main reactions occur at the char combustor and biomass pyrolysis riser, from which produced gases are carried to a heat exchanger where they condense to the bio-oil that is collected in a Dewar vessel.

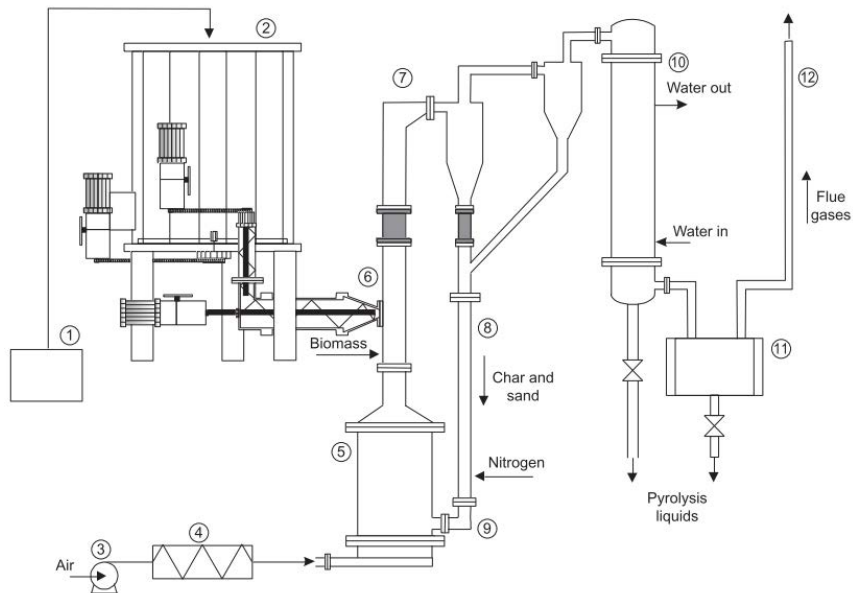


Figure 1.10: Biomass fast pyrolysis scale plant. (1) Feedstock preparator, (2) Biomass feeder, (3) Air compressor, (4) Air preheater, (5) Char combustor, (6) Biomass pyrolysis riser, (7) Solid recovery system, (8) Standpipe, (9) L-valve, (10) Shell-and-tube heat exchanger, (11) Dewar vessel and (12) Gas to vent

1.4. Bio-oil properties

Certainly, the biomass' fast pyrolysis produces a bio-oil with interesting properties to be used as fuel for internal combustion. However, the bio-oil fraction obtained in a fast pyrolysis process consists of a complex mixture whose composition (and, therefore, properties) varies with the biomass feedstock composition (see **Table 1.4**).

Table 1.4: Biomass feedstocks composition in wt.% [50]

	Corn cobs	Corn stubble	Pine	Soft- wood	Hard- wood
<i>T</i> ($^{\circ}\text{C}$)	500	500	520	500	-
<i>Reactor type</i>	Fluidized bed	Fluidized bed	Transport bed	Rotating bed	Transport bed
<i>Water</i>	25	9	24	29-32	20-21
<i>Aldehydes</i>	1	4	7	1-17	0-5
<i>Acids</i>	6	6	4	3-10	5-7
<i>Phenolics</i>	4	2	15	2-3	2-3
<i>Furan derivatives</i>	2	1	3	0-2	0-1
<i>Alcohols</i>	0	0	2	0-1	0-4
<i>Ketones</i>	11	7	4	2-4	7-8
<i>Carbohydrates</i>	5	12	34	3-7	3-4
<i>Unclassified</i>	46	57	5	24-57	47-58

Generally, this bio-oil can be identified as a dark brown, relatively dense free-flowing liquid with acrid smoky odor and limited petrol or water miscibility. Its viscosity is quite variable, ranging from 25 cSt to 1000 cSt depending on the feedstock, the water content and the amount of lights tailings collected and can also increase with aging due to the complex structures it consists of and the acidic pH [47]. Although apparently homogeneous, the substantial extractives in the lignocellulosic biomass give rise to pyrolysis products with considerable differences in solubility, polarity and density, resulting in a bio-oil that can be considered a microemulsion

formed by a water-soluble continuous phase and a micellar phase containing water-insoluble compounds [47], [51], [52].

Whilst water can help to reduce viscosity and-facilitates atomization [53], the high-water contents in bio-oil derived from lignocellulosic biomass (see **Table 1.4**) hampers its direct use in conventional engines or their blend with liquid fuels derived from fossil fuels, since water gives bio-oil a polar nature which makes it immiscible with its non-renewable counterpart. Moisture below 10 wt.% in biomass feedstock has been reported to allow favourable levels of water in the final product [47]. Besides, water increases ignition delay, reduces combustion rates and lowers bio-oil's calorific values.

The presence of water and oxygenated compounds is the major responsible for the differences in bio-oil and heavy fuel oil properties as far as high tendency to coke formation, high viscosity and corrosiveness or chemical and thermal instability is concerned [54]. Regarding calorific values, oxygenates in the bio-oil composition reduces more than 60% bio-oil the calorific values in comparison to petroleum-derived fuels. The bio-oil average calorific value ranges in $14\text{--}18 \text{ MJ} \cdot \text{kg}^{-1}$, whereas its non-renewable equivalent presents between $41\text{--}43 \text{ MJ} \cdot \text{kg}^{-1}$ [47]. Besides, the high proportion of acids lowers the pH up to mean values of 2-4, making bio-oil highly corrosive to steel, aluminium and nickel-based materials [55].

Solid and ash proportions vary depending on the biomass feedstock and can reach up to 3 wt.% and 15 wt.% respectively. Solid particles can form agglomerates during bio-oil storage and cause a viscosity increase, provoking pumping and atomization difficulties. Moreover, the metals in the ashes may promote corrosion. Nevertheless, filtration on pyrolysis vapor can reduce solid and ash contents below 1 wt.% [47].

Regarding bio-oil's instability, water and oxygenates compounds are, once again, the main responsible agents. It has been widely reported that many chemical reactions can take place during bio-oil ageing [56], [57].

For example, aldehydes, the most reactive fraction, can react with water to form hydrates; with alcohols to form acetals and water; with phenolics to form resins and water, etc. Together with polymerization, these reactions result in polarity and viscosity changes, calorific value decrease and phase separation. Cooling bio-oils during storage can reduce but ~~do~~ not prevent, these undesirable secondary reactions.

Biodegradability of liquid fuels is certainly a matter of concern. Studies carried out by Blin et al. [58] demonstrated that bio-oils can quickly degrade in 8 days and 41-50 wt.% biodegradation after a month, compared to only 24 wt.% biodegradation of an EN590 diesel fuel.

Considering the disadvantages mentioned above, bio-oils cannot meet the fuel specifications required for its direct use in internal combustion engines. Therefore, bio-oils need to be upgraded. Taking into account that the major difference between bio-oil and heavy fuel oil composition is the oxygen content (35-40 wt.% in bio-oil vs. 1 wt.% in heavy fuel oil [59]), it seems reasonable that this upgrading takes place through oxygen removal.

1.5. Bio-oil upgrading

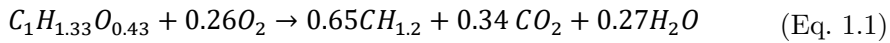
Bio-oil upgrading comprises a wide variety of processes involving complex simultaneous reactions. In respect to catalytic processing, zeolite cracking and hydrodeoxygenation reaction (HDO hereafter) of pyrolytic bio-oils are the most widely used methods to improve the H/C ratio in bio-oil, involving oxygen removal, C-C bonds saturation and minimal carbon losses in side reactions, such as decarbonylation or decarboxylation, although they may also occur, as depicted in **Table 1.5**.

Table 1.5: Typical reactions associated with bio-oil upgrading

Reaction	General reaction scheme
Cracking	$R_1-CH_2-CH_2-CH_2-R_2 \longrightarrow R_1-CH_3 + H_2C=CH-R_2$
Decarbonylation	$R_1-C(=O)H \longrightarrow R_1-H + CO$
Decarboxylation	$R-C(=O)OH \longrightarrow R-H + CO_2$
Hydrocracking	$R_1-CH_2-CH_2-R_2 + H_2 \longrightarrow R_1-CH_3 + H_3C-R_2$
Hydrogenation	$R_1-CH=CH-R_2 + H_2 \longrightarrow R_1-CH_2-CH_2-R_2$
Hydrodeoxygenation	$R-OH + H_2 \longrightarrow R-H + H_2O$

1.5.1. Zeolite cracking

Zeolite cracking of oxygenated products in bio-oil has been widely used to upgrade bio-oil thanks to the remarkable properties of zeolites to be used as catalysts, such as high specific surface area, shape selectivity or moderate acidity [60]. The reaction, expressed in Eq. 1.1 [15], usually takes place at atmospheric pressure and temperatures between 350 °C and 600 °C using zeolites like SAPO-11 or HZSM-5.



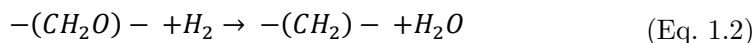
However, the short lifetime of zeolites due to coke deposition together with high Total Acid Number (TANs), undesirable by-products like water and carbon losses as CO_2 [61] have displaced zeolite cracking and promote optimization of the hydrodeoxygenation reaction.

1.5.2. Hydrodeoxygenation

Research on hydrodeoxygenation has been active since the 1980s [62] and it is consolidated as the most efficient alternative to remove oxygen

from lignocellulosic biomass-derived bio-oils, as high quality bio-oils competitive with conventional fossil fuels can be obtained with this reaction.

Closely related to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions used in the refining industry to remove sulphured and nitrogenated organic compounds, the HDO reaction uses hydrogen to eliminate oxygen heteroatom from the carbohydrate ($-(CH_2O)-$) in the bio-oil through water formation, then no carbon units are lost (see Eq. 1.2) and energy density and bio-oil's stability are increased. The reaction is exothermic, with an overall heat formation value of ca. 2.4 MJ/kg when using bio-oil as feedstock [50], [63].



During the HDO process, several reactions can take place simultaneously: water separation, dehydration due to condensation and polymerization reactions, decarboxylation, etc. as collected in **Table 1.5** [64]. Thus, the study of lignocellulosic biomass derived bio-oil model molecules such as phenol, anisole, etc. is appropriate to understand the reaction pathways and mechanisms in the presence of different catalytic systems.

To break C-O-C, C-O-H bonds, high hydrogen pressure and moderate temperature are needed, whose operating values vary depending on the main functional groups present in the bio-oil used as feedstock, with temperatures ranging between 120 and 400°C and pressure values between 10 and 50 bar to ensure the deoxygenation of less reactive compounds and also a better solubility of hydrogen in the bio-oil [65].

Due to the high oxygenates and aromatics contents in lignocellulosic biomass derived bio-oil, more than one stage may be required to achieve competitive quality. In fact, pioneering research back in 1990s by Elliott and Neuenschwander already proposed the use of a two-stage

hydrotreatment process using two fixed trickle bed reactors: the first reactor worked at 300 °C and 210 bar as an stabilization reactor and the second one worked at higher temperature and hydrogen pressure to remove the oxygen heteroatom from low-reactivity compounds like furans and phenols [64], [66]. However, these processes decreased the catalysts lifetime due to supports breakdown. Thus, the selection of one or more stages should be thoroughly studied taking into account not only the catalytic system but also the desired oxygen proportion in the final product, the future use of the upgraded bio-oil and the origin of the biomass source.

1.6. Hydrodeoxygenation catalysts

The catalyst is an essential element in HDO reactions. The development of new phases and supported multiphase catalysts that are active and selective in HDO has been the focus of HDO research since its early beginnings. Many phases have been tested in this reaction so far, presenting a bifunctional character that ensures not only hydrogen but also oxy groups activation and split, such as conventional hydrotreating catalysts, transition metal phosphides, carbides and nitrides or noble metals. In fact, the fuel specifications defined by standards could currently be attained with the benchmark hydrotreating catalyst, Co(Ni)Mo(W)/Al₂O₃ [67].

1.6.1. Transition metal sulphides

Hydrotreatment conventional catalysts like Co-MoS₂ and Ni-MoS₂ supported on alumina have been widely studied for HDO due to its resemblance with HDS and HDN reactions. According to Badawi's group [68], the active sites are sulphur vacancies allocated at the edges of MoS₂ nanocluster, which serve as a Lewis acid sites where oxygen adsorption and desorption can take place, while Co and Ni act as promoters by controlling the Mo-S bond strength [69]. The promoters may change the catalyst structure in a beneficial way. As reported by Gutierrez et al. [70], Co or Ni

atoms can form Co-M-S or Ni-Mo-S bonds at the edges of the MoS₂ phase, and S²⁺ vacancy together with Co atom are more active than that of single Mo atom, thanks to the existence of at least two hydrogenation active sites. On the other hand, since Co and Ni additives can also increase the catalyst acidity, a trade-off must be achieved as excessive acidity could result in undesirable secondary reactions like cracking. In addition, molecular hydrogen, alcohols, thiols or water activation into SH⁻ and H⁺ over the catalysts surface confer Brönsted acid characteristics on the catalyst.

CoMoS/Al₂O₃ and NiMoS/Al₂O₃ catalysts can also be tuned to improve their catalytic performance. For example, the rare earth metal Sm enhances the dispersion of the active phases on the support's surface; Cr₂O₃ helps to avoid catalyst sintering and Ce and La promoters can increase the catalyst's thermal stability [71]–[73].

However, CoMoS/Al₂O₃ and NiMoS/Al₂O₃ based catalysts present several drawbacks that have motivated the quest of new catalytic systems for HDO reaction: continuous re-sulphurization is required therefore operating costs are increased; an excess of H₂S vulcanizing agent can contaminate the final product; SO₂ may be produced from unconverted sulphur, which is an atmosphere pollutant; alumina sensitivity to water presence (one of the reaction by-products, see Eq. 1.2) and progressive deactivation due to coke formation [15], [74].

1.6.2. Noble metal-based catalysts

Platinum group noble metals have been tested in HDO reaction thanks to their remarkable capability to activate and split hydrogen at mild operating conditions due to their unfilled *d* orbital [69].

Although it is still a matter of debate, it has been generally accepted that the hydrodeoxygenation mechanism over noble metals involves several stages that require, apart from hydrogen activation on the noble metal

surface, oxygenate molecules activation either at oxophilic metal sites or at the metal-support interface [50]. Thus, in addition to the noble metal, a second component needs to be added to have a bifunctional catalyst that activates both hydrogen and oxy groups. To this end, noble metals have been used in combination with another metal or support. Transition metals such as Mo, W, Co, Ce are promising candidates, as they present variable oxidation states that ease oxy groups activation and promote C-O bond scission [75]–[77].

Considering their stability when supported on moderately acid solids, palladium, platinum, ruthenium and rhodium have been thoroughly studied in the HDO reaction. Pd and Pt produce hydrocarbons through hydrogenation reactions that saturate C=C and C=O bonds, therefore Pd-based catalysts have been reported to be selective for intermediates such as cyclohexanol and saturated hydrocarbons like cyclohexane with low hydrogen consumption and Pt-based catalysts present high selectivity to BTX and alcohols. Likewise, Ru is more active in deoxygenation reactions through the hydrogenolysis of saturated C-O bonds, thus it is known for enhancing active sites on supported catalysts and produce high hydrocarbon content fuels. Lastly, Rh is highly active in obtaining low carbon hydrocarbons [71], [78].

In these catalysts, morphological properties such as metal dispersion and particle size can affect the hydrogenation capability of the catalyst. Simakova et al. [79] reported that TOF values in stearic and palmitic acids HDO increased in 37% when the Pd dispersion on a synthetic mesoporous carbon support increased from 47% to 65%. Regarding particle size, they reported that particle sizes greater than 3 nm were not conducive for exposing the active Pd (100) plane in the Pd-catalysed HDO reaction.

On the other hand, the metallic properties can be influenced by metal-support interactions. The use of mesoporous materials with high

specific surface area has demonstrated to increase HDO performance. Niu et al. [80] studied hierarchical porous structure zeolite ZSM-5 as high dispersive support for Pt in HDO, reporting a synergistic effect between the hollow structure and the interaction of metal-acid sites, that allowed a higher dispersion (therefore exposure of Pt active sites) and also eased mass transfer of reagents and products. Zeng et al. [81] studied the catalytic performances of Pd over different supports. Strongly acid supports like alumina are believed to favour hydrogenation in metallic sites and dehydration in alumina acid sites [82], while zeolites like HBeta or HY have been proven to promote transalkylation reactions leading to phenols, cresols and xylenols thanks to their moderate acid nature [83]. Neutral supports like SiO_2 result more active in cresols to hydrocarbons conversion than alumina, as the silica surface is able to complete alcohol dehydration [78]. In fact, this kind of supports are considered the most suitable ones for m-cresol hydrogenation despite of the loss of selectivity to toluene over time due to presence of Brönsted acid sites in SiO_2 , that enhances cyclohexane selectivity [81]. Besides, oxides like ZrO_2 provides oxygen vacancies that are believed to adsorb and activate oxygenated compounds, as well as enhancing electron transfer between the noble metal and the support. Moreover, the spillover of reactive hydrogen species improves HDO performances [84].

Given the high cost of noble metals that rises the overall cost of the process, a strategy to reduce it is to add a second non-noble metal or metal oxide with which a lower amount of noble metal is needed to achieve the same HDO performances. For example, Nb in its oxidized form has been reported to act as a promoter that facilitates cleavage of C-O bonds and inhibits C-C bonds one, as well as an increasing acidity. Likewise, Re can promote the dispersion of the active phase and also C-O fracture [71]. Fe or Ni additives can modulate the Pd hydrogenation capacity to reduce decarbonylation and decarboxylation secondary reactions [85], while Mo can enhance HDO performances by increasing oxygen mobility and reducing carbon deposition [86], [87].

1.6.3. *Transition metal phosphides, carbides and nitrides.*

Despite their outstanding catalytic performance and durability, the high cost and limited existence of noble metals motivated the search of new, more available and economic catalytic phases. Non-noble metals, especially transition metals in the form of carbides, nitrides and phosphides, arose as an excellent alternative to overcome the mentioned drawbacks as they are sulphur-free, widely-abundant as well as having lower prices and presenting an oxophilic nature [88]. The incorporation of non-metal atoms into a metal lattice produces a unique electronic structure (electronic or “ligand” effect) as well as reducing the density of exposed active sites on the catalyst surface (geometrical or “ensemble” effect) [89], thus, the catalytic properties of transition metals can be tuned by choice of ligand and metal proportion.

Zhao et al. [90] studied the hydrodeoxygenation of guaiacol using Ni, Mo, Co, Fe, W phosphides supported on SiO_2 , a neutral support. Among all transition metals, Ni resulted the most active one with remarkable hydrogenation capability, weak acidity and resistance to coke formation. In the case of phosphides, reduced Ni sites act as hydrogenation sites while Brönsted acid P-OH sites serves for hydrogenolysis and dehydration reactions [91]. Together with their bifunctional nature, the superior activity of Ni phosphide catalysts has also been related to the ligand effect between Ni and P since charge transfer from Ni to P helps stabilizing Ni 3d levels and the higher d-electron density favours back-donation to aromatic rings in hydrogenation and deoxygenation reactions [92]. Besides, bimetallic phosphides have demonstrated an enhanced catalytic performance thanks to the tunability of surface properties, acidity and coordination geometry by modifying metals combination, proportion and calcination temperature of the metallic precursors. For example, it has been reported that when adding Mo or W to Ni_2P the catalyst’s acidity increases, as well as decreasing particle size [93]. Likewise, it has been reported that the combination of less active metals, like Mo and Co, produces a synergistic

effect with respect to their monometallic counterparts that allows to control products selectivity by modifying the Mo/Co ratio [94].

Regarding metal transition carbides, particularly tungsten and molybdenum, their catalytic activity in hydrotreating reactions is attributed to the noble-metal-like behaviour of these materials, with a high selectivity to C-O/C=O bonds scission, which increases the selectivity to aromatics compounds [95]. Likewise, the use of a second metal has a positive effect on catalytic performance, as the two metals are believed to form a solid solution. Smirnov et al. [96] studied the nickel and molybdenum carbides in HDO reaction, demonstrating that this alloy favours the decarboxylation pathway and also reduces coke deposition. Bimetallic molybdenum and tungsten carbides have also shown remarkable catalytic activity in the HDO of guaiacol, thanks to the greater number and exposure of metallic active sites capable of activating hydrogen molecules, as well as of increasing oxophilicity [97].

Although less selective to oxygen free products, transition metal nitrides have also shown interesting properties like ceramic-like physical properties and noble metal behaviour resemblance that make them appealing as HDO catalysts. It has been suggested that the active species in these catalysts are coordinative unsaturated metal atoms and nitrogen vacancies, which lead to non-frequent yet desirable HDO reaction pathways [98]. For example, carbon supported MoN tested in the HDO of guaiacol showed a total conversion over 50% with high selectivity to phenol and catechol, formed via demethoxylation taking place at unsaturated Mo sites and demethylation occurring at nitrogen-deficient sites [92].

Transition metals carbides, nitrides and phosphides have been traditionally prepared by thermoprogrammed reduction (TPR) of metal oxide precursors with CH₄ or C₂H₆; NH₃ or N₂/H₂ mixture; or phosphorous source, respectively [91], [99], [100]. Although the synthesis methods have

been considered the Achilles heel of these catalytic families [69], [101], this downside is currently overcome thanks to new preparation methods that have successfully reduced synthesis temperature and controlled particle growth. Regarding carbides, carbothermal hydrogen reduction (CHR) has resulted effective to reduce the synthesis temperature and allows to obtain 3-5 nm carbide particles, but their stability is still challenging with this synthetic approach, while templating methods have demonstrated to reduce particle size and improve their stability [88]. In the case of nitrides, since porous structure is desirable for the hydrodeoxygenation reaction, pyrolysis methods using metal halides or metal organic precursors traditionally used for metallic transition metals nitrides are not appropriate [102]. N_2/H_2 TPR is preferred over ammonolysis to obtain highly dispersed supported catalysts [98]. Lastly, regarding phosphides, it has been reported that metal phosphite precursors require lower temperature than phosphate ones [91]. Likewise, a new low temperature synthesis approach comprises the use of metal phosphine complexes to obtain phosphides nanoparticles by thermal decomposition. The catalysts obtained with this synthesis method at temperatures around 300 °C have similar catalytic activity as those prepared by conventional phosphorous source thermoprogrammed reduction at more than 600°C [103].

1.6.4. *Mixed oxides from layered double hydroxides*

Layered double hydroxides (LDHs) or hydrotalcite-like materials are inorganic compounds whose structure is based on $M(OH)_6$ octahedral units sharing edges so as to build brucite-like $Mg(OH)_2$ layers, in which partial Mg^{2+}/Al^{3+} substitution has taken place and the electric charge is balanced by the arrangement of anions in the interlayer space where H_2O molecules are also allocated, creating hydrogen bonds between the brucite layers [65]. Therefore, the whole structure is comprised of stacked layers, alternating charge-balancing anionic species and water molecules (see

Figure 1.11). It can be described using the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n} \cdot yH_2O]^{x-}$ [66], where M^{2+} and M^{3+} stand for divalent and trivalent metal cations, respectively, and A^{n-} is an n- valent anion.

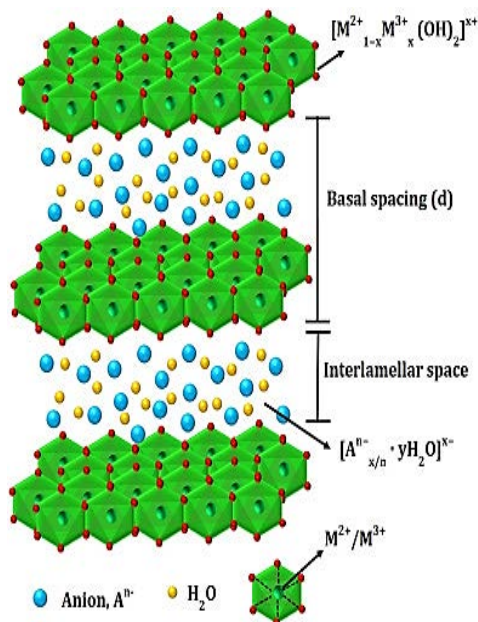


Figure 1.11: Structure of layered double hydroxide [66]

LDHs crystal structure can suffer variations according to the nature and ratio of the cations M^{2+} and M^{3+} as well as the type of anion. For x values ranging between 0.20 and 0.33, appropriate LDHs are obtained. Compositions out of this range for excess or default led to $M(OH)_3$ or $M(OH)_2$ precipitation, due to the high density of M^{2+} or M^{3+} containing octahedra, respectively [67].

By modifying the proportion of each metal during the synthesis, a great variety of LDHs with different structures and composition can be obtained, presenting promising multifunctional properties such as anion exchangeability, biocompatibility or compositional flexibility [68] that can be implemented in a wide range of applications such as adsorption [69], drug delivery [70], environmental applications [71] or catalysis [72], [73].

An interesting property of LDHs is the so called “memory effect”; it is understood that, after calcination, LDHs can recover their original layered structure from the first contact with aqueous anion-containing solutions [74]. Other properties for which LDHs have attracted attention as catalysts in bio-oil upgrading reaction are their thermal stability, high surface area and high metal dispersion [66].

Zhang et al. [75] studied Ni/Al₂O₃ derived from LDHs in anisole HDO at 20 bar and at temperatures between 200 °C and 280 °C, with remarkable catalytic performances and a high resistance to coke formation as well as easy reactivation.

LDHs have also been used as a support for transition metal active phases. Pino et al [76] studied the catalytic performance of Cu supported on MgAl and ZnAl from commercial LDHs in the HDO of furfuryl alcohol at 50 bar and 200 °C, attaining conversions of ca. 80% to cyclopentanone and cyclopentanol thanks to the interaction of the active metal phase, Cu⁰, with the support, together with the moderated acidity of the latter.

Rizescu et al. [77] have studied MgAl doped with different transition metals as mixed oxide catalyst in the HDO of benzyl alcohol at 5 bar and 230 °C in an autoclave reactor, obtaining the best catalytic performance when adding Cu, with conversions values of ca. 97% and 96% selectivity to toluene.

The synthesis method also influences the catalytic activity. As an example, the previous authors [77] also tested NiMgAl prepared by the coprecipitation method of the LDH under the same operating conditions with almost 80% conversion to toluene. On the other hand, Manikandan et al. [78] reported a similar system synthesized by thermal decomposition in HDO reaction of furfural in a downflow fixed bed reactor at atmospheric pressure and 180 °C, attaining a conversion of 98% and 95% selectivity to furfuryl alcohol.

Leveraging the compositional flexibility of LDHs, it seems interesting to add a third cation despite the fact that the ideal range could be exceeded. Transition metals with multiple oxidation states such as niobium and cerium have been studied as promoters in HDO reaction, enhancing the reaction rate and the selectivity to unsaturated compounds [79]. Cerium has shown remarkable properties as promoter in catalytic systems thanks to the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox pair, which crystalline structure provides labile oxygen species that can act as sites of direct interaction of surface defects with the gas reagents [80]. Moreover, Balasundram et al. [81] studied Ce as a promoter in HDO catalysts, reporting that it inhibited coke formation and improved sugarcane bagasse-derived bio-oil upgrading reactions.

1.7. HDO model compounds

Lignocellulosic biomass derived bio-oil comprises a wide variety of oxygenated compounds that complicate its catalytic upgrading (see Table 1.6). Thus, in an attempt to fully understand the mechanisms involved in bio-oil upgrading through hydrodeoxygenation reaction, several model molecules present in raw bio-oil have been studied.

The choice of the model compound is a crucial step when studying HDO reaction. On the one hand, the chosen molecule should be representative of that functional group in lignocellulosic biomass derived bio-oil, and simple enough to allow the study of single bond cleavage, to elucidate the reaction pathways followed by different catalysts. On the other hand, it should be stable enough to assure that its complete deoxygenation would warrantee the deoxygenation of its counterparts with similar chemical structure. To this end, model molecules containing aromatic carbon bonded to oxygen, such as phenol, dibenzofuran or guaiacol have been widely studied in HDO reaction over a wide range of catalysts, since in these molecules, $\text{C}_{\text{Ar}}\text{-O}$ bonds are present and they present higher dissociation

energy than their aliphatic counterpart [101], [104]–[108]. Some examples have been collected in **Table 1.7**.

Table 1.6: Typical oxygenated compounds present in lignocellulosic biomass derived bio-oil [55]

Functional group		Typical compounds
<i>Simple oxygenates</i>	Acids	Acetic acid, formic acid, glycolic acid, etc.
	Esters	Methyl acetate, methyl formate, etc.
	Alcohols	Ethanol, isobutanol, etc.
	Ketones	Cyclopentanone, methylcyclohexanone, acetone, etc.
	Aldehydes	Glyoxal, formaldehyde, benzaldehyde, etc.
<i>Sugars</i>		Glucose, fructose, etc.
<i>Furans</i>		Furfural, dibenzofuran, furfuryl alcohol, etc.
<i>Hydrocarbons</i>	Alkenes	Hexane, methyl-propene, etc.
	Aromatics	Benzene, toluene, xylene, etc.
<i>Phenolics</i>	Phenols	Phenol, methylphenol, etc.
	Anisoles	Anisole, methyl-anisole, etc.
	Catechols	Catechol, methoxycatechol, etc.
	Guaiacols	Guaiacol, eugenol, etc.
	Syringols	Syringol, ethyl-syringol, etc.
	Others	Vanillin, syringaldehyde, etc.
<i>High molecular weight species</i>		Lignin, hemicellulose, etc.

Table 1.7: HDO reaction of different model molecules

Model compound	Catalyst	Reaction conditions	Conversion (%)	Ref
<i>Phenol</i>	Fe ₂ P	15 bar - 275 °C	95	[109]
	NiFeP	30 bar - 300 °C	94.6	[101]
	Ni/WO ₃ -ZrO ₂	30 bar - 210 °C	100	[110]
	Pd/MCSA	50 bar - 200 °C	65	[111]
	Pd/Nb ₂ O ₅	P _{atm} - 300 °C	8.6	[112]
	Ni/Nb ₂ O ₅	P _{atm} - 300 °C	16	[112]
<i>Dibenzofuran</i>	PtMo/SBA	30 bar - 275 °C	87	[104]
	PtNi/MgO	12 bar - 240 °C	100	[113]
	Mo ₂ C/APC	41 bar - 350 °C	99.6	[114]
	Pt/MgO	30 bar - 370 °C	94	[115]
<i>Guaiacol</i>	β-Mo ₂ C	34 bar - 300 °C	80	[116]
	Pd/ZrO ₂	P _{atm} - 300 °C	11.1	[117]
	NiCo/SiO ₂ -ZrO ₂	10 bar - 240 °C	100	[118]

1.7.1. Anisole as a model compound for HDO reaction

Anisole is an organic compound with formula CH₃OC₆H₅ consisting of a benzene ring with a methoxy group. It comprises the largest contribution to the ether fraction in the lignocellulosic biomass derived bio-oil [119]. Its planar atom skeleton confers this molecule a very low reactivity, since it can hinder its adsorption on the catalyst surface [120]. On the contrary, it is a small molecule containing just one functional group, thus facilitating the study of the C_{Ar}-OCH₃ bond cleavage.

It has been reported that hydrodeoxygenation reaction of anisole can follow several reaction pathways depending on the catalyst used. Generally, it is accepted that anisole hydrodeoxygenation can occur following three main routes displayed in **Figure 1.12** [55], [83], [121], [122]: (1) direct hydrogenation (HYD) to form cyclohexyl methyl ether or cyclohexanol; (2) direct deoxygenation to form benzene or demethylation to form phenol that can be further deoxygenated to benzene and hydrogenated to form cyclohexene and cyclohexane; (3) transalkylation of methyl group

to form cresol, that could suffer deoxygenation losing water to give toluene that may be further hydrogenated to methylcyclohexane. Although less probable, the latter route is preferred, since it prevents the loss of the $-\text{CH}_3$ carbon unit and also allows the obtention of toluene, a high added-value product.

$\text{C}_{\text{Ar}}\text{-OCH}_3$ bond shows a higher dissociation energy of $422 \text{ kJ} \cdot \text{mol}^{-1}$ than $\text{C}_{\text{Ar}}\text{O-CH}_3$ bond ($339 \text{ kJ} \cdot \text{mol}^{-1}$) [122], thus, from the products distribution, it can be evidenced whether the reaction is occurring via direct demethoxylation or by demethylation and further dihydroxylation.

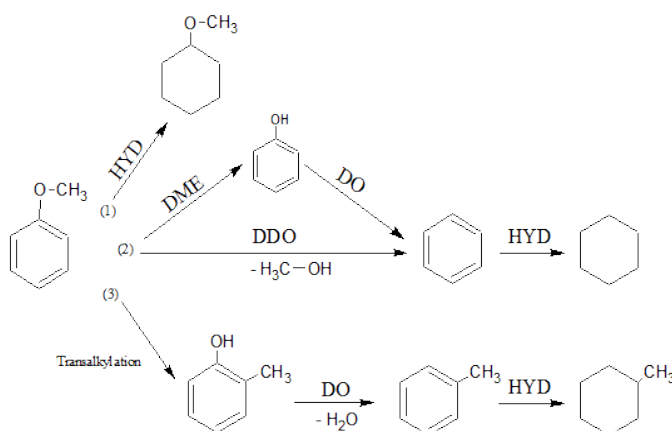


Figure 1.12: Anisole conversion routes

Operating conditions have been proven to have an influence in the followed pathway. It has been widely reported that low pressures favour the direct deoxygenation (DDO) pathway thus enhances aromatics production [121], [123]–[125]. Conversely, high hydrogen pressures favour the hydrogenation of anisole as the primary reaction [126]. Regarding temperature, it has been reported that higher temperature promotes the cleavage of $\text{C}_{\text{Ar}}\text{-O}$ bonds, thus favouring hydrogenated products obtention and, on the contrary, the CH_3 loss from methoxy group [127].

In addition to the operating conditions under which the HDO reaction is carried out, the catalyst formulation plays a crucial role in the

HDO route followed. Li et al. [128] studied HDO of anisole with nickel and molybdenum phosphides supported on silica and reported that anisole hydrodeoxygenation mainly followed the pathway of demethylation followed by DDO or HYD. Likewise, nickel and iron supported catalysts were reported to effectively induce hydrogenolysis of O-CH₃ bone and CAr-O in side chains, but not in the benzene ring [129]. Over noble metal catalyst, the hydrogenation route is preferred given the high hydrogenating capability of noble metals like Pt or Pd. In fact, it has been reported that the addition of a second phase with moderate acidity promotes the methyl transfer reaction (transalkylation) to the aromatic ring, thus significantly reducing carbon losses [83].

1.8. HDO summary

From the research exposed in this section, it can be said that all the phases studied as active catalysts for the HDO reaction share a common nexus: the bifunctionality of the catalyst. Although this bifunctionality is highly influenced by a wide range of parameters such as surface area, crystallinity, active phase's particle size and dispersion, acid sites contribution or redox properties [130], it could be summarized in two main features: an active catalyst for HDO reaction should contain a metal phase capable of activating the hydrogen molecule and the acid groups in order to activate oxy groups and promote dehydration. Among all the studied catalysts, the role of noble metals such as platinum together with some transition metals, especially nickel, stands out.

Nickel-based catalysts are by far the most popular non-noble metals catalysts in the HDO reaction thanks to their lower cost, availability and high hydrogenating ability. Many factors influence nickel-based catalysts' catalytic performance, such as distribution and dispersion of nickel active phase [131], synthesis methodology [132] or the use of a second metal. Regarding the former, it is generally accepted that nickel supported on a

mesoporous neutral solid such as SBA-15 or MCM-41 has resulted highly beneficial, since, thanks to the low interaction between nickel precursors and these neutral supports, high migration of nickel into the pores of the support leads to homogeneous distribution and better dispersion [130]. Moreover, and in relation to this last point, the use of these supports allows the incorporation of a second metal that supplies the acidity or redox properties required to achieve bifunctionality. Nickel has been combined with metals from almost all groups in the periodic table, presenting different catalytic behaviour. For example, NiCu as well as Ni₂P catalysts have been thoroughly studied in the HDO reaction of several model compounds and under varied operating conditions [133]–[139], revealing the synergy between these two phases in terms of both activity and saturated deoxygenated products selectivity in comparison to monometallic counterparts [140].

Nonetheless, special attention should be paid to the use of reducible oxides as the second phase in Ni-based catalysts, since these compounds usually present remarkable redox properties as well as acid features [141]. Zirconium, niobium or cerium oxides arise as interesting candidates and, in fact, they have been tested in model compounds for HDO reactions [142]–[144]. Thus, in this doctoral thesis the use of reducible oxides together with nickel active phase has been studied in anisole HDO.

On the one hand, NiNb catalyst supported on mesoporous SBA-15 has been studied in the anisole HDO reaction. To fully understand the role of the metal added as active site, FeNb and CoNb supported catalysts were also prepared and tested in this reaction. The results obtained from this research are included in Chapter 4.

On the other hand, a set of catalysts containing nickel and ceria as reducible oxide was prepared from hydrotalcite-like materials. The assessment of a mixed oxide catalytic system containing NiAlCe LHDs derivatives in the HDO reaction of a model molecule seems interesting, in

order to study the impact of the third cation in the LDH structure, the interactions of Ce species with both Ni and Al and the influence of Ce oxidation states on the catalytic performance. Chapter 5 collects the discussed results of this study.

Lastly, despite the high cost of noble metals, the low loadings added to the catalyst formulation and the outstanding activity of these catalysts usually compensate the overall cost of the HDO processes. Moreover, if the noble metal is combined with a second phase with lower cost and appropriate features for HDO reaction (moderate acidity, high specific surface area, etc.), the HDO process can be further optimized. To this end, in this doctoral thesis, the use of Pt-based supported catalysts containing Fe as acid and oxophilic counterpart has been studied in the anisole HDO reaction and the results are discussed in Chapter 6.

1.9. Photocatalysis potential

As thoroughly reviewed in the previous sections, the ever-increasing industrialization and population growth is engulfing modern society in a serious crisis involving not only heavy reliance on fossil fuels, but also environmental issues like global warming or water bodies pollution.

Apart from the use of biomass as an efficient, low-cost and revalorized alternative to obtain biofuels working in internal combustion engines, which is one of the most promising energy sources given its availability and the fact that its bio-oil can be processed in conventional fuel oil infrastructures, photocatalysis is surfacing as an interesting technology given its potential for solar light use and its versatility that extend its use to a wide range of scientific fields like solar-to-fuel conversion for energy production or water remediation.

1.10. Photocatalysis for energy production: Hydrogen purification for PEMFCs.

Together with lignocellulosic biomass, hydrogen is regarded as one of the most promising clean fuels. Although it is not an energy source *per se*, it is the most abundant element with the lightest weight and highest energy density compared to all known fuels ($39 \text{ kWh} \cdot \text{kg}^{-1}$ [145] vs. $12 \text{ kWh} \cdot \text{kg}^{-1}$ for crude oil [146]), which places it as a great energy vector. Moreover, hydrogen couples power consuming and power producing sectors, i.e., it links the electricity system and industry, buildings and transport, thus increasing flexibility and mitigating carbon emissions [147].

Hydrogen is a well-established industry with several decades of experience in using hydrogen as feedstock, mainly for ammonia production for fertilisers (50%) and for refining (35%). Hydrogen can be classified into grey, blue and green hydrogen depending on how it is produced: grey hydrogen is that produced from fossil-fuels via carbon intensive processes; blue hydrogen stands for hydrogen produced from fossil-fuels but whose CO_2 emissions are sequestered via carbon capture and storage (CCS) and, lastly, green hydrogen is that obtained from low or zero-emission processes using clean energy sources, as depicted in **Figure 1.13** [148].

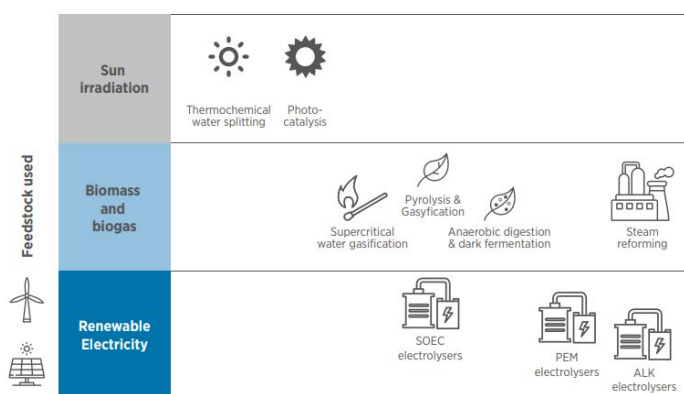


Figure 1.13: Renewable hydrogen production processes and current levels of maturity (from [145])

However, over 90% of produced hydrogen is fossil-fuel based from processes such as steam-methane reforming or coal and oil gasification; the rest is currently obtained by water electrolysis [145]. In this context, worth of mention is the role of biomass, since from its gasification syngas can be produced and, further purified, hydrogen can be obtained (**Figure 1.7**). Nonetheless, according to the Hydrogen Council, by 2030, the announced clean hydrogen production capacity is expected to stand at 11 million tons per year [149], and its applications are expected to cover other energetic demands of society. In fact, by 2040 over 45% of produced hydrogen is expected to be use for mobility, making use of fuel cells [147]. Taking into consideration the outstanding growth of hydrogen use in this sector, fuel cell technology, that combines cleaner processes and hydrogen consumption for transportation sector will be further described.

1.10.1. Fuel cells

Over the last century, the conversion of chemical energy into electrical energy has gained increasing interest as a way to reduce dependence on fossil fuels for electricity production. Fuel cells can help to reduce this heavy dependence as well as diminishing greenhouse gas emissions since they can use pure hydrogen as energy carrier, having water as the main by-product and with higher efficiencies compared to heat engines [150].

Fuel cells are galvanic cells in which free energy derived from a chemical reaction is converted into electrical energy. The unit cell comprises the core of the fuel cell, and it consists of an anode and a cathode that are in contact with an electrolyte. According to fuels and electrolyte used, fuel cells can be classified as collected in **Table 1.8**.

Table 1.8: Fuel cells classification

Fuel Cell	Fuel	Electrolyte	Electrodes	T (°C)	Ref
<i>Proton Exchange Membrane Fuel Cell (PEMFC)</i>	Pure hydrogen Reformed Natural gas	Water-based, acidic polymer membrane	Pt-based electrodes	100	[150]
<i>High Temperature Proton Exchange Membrane Fuel Cell (HT-PEMFC)</i>	Pure hydrogen Reformed Natural gas	Mineral acid-based system	Pt-based electrodes	200	[150]
<i>Direct Methanol Fuel Cell (DMFC)</i>	Liquid methanol	Polymer membrane	Pt-Ru catalysts on anode	130	[151]
<i>Molten Carbonate Fuel Cell (MCFC)</i>	Coal-derived fuel gas Methane Natural gas	Porous ceramic matrix with suspended molten carbonate salt	Ni-based catalysts, stainless steel	650	[152]
<i>Phosphoric Acid Fuel Cell (PAFC)</i>	Hydrogen Hydrogen-rich gas mixture	Phosphoric acid	Finely dispersed Pt on C- and SiC-based structures	200	[153]
<i>Solid Oxide Fuel Cell (SOFC)</i>	Coal-derived fuel gas Methane Natural gas	Solid ceramic	Ni-based catalysts	600 - 1000	[152]
<i>Alkaline Fuel Cell (AFC)</i>	Syn gas Pure hydrogen and oxygen	Alkaline electrolyte	Nickel mesh	65 - 200	[154]

Among all fuel cells, PEMFCs has gained special interest since they are environmentally friendly and highly efficient even at low operation temperatures (85-105 °C). In fact, they were the first fuel cells used in space missions [150].

In their early years, PEMFCs used polystyrene sulfonate membranes, but with the invention of Nafion® (DuPont) made of polytetrafluoroethylene (PTFE) membranes with higher stability, acidity and conductivity, their development was driven. These membranes are currently the most used membranes for PEMFCs, although other from Dow or Asahi Chemical are also in use and under extensive research [155].

1.10.2. PEMFCs functioning

In these fuel cells, whose functioning is depicted in **Figure 1. 14**, direct oxidation of hydrogen takes place in the anode and oxygen reduction occurs in the cathode, giving the overall reaction detailed in Eq. 1.3.

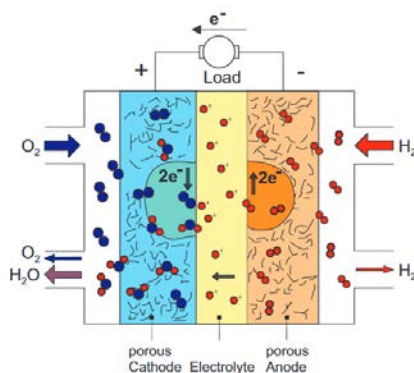
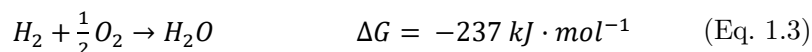
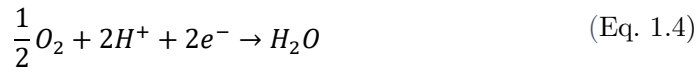


Figure 1. 14: Schematic drawing of a hydrogen/oxygen fuel cell and its reactions based on a PEMFC [150]

Electrodes for PEMFCs are usually porous gas diffusion electrodes in order to warrantee the supply of reactant gases to active zones where the noble metal catalyst is in close contact with the electronic conductor so as to ensure that electrons are supplied to or removed from the reaction site.

Cathode in PEMFCs

Even though oxygen reduction reaction (ORR in Eq. 1.4) is limited by slow reaction kinetics, dispersed Pt, usually as Pt carbon composite film, stands as the best catalyst over which this reaction can be carried out [156].



Oxygen is usually supplied by air, thus, given the lower oxygen partial pressure compared to pure oxygen and the kinetics limitations of the reaction, the use of greater Pt loadings is required. In order to overcome this limitation and also decrease the overall cost of PEMFCs fabrication, a benchmark advance in PEMFCs development was the extension of the triple-phase-boundary zone of the catalyst by means of proton-conducting ionomer and carbon-supported Pt (see **Figure 1.15**).

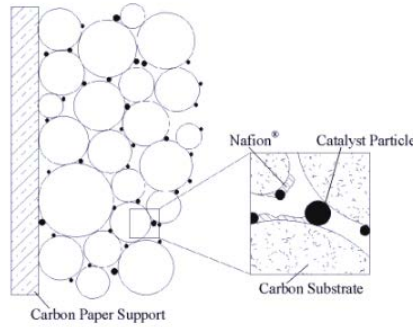
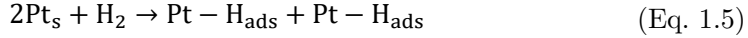


Figure 1.15: Triple-phase-boundary (TFB) cathode configuration ensuring gas, catalyst and ionic conductor close contact [150].

Anode in PEMFCs

Hydrogen oxidation reaction (HOR) takes place on Pt-based catalysts, which involves the adsorption of hydrogen onto the catalyst surface, dissociation of hydrogen molecule and electrochemical reaction to hydrogen ions, as indicated in Eq. 1.5 and Eq. 1.6, respectively [150].



These reactions are fast on Pt catalyst, and it is usually controlled by mass-transfer limitations. However, a major drawback is that it is required to work with pure hydrogen, since compounds such as CO, S and NH₃, even at trace concentrations, can cause Pt catalyst deactivation. Particularly, carbon monoxide is the main responsible of Pt catalyst poisoning in PEMFCs fuel cells [157]. Several studies have demonstrated that CO concentrations as low as 10 ppm can reduce the PEMFC performance by 50% at temperatures ranging 60-100 °C due to the strong interaction of Pt and adsorbed CO that diminishes the availability of Pt active sites [158].

Most of the hydrogen used in PEM fuel cells is produced by methane steam reforming by the reaction in Eq. 1.7, in which CO is also produced. Although the subsequent water gas shift reaction (Eq. 1.8) is usually carried out to enhance hydrogen production and diminish CO concentration up to 1%, there is still an urgent need to purify this hydrogen and decrease CO concentrations under 10 ppm. Moreover, even using novel Pt-Ru catalysts [158], [159], CO concentration should not exceed 50 ppm in order to warrant an appropriate catalyst's lifetime.



In order to decrease CO concentration up to admissible levels for Pt catalyst, several approaches have been studied, such as selective diffusion, selective carbon monoxide methanation or preferential oxidation (PROX). Likewise, adding controlled amounts of oxygen, around 1-4% O₂ into hydrogen stream, has also been studied as a way to preferentially oxidize CO [160]. However, oxidation of CO is slower than that of H₂, so added oxygen can also react with hydrogen producing water and diminishing the power output of the PEMFCs. Therefore, among the procedures abovementioned, preferential oxidation of CO in hydrogen-rich atmosphere arises as the most interesting technology to decrease CO concentrations up to few ppm.

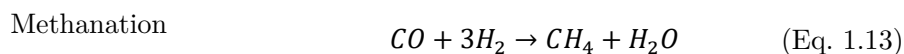
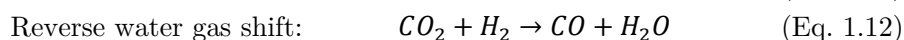
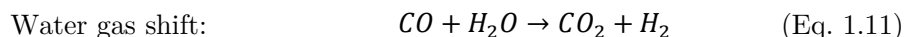
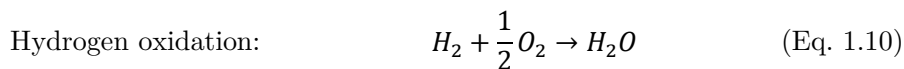
Furthermore, given the operating conditions at which this reaction occurs, the possibility of coupling this step prior to the PEMFC results appealing since it would avoid the need of hydrogen storage and it would also promote its use for automotive applications as well as for stationary and portable power generation [161].

1.10.3. CO-PROX

In CO-PROX reaction, oxygen is added to selectively oxidize CO (Eq. 1.9):



Since this reaction is usually carried out in hydrogen-rich streams, another side reactions can take place, such as hydrogen oxidation, water gas shift (WGS) and reverse water gas shift reactions (RWGS) or methanation, which are detailed in Eq. 1.10 to Eq. 1.13. Of all the mentioned side reactions, only WGS reaction is beneficial to the overall process whereas the rest of them consume hydrogen and therefore reduce the energy value of the reformat gas. Particularly, these reactions are favoured at high temperature and excess of oxygen in the stream.



Considering the side reactions that can take place during PROX process and the by-products involved, the main challenge of CO preferential oxidation is the development of effective catalysts, stable under the presence of water, CO, CO₂ and H₂, and with high selectivity for CO adsorption [162]. Apart from the catalytic active phase, other factors affect CO-PROX performance, such as the support and promoters used, as well as CO partial pressure, reaction temperature and H₂/O₂/CO ratios [163].

Regarding active phases used, noble metals, especially gold, and transition metal oxides have been studied for CO-PROX reaction:

Platinum-group metal supported on different solids presenting different acidity and textural parameters have been extensively studied in CO-PROX reaction [164], [165]. Since Pt is high sensitive to CO presence, supported Ru is a more appropriate candidate, moreover, it has been reported that it is highly active in a wide range of temperatures (80-160 °C) and also it inhibits methanation and RWGS reactions [163], [166].

Likewise, transition metal oxides such as CuO, ZnO or CeO₂ have shown remarkable activity in CO-PROX reaction. Among them, reducible oxides are preferred, since they promote oxygen mobility thanks to surface oxygen vacancies created by their redox pairs like Ce³⁺/Ce⁴⁺ [167], [168]. Also, combined catalysts containing both noble metal and transition metal oxides have been tested. For instance, Pt based catalysts have demonstrated a synergistic effect when iron oxide is added to the catalyst formulation thanks to the role of iron as oxygen reservoir [169]. Likewise, the incorporation of ceria to Pt catalyst has been reported to weaken CO adsorption over platinum active sites [170].

Special attention should be driven to Au-based catalysts, since they have shown remarkable activity in low-temperature CO oxidation reaction. The activity of these catalysts, as will be further reviewed in this chapter, is closely related to particle size [171] and nature of the solid acting as support, being reducible oxides like TiO_2 or CeO_2 the preferred ones given their ability to provide reactive oxygen to active Au sites [172]–[174]. Particularly, when supported on titania, the electron density on the surface of Au nanoparticles is increased due to electron transfer from titania, which favours CO adsorption and oxidation [175].

1.10.4. CO Photo-PROX

Even though gold-based supported TiO_2 catalyst has shown great performance in CO-PROX reaction, their catalytic activity could be further improved if the reaction is carried out using light irradiation thanks to striking photoactivity of titania semiconductor [176] and outstanding optical properties of nanosized gold like localized surface plasmon resonance, a phenomena that will be further explained in this section [177]. These properties opened up the opportunity to a new research line on the study of light-driven CO-PROX (CO Photo-PROX) reaction whose interest is ever-increasing, and **Table 1.9** collects some examples of gold-based titania catalyst used in photo-PROX reaction. Pioneer research in this field was carried out by Dai et al. [178], [179], who studied the influence of UV and visible light irradiation on PROX reaction with Au/TiO_2 catalysts, achieving not only greater activity but selectivity towards CO_2 obtention.

Considering Au/TiO_2 systems, it is generally accepted that a higher surface electron density of Au nanoparticles due to electron transfer from titania to gold, can enhance CO oxidation due to transfer of surface Au electrons to π^* orbital of CO, thus promoting the activation of CO adsorbed at Au sites [180]. In an attempt to ease electron transfer to Au surfaces, Yang et al. [181] introduced polyaniline (PANI conducting polymer) into the titania supported Au catalyst and reported that oxidation of CO was

remarkably enhanced, since PANI acted as electron transmitter to promote electron transfer from titania to gold by the formation of a TiO_2 -PANI-Au interface.

Given the high potential of these catalysts to selectively oxidize CO, the study of the influence of morphology, and co-catalysts seems a challenge to boost CO photo-PROX reaction feasibility. Thus, in this chapter, main features of titania and gold-titania nanosystems will be covered.

Table 1.9: Catalysts used in CO photo-PROX reaction

Catalyst	wt.% Au	Type of reactor	Reaction tempera- ture (°C)	X _{CO} (%)	S _{CO₂} (%)	Ref.
<i>Au/TiO₂</i>	1.0	Fixed- bed flow reactor	25	25	60	[182]
<i>Au/Meso-TiO₂</i>	0.47	Fixed- bed flow reactor	30	95	69	[183]
<i>Au/TiO₂@CuO</i>	1.0	Fixed- bed flow reactor	25	70	85	[182]
<i>Mo-MCM-41</i>	1.0	Closed system	20	98	98	[184]
<i>Au/TiO₂ nanorods</i>	1.0	Fixed- bed flow reactor	30	40	100	[185]
<i>Au/ZnCo₂O₄</i>	0.94	Fixed- bed flow reactor	25	61.7	64.5	[186]
<i>Au/TiO₂ - PANI</i>	1.0	Fixed- bed flow reactor	25	55	80	[181]

^aCO conversion. ^bCO₂ selectivity

1.11. Photocatalysis for water remediation: photodegradation of dyes

Water is an irreplaceable commodity not only for life but also for the development of innumerable socioeconomic activities like agriculture, stockbreeding, fishing, energy production or industries. Although it is widely abundant, the great demand for water to fulfil society's ever-increasing needs as far as population growth, urbanization and industrialization are concerned, has provoked the contamination of varied water bodies like lakes, rivers and other both surface and ground water resources. As a consequence, the world is experiencing a significant decrease of utilizable water supply and quality that constitutes a major concern issue to ecosystems and human health, since this environmental problem greatly varies in severity, spread and duration due to unique water properties like being a universal solvent with all states of matter aggregation present in nature. Moreover, climate change is also contributing to its aggravation due to water temperature rising, glaciers melting and intensification of water cycle [187].

It comes as no surprise that almost all water pollution is derived from anthropogenic activities involving chemical pollutants. These can be roughly classified into two categories: macro and micropollutants. The former comprise nutrients like nitrogen, phosphorous and natural organic constituents from varied origins like fertilizers or pesticides [188]–[190], that are present at concentrations of $\text{mg} \cdot \text{L}^{-1}$. Micropollutants category covers a wide variety of natural and synthetic compounds with complex chemical structures that are present in water bodies in trace concentrations, which may or may not be persistent or bio-accumulative, with potentially hazardous and/or synergistic environmental effects that may be acute or chronic, affecting aquatic and human life development.

1.11.1. Water remediation processes

Given the wide variety of chemical structures and concentrations of pollutants, the assessment of appropriate removal techniques for water

remediation is still a challenging task, and huge work has been dedicated to the quest of affordable, environmentally friendly and efficient treatments for contaminated water. Generally, they can be divided into biological, physical or chemical methods.

Biological methods involve the use of microorganisms (mainly bacteria) and enzymes that, through aerobic and anaerobic processes can reduce biodegradable organic matter and nutrients concentration as well as removing pathogens. Biological processes can be carried out in liquid suspension (suspended growth processes), biofilms (attached growth processes) or a combination of thereof [191]. However, the increasing need of recycling and recovering valuable products from water effluents has exposed the limitation of biological systems but, in turn, it has also promoted their integration with physical and chemical treatments, in different reaction systems such as microbial fuel cells (MFC) membrane bioreactors (MBR) or biological aerated filters (BAF), according to the type of water residue to be treated [192].

Physical treatments are applied to remove solid particles and non-water-soluble components like oils. Sieving, sedimentation, sorption techniques and filtration processes are included in this category. Adsorption methods present a low cost, simple technique for the removal of a great number of pollutants, but adsorbents' reusability and limited versatility has stepped membrane filtration technology such as nanofiltration, reverse osmosis or electrodialysis onto the podium as the most used and effective ones thanks to its wide range of application at small and large scales and its versatility, being able to remove solid particles, bacteria and even ions [193].

Chemical methods imply the use of chemical components and reactions to improve water quality. Applied since 1900s, coagulation/flocculation are considered indispensable treatment units in water remediation, since the efficiency of the next treatments highly

depends on this one. Moreover, this treatment present numerous advantages like plant design flexibility, adaptation to a wide range of water effluents and water flow and composition independence [194]. It consists in combining small particles or adsorbing dissolved organic matter into larger aggregates called flocs that separate from water phase and can be further removed in separation processes [195]. However, in some cases a more exhaustive treatment is needed to reach the degree of purity required for certain applications or to meet local environmental criteria and in this context conventional oxidation processes like chlorine oxidation has also been traditionally used, although it is well-known that chlorine can react with natural organic matter in water bodies forming carcinogenic halogenated disinfection by-products like trihalomethanes (THMs) [196]. This fact has motivated the development of advanced oxidation processes (AOPs), capable of replacing conventional technologies without generating toxic by-products.

1.11.2. Advanced oxidation processes for water remediation

AOPs processes involve the *in-situ* generation of short lifetime reactive oxygen species (ROS), like $\cdot\text{OH}$ radicals by means of chemical, photochemical, sonochemical or electrochemical reactions. These ROS are electrophilic, non-selective, highly oxidative species able to oxidize a wide variety of recalcitrant, refractory and toxic organic and inorganic compounds thanks to their high redox potential (2.8 eV), which accelerates the oxidation and degradation either by abstracting a hydrogen atom from aliphatic carbon or by adding a hydrogen atom to double bonds and aromatic rings [197]. Together with the most common $\cdot\text{OH}$ radicals, other ROS are superoxide radicals $\cdot\text{O}_2^-$, hydroperoxyl radical $\cdot\text{HO}_2^-$ and organic peroxy radicals ($\cdot\text{ROO}$) [198]. Examples of AOPs technologies are listed in **Table 1.10**, of which are worth noting $\text{Fe}/\text{H}_2\text{O}_2$ (Fenton reaction), $\text{Fe}/\text{H}_2\text{O}_2/\text{UV}$ (photo-Fenton reaction), O_3/UV and TiO_2/UV [199], [200].

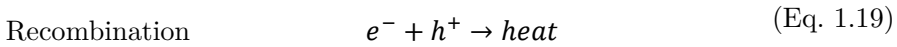
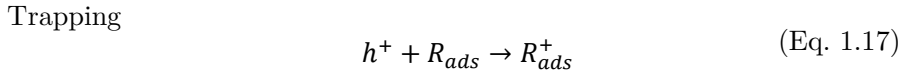
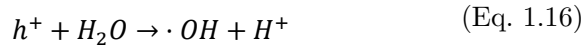
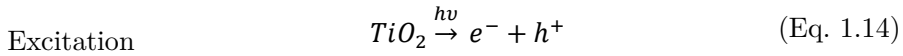
Table 1.10: Advanced oxidation processes (adapted from [200])

Photochemical processes		
Process	Irradiation wavelength (nm)	Non-photochemical processes
Water photolysis in vacuum ultraviolet (VUV)	< 190	Alkaline ozonation
UV/Ozone (UV/O ₃)	280-315	Fenton processes
Photo-Fenton	<450	Electrochemical oxidation
Heterogeneous photocatalysis with TiO ₂	380-400	Wet air oxidation

Especial attention should be driven to photochemical AOPs that combine the use of oxidizing agents and catalysts, since they represent an attractive, efficient treatment technology for water effluents containing high concentration of hazardous and nonbiodegradable pollutants that cannot be treated with conventional biological processes. These photocatalytic treatment processes are based on the initiation of $\cdot\text{OH}$ radicals by photons produced by electromagnetic radiation.

Briefly, the solid catalyst is excited by photons whose energy is enough to produce the movement of electrons from valence band to conduction band, therefore creating valence band holes (h^+) and conduction band electrons (e^-) that eventually migrate to the surface of the solid material and react with redox species present in the environment forming $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ reactive oxygen species [197]. In this context, many semiconductors like TiO₂, ZnO, Bi₂WO₆, Nb₂O₅ or CuS/ZnS, among others [201]–[204], have been studied, being TiO₂ semiconductor the benchmark catalyst for UV-based AOPs operating at mild conditions, i.e., atmospheric pressure and ambient temperature, thanks to its outstanding photocatalytic properties as well as its great thermal and chemical stability, non-toxicity, remarkable oxidation power and affordability [205]. Steps involved in

heterogeneous photocatalytic degradation over titania semiconductor have been thoroughly studied and can be resumed in equations Eq. 1.14 to Eq. 1.19, which can be described as follows: (1) excitation of TiO_2 particles giving rise to holes in the valence band and electrons in the conduction band with oxidative and reductive capacity, respectively, that migrate towards the surface of the semiconductor; (2) trapping of electron-hole charge carriers and (3) chain redox reactions with electron acceptor or electron donor adsorbed on TiO_2 surface or (4) recombination of photogenerated electron-holes in defect sites on the surface, thus end of the photodegradation process [206], [207].



1.11.3. Photo assisted AOPS for water remediation: dyes photodegradation

Considering water pollutants derived from industry, noteworthy is the contribution of strong and consolidated industries like textile, leather, paper printing, pharmaceutical, cosmetic and breweries food industries, all of them sharing a common factor: the use of dyes with complex and varied composition that are discharged in waste effluents. Nowadays, this market is expected to reach USD 15 billion in the next five years [208].

Textile industry has been reported to be the second most contaminant industry after oil sector, not only for the greenhouse effect

gases emissions derived from clothing production but also for microplastics and water effluents that are eventually discharged in water bodies. In fact, the United Nations Organization has estimated that this industry is responsible for 20% of world wastewater and 10% of CO₂ emissions [209]. Particularly, it should be appreciated that global dyes and pigments are an ever-increasing market that currently reports more than USD 36 billion and it is expected to continue growing with an annual growth rate of about 5% [210]. With more than 10000 dyes available nowadays, most of them absorbing in the visible light region, it constitutes an issue of major concern in terms of water pollution [208]. Even at trace concentrations, their bright pigmentation can provoke the reflection on sunlight entering water bodies, thus hindering the normal development of aquatic ecosystems and also causing water scarceness. Moreover, these compounds could be recalcitrant or eventually degrade to potentially carcinogenic substances [211], [212].

Synthetic dyes are in the forefront of dyes consumption, since they present remarkable advantages compared to natural ones: lower cost, higher resistance towards washing and heat, better solubility limits, enhanced brightness and stability, and wider colour range. Although there is vast variety of chemical structures, azo dyes like methylene blue, methyl red or methyl orange, represent over 70% of the total consumption [213] since they are widely used in textile, leather, paper and plastic industries.

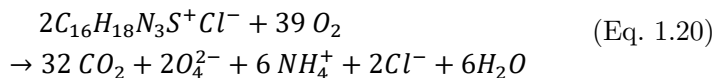
Methylene blue photodegradation

The photodegradation of textile dyes should be carefully considered since some dye molecules can act as photosensitizers thus covering real photocatalytic performance. In fact, Vinodgopal et al. [214] confirmed charge injection from excited acid orange 7 dye molecule to titania's conduction band through diffuse reflectance laser flash photolysis, but also reported that this reaction pathway is not the main one and that complete mineralization of the dye is not achieved by photosensitization process. Furthermore, for photosensitization to occur, several requirements need to

be attained: (1) it is necessary that the excited state of the dye molecule lies above the bottom of titania's conduction band; (2) a strong binding of the dye onto titania surface is needed; (3) back electron transfer to dye after charge injection should be minimal and (4) the dye molecule must have a strong absorption in the visible light region of the spectrum [215]. Considering all the conditions above mentioned, methylene blue (MB) could be used as model molecule for the assessment of the photo-response of titania based photocatalysts. In fact, International Organization for Standardization (ISO) test 10678:2010 [216] specifies a method based on methylene blue photodegradation in aqueous media under artificial UV light irradiation as the standard way to determine the photocatalytic activity of a certain surface. Thus, MB test is appropriate to test the water purification ability of photocatalysts. Moreover, this method is also valid to evaluate the specific photocatalytic self-cleaning activity of surface covered with respective coatings and it is in fact industrially used as a standard in Japan (JIS-R-1703-2:2007) [217].

Apart from its potential to assess photocatalytic performance, methylene blue dye also represents a water pollutant from textile- or paper-based industries. Moreover, it has been reported that high MB concentrations could have detrimental effects on human health, such as reproductive disorders, abdominal pain, nausea and vomit and more serious problems related to its mutagenic potential [208].

The pathway for MB photodegradation collected in **Figure 1.16** is well-known and it has been thoroughly studied by means of LC/MS and GC/MS analyses of the intermediate compounds, involving the conversion of the dye into harmless CO₂, nitrate, ammonium and sulphated ions [218]. Thus, the photodegradation reaction could be written as detailed in Eq. 1.20:



When performing MB photocatalytic tests, special attention should be paid to pH at which the reaction occurs in order to minimize adsorption of the dye onto the catalysts surface due to coulombic attraction forces.

Solid metal oxides suspended in aqueous solutions usually become hydrated, forming a hydroxyl monolayer on their surface. This layer may be protonated or deprotonated according to the pH of the solution, thus exhibiting ion exchange properties.

Point of zero charge (PZC) is defined as the pH value at which the net surface charge is zero. At solution pH values below the PZC of the semiconductor, the adsorption of the dye⁺ is likely to be negligible, since the oxide surface sites become protonated therefore MB⁺ adsorption is hampered.

Although it can be influenced by crystalline phases present, synthesis methodology or particle size, titania's PZC is estimated to be *ca.* 6.0 [219]. Thus, it has been reported that pH value of 5.5 is appropriate for methylene blue photodegradation in aqueous media when using titania-based photocatalysts [216].

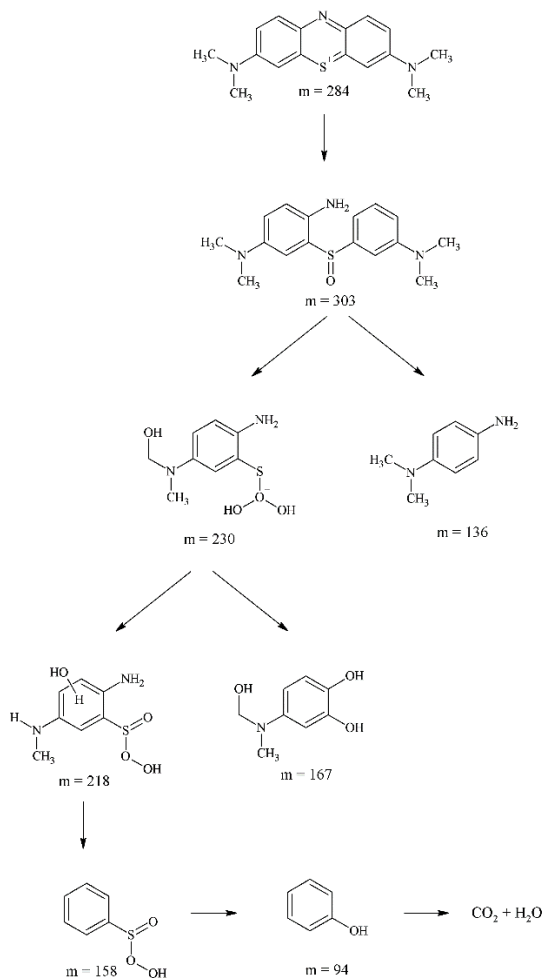


Figure 1.16: Methylene blue photodegradation pathway

1.12. TiO_2 photocatalytic performance

Taking into consideration the AOPs related processes described above in 1.11.2. section for titania semiconductor, it is clear that electron-hole charge carriers' generation and efficient separation of thereof are key factors in photodegradation processes. These can be improved by modifying different properties of the semiconductor which are responsible for its catalytic performance. In fact, titania's photocatalytic activity strongly depends on parameters like crystallinity, morphology (in terms of pore size distribution, porosity or specific surface area) and optical properties,

therefore one of the most common strategies to improve the photocatalytic performance relies on the synthesis of the semiconductor.

In respect to crystallinity, titania naturally exists as three polymorphs in nature, with different physical properties and photocatalytic behaviour. Anatase and rutile present tetragonal structure with four and two shared octahedrons of TiO_6 , respectively, whereas brookite forms an orthorhombic structure with three shared octahedrons (see **Figure 1.17**) [220]. Both anatase and brookite are metastable crystalline phases on the bulk form, and are exothermically and irreversibly transformed into rutile when heated above 600 °C [221]. Nonetheless, anatase is regarded as the most photoactive phase thanks to its improved charge-carrier mobility and greater number of surface hydroxyl groups [207].

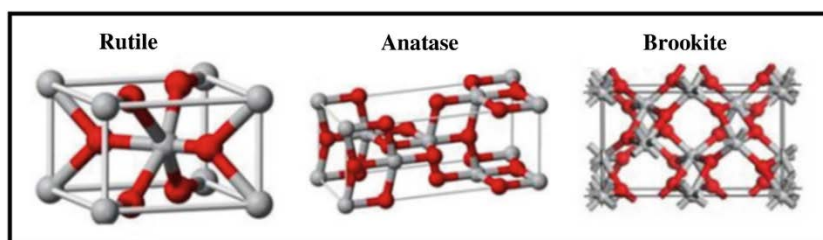


Figure 1.17: Titania polymorphs: rutile, anatase and brookite [222]

Regarding morphology, titania photocatalysts are commonly found in nanoscale structures like monodispersed nanoparticles of controlled diameter with considerable stability. In the case of the most photoactive phase, anatase, nanoparticles of 11 nm and smaller, result stable even at high temperatures. For particle sizes between 11 and 25 nm, brookite is the most stable phase, whereas for rutile phase, a good stability is achieved for particle sizes greater than 35 nm [222], [223].

Several synthesis approaches have been developed and optimised, being the most used one sol-gel method [224], but also worth mentioning chemical vapor deposition [225] or hydrothermal and solvothermal techniques using titanium alkoxides [226], [227], among others. According

to the synthesis method, titania can be found in one-, two- or three-dimensional structures like nanotubes, nanosheets or hierarchical structures and microspheres, respectively, each of them with unique properties to photocatalytic processes. For example, 1D structures with layered walls can be prepared by hydrothermal synthesis [226], obtaining nanotubular structures with high surface-to-volume ratio that promotes the reduction of electron-hole pairs recombination as well as enabling a high interfacial charge carrier transfer rate, whereas 2D structures, like nanosheets or nanofilms, can be obtained by sol-gel dip-coating techniques that, with low equipment and production costs, are able to produce nanostructures with great adhesion to substrates and highly smooth surface that make them excellent candidates for self-cleaning coatings [228]. Lastly, 3D structures can provide superior photocatalytic behaviour thanks to their potential ability to combine properties of the former morphologies, providing efficient diffusion pathways and greater carrier mobility [227].

Another strategy to enhance titania's photocatalytic activity through morphological modifications consist in increasing titania's specific surface area. Although the use of surfactants during the synthesis improves the specific surface area of titania semiconductor up to two times compared to P25 [229], it has been reported that the incorporation of titania nanoparticles in mesoporous structures enable both particle size control and greater dispersion of active sites due to a much higher specific surface area [230]. Zhou et al. [231] studied the incorporation of Ti in MCM-41 mesoporous material, which resulted in a considerable increase of specific surface area compared to TiO_2 prepared by conventional sol-gel method. Likewise, Shindo and co-workers [232] optimized a post-synthesis route to incorporate titania nanoparticles inside the pore channels of SBA-15, obtaining a more stable and active catalyst in the degradation of methylene blue dye than P25 titania counterpart.

Regarding the optical properties of titania, its wide band gap of 3.2 eV for anatase (considered the most photoactive phase) [233] and 3.0 eV for rutile [234], limits the operating radiation to the UV region ($\lambda < 387$ nm). Likewise, undesired electron-hole recombination dominates in the absence of electron acceptor or donor, resulting in low quantum yields and considerable energy loss [215]. Thus, great attention has been paid to reduce the band gap in order to operate in the UV-Visible region spectrum, as discussed in the next section.

1.13. TiO_2 optical properties and tuning

Despite the efficiency and environmental friendliness of AOPs, the high operating costs derived from the use of UV radiation has hindered their further development. Considering that just 8% of total solar spectrum consists in UV radiation, great attention has been paid to the use of the visible light scope, since it accounts for 40% of the total solar spectrum [235].

In this context, multiple efforts have been devoted to narrow titania's wide band gap, so that it is possible to operate with UV-visible radiation. Doping titania with both non-metals and metals is regarded as the most popular and efficient approach to decrease titania's band gap. In doping processes, the decrease of electron-hole recombination rates and the increase of the light absorption range are possible thanks to the defect states or the introduction of energy levels created between titania's conduction and valence bands [236], [237]. As already discussed, doping efficiency depends on several parameters like titania's morphology or crystalline phases present, but also on dopant concentration and distribution on titania's surface [238].

1.13.1. Non-metal doping

The use of non-metal dopants for improving titania's photo-absorption properties in order to harvest solar light has been subject of

study in computational chemistry and has effectively helped to understand the electronic structures and possible configurations of these non-metal-titania systems [239]. In this way, it has been reported that non-metal such as N, B, F or C doping can modify titania's cell parameters, affecting band edges or introducing intermediate energy levels that can decrease the energy gap value.

Among all non-metal dopants, nitrogen arises as the most promising one to promote visible light photoactivity, not only due to its synthesis versatility but also for its high stability [205]. Nitrogen presents an atomic radius comparable to that of oxygen and a low ionization potential, so the introduction of nitrogen into titania lattice is facilitated, with nitrogen occupying either interstitial sites (suggesting N-O bonding) or substitutional sites (involving N replacement of O in titania matrix) [205], [240]. The latter is preferred, since substitutional nitrogen is believed to decrease titania's band gap and also enhance visible light absorption [241]. Liu et al. [242] studied nitrogen doping in mesoporous TiO_2 , reporting that the substitution of nitrogen altered both the electronic properties and surface structure of TiO_2 , in which the former is responsible for light response range and redox power carriers and the latter for surface transfer of charge carriers. However, although a big deal of research has been devoted to the study of these structures, the improvement of low quantum efficiency and poor oxidative ability of photogenerated holes in N- TiO_2 is still a challenging task.

Boron doping has also been a spotlight, since it has been reported that boron atom tends to either replace oxygen or incorporate in interstitial positions in titania matrix, which provokes a red-shift in the absorption thus enhancing the photocatalytic efficiency [243].

Carbon is also one of most used non-metal dopants, since it can be incorporated into titania's structure in a wide range of concentrations. When carbon is introduced in titania network, localized extrinsic energy levels inside TiO_2 band gap are created. The optical transitions between

these levels and Ti 3d energy levels (main component of the conduction band edge) improve the absorption properties of pure titania [244].

1.13.2. Metal doping

A wide range of metals has been studied as dopants in titania structures, which can be organized in three main groups: transition, noble and rare earth metals. The activity of these doped structures are influenced by several parameters such as metal concentration, energy level of the metal within the titania matrix, electronic configuration at *d* energy level, distribution on the surface, electron donor density or incident light intensity [215].

1.13.2.1. Transition metal doping

Regarding transition metals, many of them present redox energy states within the band gap states on titania, thus, the use of these metals as dopants in titania structures would introduce an intraband state close to conduction or valence band edges that would extend absorption to the visible light scope. Among all transition metals, noteworthy is the doping with iron, given the Fe^{3+} ionic radius very similar to that of Ti^{4+} (0.79 Å and 0.75 Å, respectively), and its half-filled electronic configuration that serves as shallow traps [245]. Likewise, Mn has been also studied thanks to its ability to introduce defect levels into titania's forbidden gap [246]. Copper has also been reported as an enhancer of the photocatalytic activity of titania, since it can extend the absorption of titania to the visible region by forming doping states above its valence band caused by Cu 3d – Ti 3d optical transition [247], [248].

1.13.2.2. Noble metal doping

Their outstanding optical properties when nano-sized [249]–[251], like high absorption in a wide range of solar light as well as low cytotoxicity and reactivity at low temperatures [252] has motivated the use of precious

metals in photocatalysis. The enhancement in the photoactivity of titania semiconductor when noble metals are incorporated to the catalyst formulation was firstly reported by in water splitting reaction with Pt/TiO₂ by Sato et al. [253], and ever since a great deal of research has been dedicated to the study of these systems for a wide range of photocatalytic applications like water splitting, photo- oxidation and reduction reactions and photodegradation, with the aim to develop industrially scalable and sustainable processes. [249], [251], [252], [254], [255].

Two main phenomena are responsible for the photocatalytic enhancement of noble metal doped titania: Localized Surface Plasmonic Resonance and Schottky barrier formation.

a. Localized Surface Plasmonic Resonance (LSPR)

LSPR is a nanoscale phenomenon occurring in nanosized noble metals consisting in the absorption of photon energies of incident light at the resonance frequency of these nanostructures. This peculiar situation takes place in some metals that, as well as reflecting light, under appropriate conditions, light can travel in their metallic surface without losing contact with them, thus, light is somehow confined. Moreover, apart from its electromagnetic field, this light involves free electrons in the metal surface that are called superficial plasmons [256], [257]. When a superficial plasmon is confined to a particle whose size is similar to that of the wavelength of the incident light, the particle's free electrons participate in the collective oscillation, and it is called localized surface plasmon (LSP) (see **Figure 1.18**). LSP has two crucial effects: On the one hand, the electromagnetic near-field is greatly enhanced and, on the other hand, the particle's optical extinction has a maximum at the plasmon resonant frequency [258]. Interestingly, for noble metals this occurs at visible wavelengths and, predictably, it is highly influenced by particle size. For example, for gold nanospheres, the LSPR wavelength can be tuned over 60 nm changing particle size from 10 to 100 nm [259].

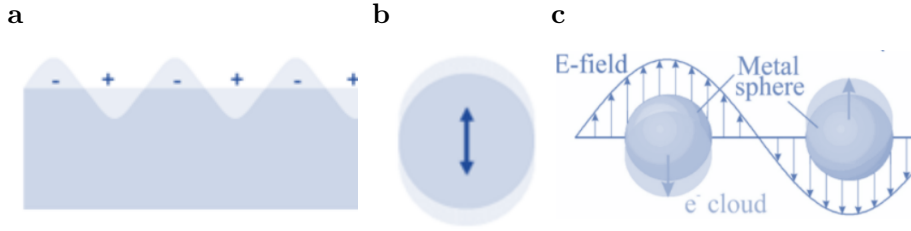


Figure 1.18: (a) Surface plasmon and (b) Localized surface plasmon and (c) Localized surface plasmon resonance (LSPR) [258], [260]

b. Schottky barrier

The Schottky barrier is a potential energy barrier for electrons formed at a metal-semiconductor junction that leads to a rectifying behaviour of the electrical contact. For an isolated metal, the work function (ϕ_m) can be expressed as the difference between the minimum energy required to free an electron for the metal surface (vacuum energy, E_{VAC}) and Fermi energy (E_F), i.e., it is the energy barrier to free space that prevents an electron at the Fermi level from scaping the metal [261].

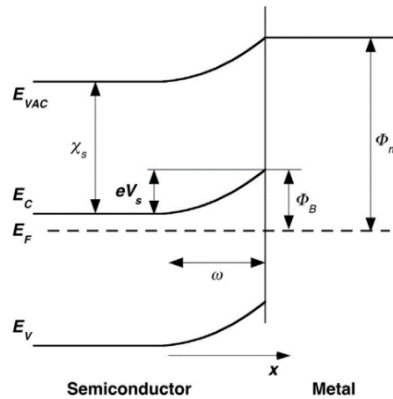


Figure 1.19: Schottky barrier formation at a metal-semiconductor interface. E_C and E_V stand for conduction and valence band minimum, respectively and ω is the thickness of the space-charge layer

When the metal is in close contact with a semiconductor, a Schottky barrier is formed, whose height (ϕ_B) equals to the difference between the

metal work function and the semiconductor conduction band electron affinity (χ_s), as depicted in **Figure 1.19** [262].

However, this theoretical model is not followed by most metal-semiconductor interfaces, since it depends not only in the metal work function but on a wide range of parameters like metallic dopant concentration or distribution. Nevertheless, the resulting potential that increases linearly from the edge of the depletion region up to the metal-semiconductor interface is usually referred as a Schottky barrier [263].

In the case of titania semiconductor, this phenomenon gains great interest especially when doping with noble metals. Noble metals present a Fermi level lower than that of titania [263], thus, electrons can be transferred from conduction band to metal particles and this barrier could promote the trapping of electrons in the metal, hindering their backflow to titania and therefore diminishing electron-hole recombination rate. It should be appreciated that Schottky barrier phenomenon is strongly influenced by the addition of a second metal, often alloyed with the main one, since it can decrease the metal work function and prevent recombination of charge carriers [255], [262], [264], which is one of the main drawback of titania semiconductor as a photocatalyst.

c. Gold doping

Among all noble metals, gold arises as the most promising candidate for photocatalytic processes operating at mild conditions (atmospheric pressure and moderate temperatures between 30 and 200 °C) [265], [266] since Haruta demonstrated their potential in CO oxidation by virtue of particle size manipulation and of the modification of the metal-support interaction architecture [267], [268]. Gold presents a peculiar behaviour due to charge transfer to and from the support, high resistance to oxidation, oxygen spill-over and role of low-coordinated gold atoms [260]. Moreover, gold can extend the operating irradiation scope to the visible light region

and it forms alloys with lower cost metals, improving its photocatalytic activity [255].

The photoactivity of gold nanoparticles (Au NPs) is strongly influenced by the synthesis methodology followed to obtain the nanoparticles as well as by their size. Although several approaches have been widely investigated, such as impregnation [269], deposition-precipitation [175], chemical vapor deposition [270] or surface functionalization [271], deposition-precipitation procedure arises as the most popular one, since it allows the modification of the nanoparticles' size by controlling pH and calcination temperature [272]. Regarding the size, it has been reported that titania photocatalytic activity improves with decreasing size of Au NPs and increasing surface-to-volume ratio [273].

Titania supported Au NPs have been extensively studied in the photocatalytic removal of water pollutants [274]–[276] as well as in oxidation reactions [172], [277], [278].

Although Au-doped titania has demonstrated great potential in a wide range of reactions involving water pollutants, noteworthy is the remarkable enhancement in the photodegradation of azo dyes like methylene blue or methyl orange, since Au NPs can attract electrons from the organic dye on the nanoparticles. Furthermore, light irradiation can excite the dye molecule that can inject their electrons to the substrate thus easing the formation of O^{2-} species [279]. For example, when Au NPs were supported on titania for photodegradation of the azo dye methyl orange, a 9-fold improvement in the reaction rate was observed operating under visible light irradiation [280].

Regarding photo-oxidation reactions, it has been reported that the enhancement in the photocatalytic performance could be related to the strong interaction between gold and titania that favours the electron transfer from Au to TiO_2 , thus increasing surface electron density of Au sites and promoting oxidation [265], [281]. Nevertheless, when using Au-

doped titania for oxidation processes that involves oxygen adsorption and activation steps, it must be taking into consideration that oxygen dissociation is believed to be inhibited on single gold crystals [282]. In other to overcome this drawback, one of the strategies comprises the use gold alloys with a second metal capable of adsorbing and activating oxygen. In this context, Au-Ag alloyed nanoparticles have been investigated, reporting a synergistic effect between these metals in CO oxidation [283]. However, apart from the increased cost associated with the use of two noble metals, Au-Ag based catalysts present serious reproducibility issues, since the control of particle size is complex [284].

Given the limitations when using noble metals alloys, research in this field has been dedicated to the obtention of sustainable and economic gold alloys with a lower cost and abundant second metal, like Fe, Cu, Co or Ni. In fact, they have shown synergistic effects not only in oxidation reactions like CO to CO₂, but also in pollutants removal [285], [286].

The behaviour of alloyed bimetallic catalysts supported on oxidic supports is complex and it depends on several parameters such as the type or metals and oxides used and the post-synthesis treatment at which they are subjected. For instance, it has been reported that the structure of bimetallic catalysts varies as a function of the support whether it is a carbon-based support or a refractory oxide. If refractory oxides are considered, the structure of the bimetallic particles is influenced by the metals used. Thus, in this case there is a preferential interaction between the more “base” metal and the support, which would eventually lead to preferential segregation of that metal to the refractory oxide interface, leaving the more noble metal with greater presence the catalytic interface [287]. Regarding the post-treatment, it has been reported that calcination with air lead to a core-shell structure with an enrichment of the less noble metal on the surface of the catalyst in an oxidized form. Conversely, when exposed to hydrogen, the formation of an alloy is favoured [286].

Although several bimetallic catalysts with gold and a second, less noble metal have been investigated, such as Au-Ni [288] or Au-Fe [289], Au-Cu catalysts arise as the most promising alternative to noble metal – noble metal bimetallic systems, since Cu is an abundant, low cost material that, when combined with Au, presents a higher resistance to oxidation, a great enhancement of the photoactivity of gold and an improvement of the bimetallic catalyst lifetime [290]. In fact, Au-Cu catalysts has shown their efficiency in a wide range of reactions like oxidation of propene [291], [292] or CO [293], [294], as well as in the hydrogenation of dimethyl oxalate [295] and CO₂ photo-assisted reduction to methane [296].

1.13.2.3. Rare earth metal doping

Given their abundant energy levels intrinsic to electron-photon transitions between $4f$ and $5d$ orbitals, rare earth noble metals are considered effective dopants to modify semiconductors structure as well as to improve its optical and electrical properties [297]. For instance, La doping has been reported to inhibit anatase to rutile transition, control crystal growth and increase the concentration of oxygen vacancies [298].

Cerium has risen special interest since it presents excellent physical and chemical properties. Considering the numerous advantages detailed below, it can be concluded that ceria could play a key role in photocatalytic processes.

It has low toxicity, high oxygen storage capacity (OSC) so it serves as oxygen buffer and it promotes oxygen mobility, as it can be found at two oxidation states, Ce³⁺ and Ce⁴⁺, conforming a redox pair that allows the shuttle between Ce₂O₃ and CeO₂ depending on the reducing and oxidizing environment. Moreover, nonstoichiometric CeO_{2-x} oxides can be formed in a reducing environment [299]–[301]. Considering the key role of oxygen in photocatalytic processes, cerium is a promising dopant for titania nanostructures.

Superficial Ce atoms can easily interact via weak coordination with electron-rich heteroatoms, such as nitrogen, which would result beneficial for catalytic reactions such as water pollutants remotion [302].

Even though the theoretical band gap of cerium oxide CeO_2 (ceria) is *ca.* 6.0 eV [303], its experimental band gap is close to that of most used semiconductors titania and zirconia, around 3.4 eV. This reduced band gap's origin is still a subject of debate, although it is believed to the transition occurs between fully occupied O 2*p* and empty Ce 4*f* states [299]. Xu et al. [304] reported that coupling ceria with titania suppressed electron-hole recombination by electron trapping at Ce^{4+} sites, thus improved photocatalytic performance in formaldehyde photodegradation. Likewise, Li et al. [305] reported a reduced the band gap of pure titania when doped with ceria, extending the photodegradation of 2-mercaptobenzothiazole to the visible light region.

1.14. Photocatalysis summary

Water pollution and clean energy production are two major issues the scientific community is facing nowadays. Photocatalysis have been proven as one of the most feasible and cost-effective strategies to overcome these problems, since reactions can be carried out at mild operating conditions and make use of incident solar spectrum, which is a vast, not enough exploited, renewable energy source.

A wide range of catalysts involving different morphologies, structures and optical properties have been investigated in energy production and water remediation processes, of which titania arises as the benchmark photocatalysis working under UV irradiation. However, the need of working under visible light irradiation to make the most of incident solar scope has promoted the quest of tuned titania structures with enhanced photocatalytic performance in the visible region. Band gap decreasing, hindering of electron-holes recombination or improved morphology are some

of the most popular strategies to improve titania's photocatalytic performance.

The use of gold nanoparticles has demonstrated a key role in the enhancement of titania's photoactivity, especially in photo-oxidation processes. With the aim of developing a sustainable, cost-effective gold-based catalyst, in this doctoral thesis the synthesis of a set of catalysts based on Au-Cu nanoparticles supported on Ti-containing SBA-15 mesoporous support has been studied, given the synergy of AuCu system in Ti-associated photocatalytic processes. The catalysts have been tested in preferential oxidation of CO in high-hydrogen stream under simulated solar light. In addition, considering the enhancement of the photocatalytic activity observed for these materials, they were also tested in the photodegradation of methylene blue dye in aqueous media under UV light irradiation. The results obtained with this research have been discussed in Chapter 7.

Likewise, considering the unique redox properties of cerium oxide and its physical and chemical properties, the study of the influence of morphology of ceria-titania structures in the photodegradation of methylene blue in aqueous media, both under UV light irradiation and simulated solar light has been covered in this thesis, which results have been collected in Chapter 8.

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2. OBJECTIVES

2. Objectives

In the present doctoral thesis, two main concerns modern society is experiencing have been addressed: on the one hand, the need of developing clean, renewable energy sources that help to reduce the heavy reliance on fossil fuels and, on the other hand, the urgency to unfold greener processes to palliate water pollution.

Regarding the first covered issue, several catalysts families based on transition and noble metals have been synthesized, fully characterized and tested in hydrodeoxygenation (HDO) reaction. Specifically, the main objectives related to HDO (chapters 4, 5 and 6) have been the following:

- Synthesis of Nb-based supported on SBA-15 materials with Ni, Fe and Co as co-catalysts. Evaluation of the role of the second metal added in the catalytic activity and selectivity to deoxygenated compounds in anisole HDO.
- Synthesis of mixed oxides derived from layered double hydroxides (LDH) containing Ni, Al and Ce obtained from Ce^{3+} and/or Ce^{4+} precursors. Assessment of the influence of Ce precursor on the obtention of LDH and LDH-derived mixed oxides on the catalytic activity and selectivity to deoxygenated compounds in anisole HDO.
- Synthesis of Pt- and Fe-based catalysts supported on SBA-15. Analysis of the role of Fe_2O_3 as an oxophilic and acid compound in the catalytic activity and selectivity to deoxygenated products in anisole HDO.

In order to fully understand the catalytic behaviour of the three prepared sets, crystalline nature, textural properties, morphology, acidic nature and surface chemical composition of all catalysts (and precursors, when required) were characterized by X-ray powder diffraction (XRD), N_2 adsorption-desorption isotherms, transmission electron microscopy (TEM), ammonia thermoprogrammed desorption (NH_3 -TPD) and X-ray

photoelectron spectroscopy (XPS). Other characterization techniques have been performed for some but not all catalysts, such as hydrogen thermoprogrammed reduction (H_2 -TPR), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and scanning electron microscopy (SEM).

With respect to the second discussed topic, two sets of photoactive catalysts based on gold and reducible oxide CeO_2 as dopants for titania-based nanostructures have been studied in photocatalytic processes carried out at ambient conditions. Thus, the main objectives of this topic (chapters 7 and 8) are the following:

- Synthesis of AuCu-based catalysts supported on Ti-containing SBA-15 support. Evaluation of the role of both the mesoporous titania structure and of the bimetallic nanoparticles in two photocatalytic reaction systems: methylene blue photodegradation under UV light irradiation and preferential oxidation of CO in H_2 -rich stream under simulated solar light.
- Synthesis of ceria-titania nanostructures with different morphologies. Study of the influence of morphology and ceria doping in methylene blue photodegradation under UV light irradiation as well as under simulated solar light.

Both photocatalysts families were characterized by XRD, N_2 adsorption-desorption isotherms, TEM, XPS and diffuse reflectance UV-visible spectroscopy (DRUV-vis) in order to assess the crystalline phases present, textural properties, morphology and metallic dispersion, surface chemical composition and optical properties, respectively. Additionally, RMN-ss was performed for AuCu supported on Ti-SBA catalysts and Raman spectroscopy and time-resolved photoluminescence (TRPL) for ceria-titania nanostructures.

3. MATERIALS AND METHODS

Summary

In this chapter, synthesis procedures, methods used for characterization purposes and catalytic reaction systems are detailed. Several tables and figures indicating reagents, solvents and gases are also included. In addition, brief theoretical foundation of the different characterization techniques studied can be found.

3.1. Chemical reagents for HDO reaction

Mesoporous support SBA-15 was synthesized with sodium silicate solution as silica precursor. Titanium oxide was incorporated after SBA-15 synthesis using titanium butoxide as Ti source. All reagents are commercially available and detailed information about brand and purity is listed in **Table 3.1**:

Table 3.1: Chemical reagents for the synthesis of SBA-15 support

Reagent	Molecular formula	Purity (%)	Commercial brand
<i>Sulphuric acid</i>	H ₂ SO ₄	95	VWR
<i>Sodium hydroxide</i>	NaOH	97	VWR
<i>Pluronic</i>	-	98.5	Aldrich
<i>Sodium silicate solution</i>	Na ₂ O(SiO ₂) _x · xH ₂ O	Reagent grade	Sigma-Aldrich
<i>Hexadecyltrimethylammonium bromide (CTAB)</i>	C ₁₉ H ₄₂ BrN	98	Sigma
<i>Titanium (IV) butoxide</i>	Ti(C ₄ H ₉ O) ₄	97	Aldrich
<i>(3-aminopropyl) triethoxysilane (APTES)</i>	C ₉ H ₂₃ NO ₃ Si	98	Sigma-Aldrich
<i>Ethanol absolute</i>	C ₂ H ₅ OH	100	VWR

Table 3.2 displays the chemical reagents and gases used for the synthesis of the HDO catalysts

Table 3.2: Chemical reagents for synthesis of HDO catalysts

Reagent	Molecular formula	Purity (%)	Commercial brand
<i>Iron (III) nitrate nonahydrate</i>	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	99	Sigma
<i>Ammonium tetrachloroplatinate (II)</i>	$(\text{NH}_4)_2\text{PtCl}_4$	99	Aldrich
<i>Silica, fused</i>	SiO_2		Aldrich
<i>Nickel nitrate hexahydrate</i>	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	97	VETEC
<i>Aluminium nitrate nonahydrate</i>	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	98.5	Dinâmica
<i>Cerium nitrate hexahydrate</i>	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	98.5	Merck
<i>Ceria ammonium nitrate</i>	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	99	VETEC
<i>Sodium hydroxide</i>	NaOH	99	Merck
<i>Terephthalic acid</i>	$\text{C}_8\text{H}_6\text{O}_4$	99	AcrosOrganics
<i>Cobalt (II) nitrate hexahydrate</i>	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	98	Sigma-Aldrich
<i>Niobium (V) oxalate hydrate</i>	$\text{C}_{10}\text{H}_5\text{NbO}_{20} \cdot \text{H}_2\text{O}$	19.9% Nb_2O_5 min	Alfa Aesar
<i>Oxalic acid dihydrate</i>	$\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	99.5	Scharlau Chemie

Reagents in **Table 3.3** were used for hydrodeoxygenation (HDO) reaction with the prepared catalysts.

Table 3.3: Chemical reagents for HDO reaction

Reagent	Molecular formula	Purity (%)	Commercial brand
<i>Anisole</i>	C ₇ H ₈ O	99	Fluka
<i>Decahydronaphtalene</i> (<i>cis-</i> and <i>trans-</i> isomers)	C ₁₀ H ₁₈	98	Alfa Aesar
<i>Dodecane</i>	C ₁₂ H ₂₆	99	Honeywell
<i>Carborundum, 1.68 mm</i>	SiC	100	Prolabo

Table 3.4 contains information about the gases used both for HDO catalytic tests and for characterization purposes.

Table 3.4: Gases for HDO catalytic tests and for characterization purposes

Gas	Molecular formula	Purity (%)	Commercial brand
<i>Helium</i>	He	99.9999	Air liquide
<i>Hydrogen</i>	H ₂	99.999	Air liquid
<i>Nitrogen</i>	N ₂	99.9999	Air liquide
<i>Ammonia</i>	NH ₃	99.9	Air liquide
<i>Synthetic air</i>	-	-	Air liquide

It is generally accepted that, in order to avoid mass and heat transfer diffusion issues, the catalysts' particle size should be one tenth of the reactor's inner diameter. Therefore, the catalyst's powders synthesized as below described were placed in a hydraulic press and exposed to 10 ton · cm⁻² pressure for five minutes to obtain a compressed tablet that was eventually milled and sieved between 1 mm and 0.85 mm.

3.1.1. Synthesis of SBA-15 support

SBA-15 was synthesized following the procedure by Cazalilla et al. [1]. First, 1 litre of H₂SO₄ 0.4 M and 25 grams of pluronic were stirred for 24 hours at ambient temperature. Once pluronic was completely dissolved,

1 gram of NaOH was added and stirred until dissolved. After, a known concentration solution of sodium silicate (6.73 vol.%) was added dropwise, forming a suspension that was kept with agitation for five days. The suspension was filtered and washed with deionized water, which removed the surfactant. The recovered solid was dry at 60 °C overnight and calcined in static air at 550 °C for six hours with a 10 °C · min⁻¹ heating rate.

Prior to Ti incorporation, synthesized SBA-15 was functionalized with (3-aminopropyl)triethoxysilane (APTES) in order to ease Ti incorporation, since it has been reported that mesoporous materials' pore structure can be modified within the nanometre range by means of organic groups grafting inside [2]. To this end, a well-known APTES volume (2.5 g per SBA-15 gram) was mixed with ethanol (50 g per SBA-15 gram) and SBA-15 was added afterwards. The suspension was kept in reflux for 24 hours at ambient temperature before being filtered, washed with ethanol and dried overnight at 60 °C.

Post-synthesis SBA-Ti with a nominal Si/Ti ratio of 3 was prepared using the method reported by Shindo et al. [3] using H₂O/Ti ratio of 2. In a typical procedure for 1 gram of SBA-15, 1 gram of a micelle solution of CTAB and 6.76 mL of ethanol was heated at 321 K for one hour, prior to grafted APTES-SBA-15 addition. Afterwards, 18.95 mL of ethanol and 0.19 mL of deionized water were added, and the solution was stirred for one hour and ambient temperature before adding 1.93 mL of titanium butoxide dropwise. The suspension was kept with agitation for two more hours at ambient temperature before filtering and drying at 60 °C for 48 hours. Finally, the recovered solid was calcined in static air at 550 °C for 5 hours with a 10 °C · min⁻¹ heating rate.

3.1.2. Synthesis of bimetallic Nb-based supported catalysts

For the synthesis of Nb based supported catalysts, SBA-15 support was used, synthesized using the same procedure described above. All

catalysts were synthesized by incipient wetness impregnation. First, the support was impregnated with a well-known volume of a niobium oxalate solution (0.1 M) and dried at 60 °C overnight before calcination at 450 °C for 2 hours with a heating rate of 10 °C · min⁻¹. Afterwards, in order to obtain FeNb, CoNb and NiNb catalysts, a certain volume of Fe, Co and Ni salts aqueous solutions, respectively, were added dropwise, in order to obtain a total metal loading of 12% and a metal/Nb molar ratio equal to 1. These precursors were then dried at 60 °C overnight and calcined at 450 °C for two hours with the same heating rate. Finally, the catalysts were pelletized with a particle size between 0.85 mm and 1 mm and reduced *in situ* using 100 mL · min⁻¹ flowing hydrogen at 450 °C for 2 hours, with a heating rate of 10 °C · min⁻¹.

3.1.3. Synthesis of Ni, Al, Ce derived mixed oxides derived from layered double hydroxides catalysts

Layered double hydroxides (LDHs) were synthesized by pH-controlled co-precipitation method described by Arias et al. [4], using the general LDHs formula $[M^{2+}_{(1-x)} M^{3+}_x (OH)_2]^{x+} A^{m-}_{x/m} \cdot H_2O$, with x value corresponding to 0.5 (mol) for calculations. Additionally, a molar Ni/(Al+Ce) ratio of 1.0 and with a partial replacement of Al³⁺ with Ce³⁺ and/or Ce⁴⁺ in molar percentages of 10% and 50% was applied.

In a typical synthesis, the solutions of the metallic salts were mixed in continuous stirring with NaOH as a precipitating agent and a terephthalic acid solution, keeping pH values at 6.3-6.8 and temperature at 50 °C. The resulting solution was then aged for 16 hours at ambient temperature, filtered and washed with deionized water and finally dried at 70 °C overnight to obtain the layered double hydroxides name as LDH-NAC-y,z, where NAC stands for Nickel, Aluminium and Cerium and y and z are indicators of cerium oxidation state (3 for Ce³⁺ and 4 for Ce⁴⁺) and cerium molar percentage added (z = 10%, 50%) , respectively. Thus, the five

samples prepared are referred as LDH-NAC-4,10 (Ce^{4+} , 10%), LDH-NAC-4,50 (Ce^{4+} , 50%) y LDH-NAC-3-4,50 (Ce^{3+} and Ce^{4+} , 50%).

In order to obtain the mixed oxides derived from the samples described above, they were calcined in static air at 500 °C for three hours with a heating rate of 10 °C · min⁻¹. These precursors were named c-NAC-y,z, being c the indicator of calcined samples. In this case, the prepared samples were named c -NAC-3,10; c-NAC-3,50; c-NAC-4,10; c-NAC-4,50; c-NAC-3-4,50.

Lastly, in order to obtain the active phase for the catalytic test, the calcined samples were reduced *in situ* using a hydrogen flow of 60 mL · min⁻¹, with a heating rate of 10 °C · min⁻¹ from room temperature to 500 °C and was kept at this temperature for 3 hours. The reduced samples are referred as NAC-3,10; NAC-3,50; NAC-4,10; NAC-4,50 and NAC-3-4,50.

3.1.4. Synthesis of Pt- and Fe-based catalysts

Fe_2O_3 , Pt and bimetallic counterpart catalysts were prepared by incipient wetness impregnation using aqueous solutions of the Fe and Pt metal precursors listed above (see **Table 3.2**). The incipient volumes for both supports (see **Table 3.5**) were determined by adding deionized water to 1 gram of dry support, mixing with a mortar until a gel texture is achieved.

Table 3.5: Incipient volumes for supports used for catalysts synthesis

Support	Incipient volume (mL · g ⁻¹)
Silica, fused	3
SBA-15	1.1

For Fe supported catalysts, well-known volumes of iron nitrate aqueous solution were added to the support in order to obtain iron loadings of 5 wt.%, 15 wt.% and 30 wt.%. Then, the catalysts were dried at 60 °C overnight and calcined at 500 °C for six hours with a heating rate of 1 °C · min⁻¹. These catalysts are referred to as 5Fe, 15Fe, 30Fe, respectively.

For Pt supported catalyst, the same procedure was carried out, in order to obtain a monometallic Pt catalyst with a loading of 1 wt.% Pt. Analogously, the catalyst was dried at 60 °C overnight and calcined in static air at 500 °C for six hours with a heating rate of 1 °C · min⁻¹ and is referred as Pt.

For bimetallic catalysts, Fe supported catalysts were impregnated with a Pt salt aqueous solution in order to obtain bimetallic catalysts with 1 wt.% and 5 wt.%, 15 wt.% and 30 wt.% Fe. After drying at 60 °C overnight, the catalysts were calcined at 500 °C for six hours with a heating rate of 1 °C · min⁻¹. These catalysts are referred as Pt5Fe, Pt15Fe and Pt30Fe, respectively.

3.1.5. HDO catalytic tests

Anisole hydrodeoxygenation was performed in continuous down flow in a high pressure, fixed-bed stainless steel reactor with an inner diameter of 9 mm and length of 30.5 cm (**Figure 3.1**). The catalytic bed consisted of 250 mg of pelletised catalyst, with a particle size in the range of 0.85-1 mm, together with 3 cm³ of SiC in order to reduce dead volume. The temperature was controlled with a type K thermocouple in close contact with the catalytic bed.

The reactions were carried out for six hours at 275 °C and 15 bar with a hydrogen flow of 30 mL · min⁻¹ and a feed flow (2 wt.% anisole in decalin) of 0.18 mL · min⁻¹ that was pumped with a Gilson 307SC HPLC piston pump. Prior to the catalytic test, the samples were reduced in situ when required following the requirements specified in sections 3.1.2. and 3.1.3. The liquid reactions products were collected every hour and analysed offline by gas chromatography using a Shimadzu GC-14B equipped with a TBR-14 capillary column, a flame ionization detector and an automatic Shimadzu AOC-20i injector. Dodecane was used as an internal standard. Gas phase products were also monitored by gas chromatography.

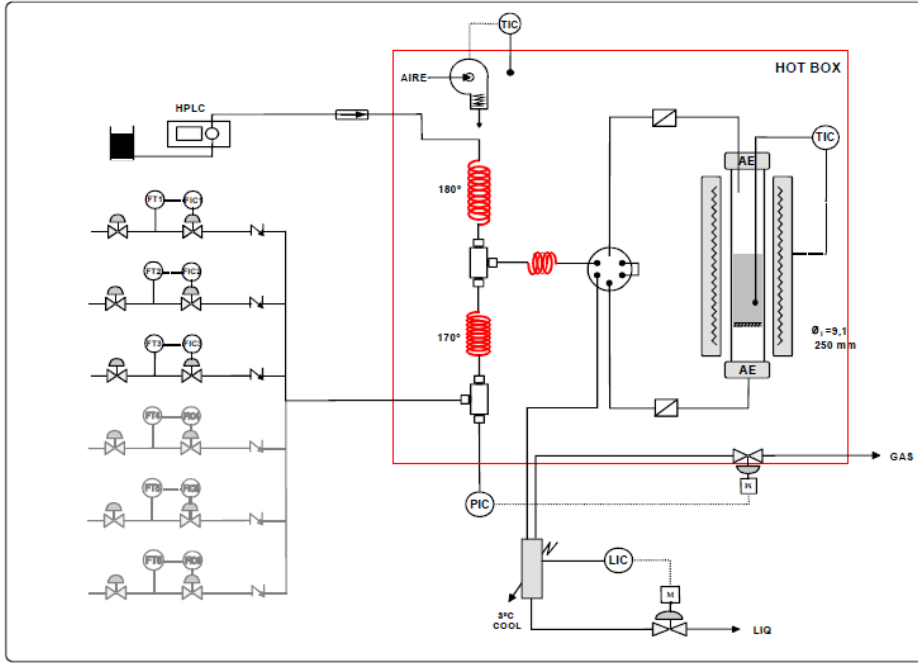


Figure 3.1: Scheme of Microactivity PRO reactor [5]

Total conversion was calculated as the ratio between anisole concentration at each hour and anisole initial concentration in the feed (Eq. 3.1):

$$X_{total} = \frac{C_A}{C_{A_0}} \cdot 100 \quad (\text{Eq. 3.1})$$

On the other hand, HDO conversion was calculated as the converted anisole minus the concentration of oxygenated intermediates, as follows (Eq. 3.2):

$$X_{HDO} = \frac{C_{A_0} - C_A - C_{oxy}}{C_{A_0}} \cdot 100 \quad (\text{Eq. 3.2})$$

Finally, the selectivity to deoxygenated products was calculated with Eq. 3.3:

$$S = \frac{C_{deoxy}}{C_{A_0} - C_A} \cdot 100 \quad (\text{Eq. 3.3})$$

3.2. Chemical reagents for CO photo-PROX and Methylene Blue Photodegradation reactions

Au and AuCu supported catalysts used for both reactions were synthesized using the chemical reagents listed in **Table 3.6** without further purification. The SBA-15 support was prepared as detailed in the previous section using reagents in **Table 3.1**.

Table 3.6: Chemical reagents for AuCu based photocatalysts

Reagent	Molecular formula	Purity (%)	Commercial brand
<i>Copper nitrate trihydrate</i>	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	99.5	Merck
<i>Sodium borohydride</i>	NaBH_4	98	Sigma-Aldrich
<i>Gold (III) chloride trihydrate</i>	$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	99.9	Sigma-Aldrich

Likewise, chemical reagents collected in **Table 3.7** were used for Ce-doped titania nanotubes and nanoparticles synthesis.

Table 3.7: Chemical reagents for CeTNTx and CeTNPx synthesis

Reagent	Molecular formula	Purity (%)	Commercial brand
<i>Titanium tetraisopropoxide</i>	$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$	97	Sigma-Aldrich
<i>Titanium oxide P25</i>	TiO_2	-	Aeroxide Evonik
<i>2-propanol</i>	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	99.5	Sigma-Aldrich
<i>Hydrochloric acid</i>	HCl	37	Sigma-Aldrich
<i>Ethanol absolute</i>	$\text{C}_2\text{H}_5\text{OH}$	> 99	Sigma-Aldrich
<i>Sodium hydroxide</i>	NaOH	-	VWR Chemicals
<i>Potassium hydroxide</i>	KOH	-	VWR Chemicals
<i>Nitric acid</i>	HNO_3	> 90	VWR Chemicals
<i>Cerium nitrate hexahydrate</i>	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	-	Sigma-Aldrich

3.2.1. Synthesis of mono- and bimetallic catalysts AuCu-based catalysts

For Au-based supported catalysts, the synthesis method reported by Liu et al. [6], with a gold loading of 1.5 wt.%. The procedure was followed analogously for both SBA and SBA-Ti support. For one gram of support, 15 mL of Milli-Q water were added in continuous stirring. A volume of 7.75 mL HAuCl₄ 10 mM solution was added, and the suspension was stirred for two hours in the absence of light using aluminium foil. The suspension was filtered and washed with Milli-Q water. Following, the recovered solid was redispersed in 15 mL of Milli-Q water, obtaining a yellowish suspension that turned reddish brown after the addition of 5 mL of NaBH₄ 0.2 M as reduction agent. The suspension was kept in dark with vigorous agitation for 30 minutes before being filtered and washed with Milli-Q water. The solid was dried at 60 °C overnight and calcined in static air at 500 °C for six hours with a heating rate of 10 °C · min⁻¹.

In the case of AuCu-based supported catalyst, the amount of precursor salts was calculated to obtain Au catalysts with a loading of 1.5 wt.% of Au, a total metal loading of 2.0 wt.% and an Au/Cu molar ratio of 1. For Au incorporation, the above detailed methodology was followed, except that before the drying step, the sample was again dispersed in 15 mL Milli-Q water, 7.75 mL of Cu(NO₃)₂ 10 mM solution were added and the suspension was kept with agitation for two hours at ambient temperature covered with aluminium foil. Then, it was filtered and washed for Milli-Q water before redispersion in 15 mL Milli-Q water. Once redispersed, 5 mL of NaBH₄ 0.2 M reduction agent were added, and the suspension was kept in dark with vigorous stirring for 30 minutes. Finally, the solid was recovered by filtration and Milli-Q water washing, dried at 60 °C overnight and calcined in static air at 500 °C for six hours with a heating rate of 10 °C · min⁻¹. In order to obtain the Au-Cu alloy, the catalyst was reduced with a 50 mL · min⁻¹ flow of pure hydrogen at 500 °C for two hours with a heating rate of 10 °C · min⁻¹.

3.2.2. *Synthesis of CeTNTx and CeTNPx catalysts*

3.2.2.1. Synthesis of Ce-doped TiO₂ nanotubes (CeTNTx)

Pure titania nanotubes were prepared following a two-step hydrothermal procedure. Firstly, titania nanopowder was obtained by a sol-gel process, in which 5 mL of titanium tetraisopropoxide (TTIP) were added to 15 mL of 2-propanol and 250 mL Milli-Q water. The solution was kept under vigorous stirring and aged at 70 °C for 10 hours, afterwards pH was fixed at 2 by adding a certain volume of 0.6 M HCl. The solid was recovered by centrifugation, washed with ethanol absolute and dried at 80 °C overnight before the second step of the synthesis: dehydration reaction under autogenous pressure. For this process, 30 mL of 10 M NaOH were added to 0.5 g of the dried nanopowder solid, transferred to a Teflon autoclave and kept at 130 °C for 24 hours. The obtained product was filtered, washed with Milli-Q water and 0.1 M HNO₃ and lastly with hot Milli-Q water until neutral pH was obtained. Finally, the recovered solid was dried at 80 °C overnight and calcined in static air at 400 °C for 2 hours with a heating rate of 1 °C · min⁻¹.

To obtain Ce-doped titania nanotubes samples, the same procedure was followed adding the appropriate amount of Ce(NO₃)₃ · 6H₂O aqueous solution to that of TTIP, 2-propanol and Milli-Q water, in order to obtain samples containing 0.25, 0.5, 1.0, 2.5 and 5 wt.% CeO₂.

3.2.2.2. Synthesis of Ce-doped TiO₂ nanoparticles (CeTNPx)

Titania nanoparticles were also prepared following the scheme of the hydrothermal procedure proposed by Wei et al. [7]: 1 gram of P25 titania was dispersed in 80 mL of 10 M KOH aqueous solution under vigorous stirring for 1 hour. The suspension was placed in a Teflon-lined autoclave and heated at 160 °C for 6 hours. The solid was recovered by centrifugation and washed with Milli-Q water, 0.1 M HNO₃ and hot Milli-Q water until neutral pH. The product was dried at 80 °C overnight prior to calcination

in static air flow at 400 °C with a heating rate of 1 °C · min⁻¹ and kept at 400 °C for 2 hours.

For Ce-doped counterparts, the required amount of Ce(NO₃)₃ · 6H₂O aqueous solution was added to the KOH solution to obtain CeTNPx catalysts with x = 0.25, 0.5, 1.0, 2.5 and 5 wt.% CeO₂.

3.2.3. CO Photo-PROX catalytic tests

Catalytic tests were performed at ambient temperature (approximately 30 °C, measured by a thermocouple inside de catalytic bed) and atmospheric pressure in a laboratory flow apparatus with a fixed bed reactor fed with a gas mixture containing 1.25% CO, 1.25% O₂ and 50% H₂ balanced with He, with gas hourly space velocity of 22000 h⁻¹. 150 mg of catalyst were placed in a quartz cell equipped with a cooling water system.

The catalysts were first tested in dark, covering the quartz cell with aluminium foil. For light-irradiated measurements, a visible light simulator lamp (Sunlight Solar Simulator, AM1.5G filter, 100 watts Xenon arc lamp, Abet Technologies, Milford, CT, USA) was placed into the surface of the quartz cell.

Oxygen and carbon monoxide conversions were calculated by means of their consumption with Eq. 3.4 and Eq. 3.5, where n stands for mol:

$$CO \text{ conversion } (\%) = \frac{n_{CO}^{in} - n_{CO}^{out}}{n_{CO}^{in}} \cdot 100 \quad (\text{Eq. 3.4})$$

$$O_2 \text{ conversion } (\%) = \frac{n_{O_2}^{in} - n_{O_2}^{out}}{n_{O_2}^{in}} \cdot 100 \quad (\text{Eq. 3.5})$$

CO selectivity was calculated from the oxygen mass balance following Eq. 3.6:

$$CO \text{ selectivity } (\%) = \frac{n_{CO}^{in} - n_{CO}^{out}}{2 \cdot (n_{O_2}^{in} - n_{O_2}^{out})} \cdot 100 \quad (\text{Eq. 3.6})$$

Lastly, the excess of oxygen factor, λ (Eq. 3.7), has been reported to have an optimal value of 2 for this reaction [8]:

$$\lambda = 2 \cdot \frac{n_{O_2}^{in}}{n_{CO}^{in}} \quad (\text{Eq. 3.7})$$

3.2.4. Methylene blue photodegradation catalytic tests

The prepared samples were tested in the photodegradation of the cationic dye methylene blue, at room temperature (20 °C) and atmospheric pressure. The catalytic tests under UV light irradiation were performed in a 100 mL Pyrex photochemical reactor equipped with a 125 W high pressure mercury lamp (model UV13F, Helios Italquartz, Cambiago, Italy) operating at wavelengths between 180-420 nm with a peak at 366 nm. A DeltaOHM HS2302.0 (Selvazzano Dentro, Italy) radiometer with pure water leaned against the external wall of the photoreactor was used to measure photon flux. For simulated solar light tests, a Sunlight Solar Simulator with an AM1.5G filter and a 100 watts xenon arc lamp (Abet Technologies) was used. To set the intensity of the light source to standard illumination conditions, a reference cell was used before each photocatalytic test.

An aqueous methylene blue solution $6 \cdot 10^{-5}$ M was placed in the photoreactor together with a fixed catalyst amount of $1.25 \text{ g} \cdot \text{L}^{-1}$. Before each photodegradation test, the suspension was stirred for 30 min in the dark covering the surface with aluminium foils in order to reach the adsorption equilibrium. It is generally accepted that the amount of the organic molecule adsorbed on the catalyst's surface is affected by the pH of the solution and depends both on specific surface area and the point of zero charge (PZC) of the material. Therefore, considering the composition of the materials used (titania presents a PZC around pH 6.0-6.5 [9] and ceria at *ca.* pH 7.2 [10]), pH was fixed at 5.5, since the adsorption of methylene blue via coulombic attraction is likely to be negligible in solutions with a pH below PZC values [11], [12]. After the adsorption period, the lamp was

switched on and aliquots of 2 mL of the suspension were collected using a 0.45 μm PTFE Millipore disc to remove the catalyst powder.

The dye concentration was determined by UV/Vis spectrometry using a Shimadzu UV-2450 UV/Vis spectrometer (Maston Technology, Dublin, Ireland). The maximum absorption of methylene blue is found at 664 nm [13], thus the degradation process was monitored following the evolution of absorbance at this maximum. In order to monitor the potential by-products formation, such as colourless leucomethylene blue, the overall UV-Vis spectrum was acquired.

It has been reported that, in systems where both adsorption and photocatalysis are present, the adsorption of the reactant generally occurs faster than the photocatalysis, being the former the rate-determining step [14], which justifies the necessity of a dark period before turning the light on, so adsorption-desorption equilibrium is reached.

Methylene blue's degradation pathway on TiO_2 -based materials is known with high reliability [15], [16], following a first order Langmuir-Hinshelwood mechanism (Eq. 3.8). It has been investigated by intermediate analysis by LC/MS and GC/MS, reporting that the organic dye is transformed into harmless CO_2 , ammonium, nitrate and sulfate ions [15].

$$\ln \frac{C}{C_0} = -k \cdot t \quad (\text{Eq. 3.8})$$

Where C is the reactant concentration after time t , C_0 represents the initial reactant concentration after adsorption equilibrium and k is a pseudo-first order rate constant, calculated as Eq. 3.9 using data from the non-stationary regime during the light phase:

$$k \text{ (min}^{-1}\text{)} = 2.303 \cdot \text{slope} \quad (\text{Eq. 3.9})$$

The reusability of the photocatalysts was evaluated by a 3-cycle recycling test, for which the solid catalyst was recovered by centrifugation,

washed with Milli-Q water and dried overnight after each photocatalytic cycle.

3.3. Characterization techniques

3.3.1. X-Ray Diffraction (XRD)

X-Ray powder diffraction was used to obtain both qualitative and quantitative information about the crystalline phases present in the catalysts. This is a non-destructive technique based on the analysis of the radiation diffracted by a solid material in which a monochromatic X-ray beam falls upon with a variable angle.

This technique is based on a scattering phenomenon involving a great number of atoms that are periodically arranged in a crystal. Thus, when X-ray are diffracted by a crystalline material, the re-emitted scattered electromagnetic waves only interfere with each other in certain directions, those in which the distance between the atomic layers is proportional to a positive integer of the radiation wavelength used (**Figure 3.2**).

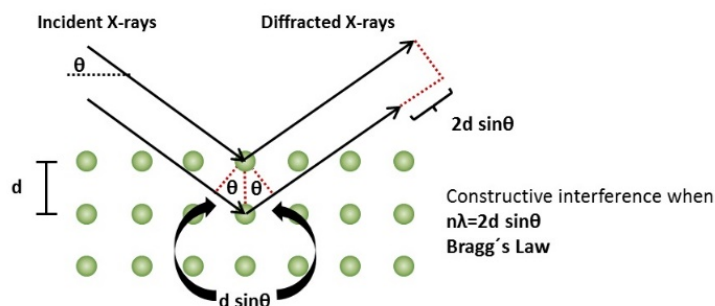


Figure 3.2: Schematic representation of the Bragg equation [17]

Bragg's law states that the incident and diffracted beams are coplanar, equally tilted at $(90^\circ - \theta)$ to the normal to the lattice plane [18]. This θ is known as Bragg's angle, and it is related to the wavelength of the incident X-ray beam and to the interplanar spacing.

The angles in which constructive interferences from a crystal lattice are produced are those that satisfy Bragg's equation (Eq. 3.10):

$$n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin(\theta) \quad (\text{Eq. 3.10})$$

Where n is a positive integer ($n = 1, 2, 3, \dots$) that represents diffraction order, λ is the incident radiation wavelength, d_{hkl} is the interplanar distance of crystalline planes and θ is the diffraction angle. That is to say, when the path length difference is equal to a whole number of wavelengths, the reflected waves are in phase and constructively interfere to form a diffracted beam in the given direction [18]. In any other case, scattered waves in different directions would eventually cancel one another.

Analysing Eq. 3.10, it can be noted that, given wavelength λ and interplanar distance d_{hkl} , several incidence angles can exist considering several diffraction orders (see **Figure 3.3**), which eventually allows the reformulation of Bragg's equation simply as in Eq. 3.11, which is the prevailed equation used in X-ray diffraction:

$$\lambda = 2 \cdot d \cdot \sin(\theta) \quad (\text{Eq. 3.11})$$

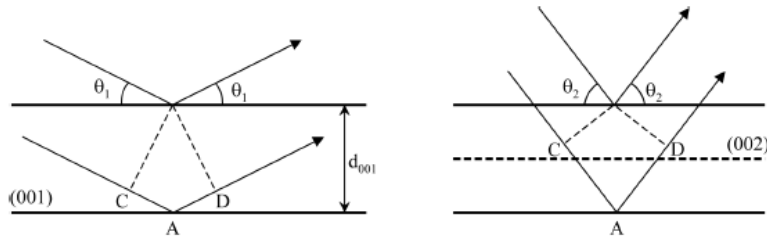


Figure 3.3: First order and second order reflections from (001) planes. Picture from [18]

X-rays have wavelengths similar to those of interatomic distances in crystalline materials, so it is possible to use this technique as a manner to study the crystalline structure and interatomic planes distances of a material. Materials identification using a diffractogram (radiation intensity vs θ angle) is a function of the diffraction lines positions and their relative

intensities, which are related to the material composition and also to the atoms positions inside the crystalline structure [19].

XRD measurements were carried out in a Shimadzu model XRD-600 diffractometer, at 40 kV and 30 mA, with a step size of 0.02θ , 1.0 s of time per step with an angle 2θ ranging from 5° to 70° . ICSD database was used to compare crystalline phases present in the samples.

Crystallite size was calculated from Scherrer equation (Eq. 3.12), where τ is the mean size of the ordered domains, θ is Bragg's angle, λ is the X-ray wavelength, β stands for full width at half maximum and K is a dimensionless shape factor with a typical value of 0.9.

$$\tau = \frac{K \cdot \lambda}{\beta \cos \theta} \quad (\text{Eq. 3.12})$$

3.3.2. Nitrogen adsorption-desorption at -196°C

Nitrogen adsorption-desorption isotherms at -196°C were performed in order to obtain information about the surface and textural properties (pore volume, pore size distribution and specific surface area) of the prepared catalysts.

Given the gas/solid interface, adsorption-desorption is the enrichment or depletion of one or more components in the interfacial layer [19]. This physical interaction between the solid material (adsorbent) and the gas molecules (adsorbate) in the gas phase (adsorbable) is named physisorption, and it is governed by attractive dispersion forces (Van der Waals forces). In these systems, when temperature is constant as a value lower than the gas critical temperature, the adsorbed gas volume per adsorbent mass unit is related to the gas relative pressure. Thus, by plotting the amount of adsorbed gas (usually nitrogen) at a fixed temperature (liquid nitrogen temperature, -196°C) versus the partial pressure applied, adsorption-desorption isotherms can be obtained. IUPAC isotherms classification [20] is by far the most referenced one, and it classifies isotherms

in six groups, depending on their shape, which is related to the adsorbible-adsorbent interaction as well as to the material's texture.

Specific surface area of a solid material can be calculated using different mathematical approaches like Freundlich, Langmuir or Brunauer-Emmett-Teller (BET), among others [21], being the former the most used one, and it assumes that the adsorption of nitrogen at its boiling point is monolayer-driven. Following this method, the monolayer value can be calculated with Eq. 3.13:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m \cdot C} + \frac{C - 1}{V_m \cdot C} \cdot \frac{P}{P_0} \quad (\text{Eq. 3.13})$$

$$C = e^{\frac{-(\Delta H_L - \Delta H_1)}{RT}} \quad (\text{Eq. 3.14})$$

Where P stands for equilibrium pressure, V is the volume of adsorbed gas per gram of solid, P₀ is the adsorbate's saturation vapor pressure, V_m is the adsorbate volume necessary to cover the solid with a monolayer and C is the BET constant, related to the net adsorption heat (Eq. 3.14). Equation Eq. 3.13 considers the solid's surface as a distribution of adsorption sites in equilibrium with the adsorbate, in which the condensation rate of molecules on empty places equals the evaporation rate of molecules in occupied sites. Taking into consideration the lineal range of Eq. 3.14 which occurs at $0.05 < P/P_0 < 0.35$ and knowing the slope value, it is possible to know the BET constant (C).

The nitrogen volume V_m is calculated with the y-intercept of the previous equation, $\left(\frac{1}{V_m \cdot C}\right)$, once C is known. BET area is obtained through the following Eq. 3.15:

$$S_{BET} = \frac{V_m \cdot N \cdot A}{V_0} \quad (\text{Eq. 3.15})$$

Where N is Avogadro number, A the transversal section of N₂ molecule (16.2 Å) and V₀ is the molar volume.

N₂ adsorption-desorption isotherms were carried out in a ASAP 2020 Micromeritics equipment at liquid nitrogen condensation temperature (-196 °C), thermostating the sample holders with a liquid nitrogen Dewar. Before nitrogen adsorption, all samples were degassed at 200 °C and 27 bar for 12 hours. Pore size distribution can be calculated by Barret, Joyner and Hellenda (BJH) method, considering the desorption branch of the isotherm, and total pore volume was calculated at a gas relative pressure of 0.95.

3.3.3. Ammonia Thermoprogrammed Desorption (NH₃-TPD)

The acidic properties of the prepared catalysts were studied by thermoprogrammed desorption of a base molecule. Ammonia was chosen as the target molecule thanks to its small size and strong basicity, able to neutralize both Lewis and Bronsted acid sites, which allows a quantitative determination of available acid sites in the catalysts. To this end, the equipment was previously calibrated with Ni(NH₃)₆Cl₂ (Aldrich).

The acidity assays were performed in a homemade apparatus equipped with a tubular oven and an online gas chromatograph with a thermal conductivity detector. In a typical experiment, 80 mg of catalyst powder were introduced in a U-shaped quartz reactor that was then placed inside a tubular oven with programmable heating rate, and 40 mL/min of pure helium were flowing continuously as carrier gas.

Figure 3.4. depicts the possible TPD-NH₃ schemes. In the case of non-reduced samples (**Figure 3.4 A**), for which the catalyst surface was cleaned in flowing He (40 mL · min⁻¹) raising temperature up to 500 °C with a heating rate of 10 °C · min⁻¹, and then cooled to 100 °C. Once the temperature was stabilized, pure NH₃ was adsorbed for 10 minutes and cleaned in He for half an hour. Lastly, NH₃ desorption was registered on-line with a Shimadzu GC-14B chromatograph, heating the sample up to 500 °C with a heating rate of 10 °C · min⁻¹. Helium was chosen as the carrier gas due to its higher thermal conductivity [22] compared to that of ammonia [23].

For reduced samples (**Figure 3.4 B**), the reduction was carried out in-situ, instead of the cleaning step. Hydrogen flow, temperature and heating rate were chosen according to the catalysts set, and they will be detailed in the discussion section.

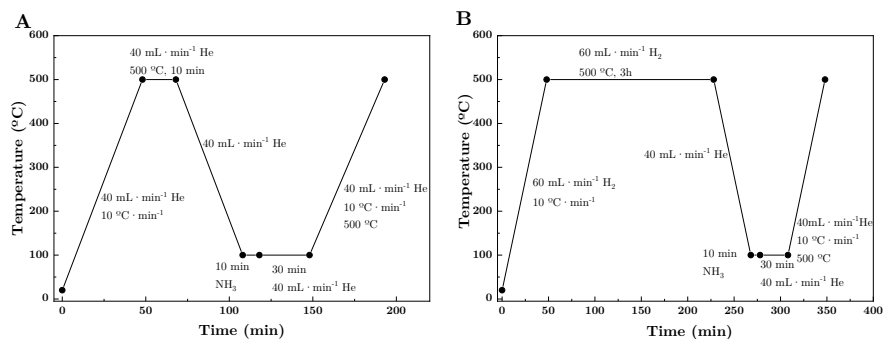


Figure 3.4: Ammonia thermoprogrammed desorption schemes for (A) non-reduced samples and (B) reduced samples

3.3.4. Hydrogen Thermoprogrammed Reduction (H_2 -TPR)

Hydrogen thermoprogrammed reduction experiments were carried out in order to study the catalysts' reproducibility, i.e., the potentially reducible species and their amount, the optimal reduction temperature as well as possible metal-support interactions and reduction kinetics.

The experiments were performed in a Autochem 2920 Micromeritics equipment. Typically, the scheme in **Figure 3.5** was followed: 400 mg of the sample was cleaned with flowing Ar up to 100 °C, with a heating rate of 10 °C · min⁻¹ for 30 minutes. Then, the sample was cooled at 45 °C before starting the reduction process with 50 mL · min⁻¹ of H₂/Ar (10% H₂) gas mixture and heating at 10 °C · min⁻¹ up to 900 °C.

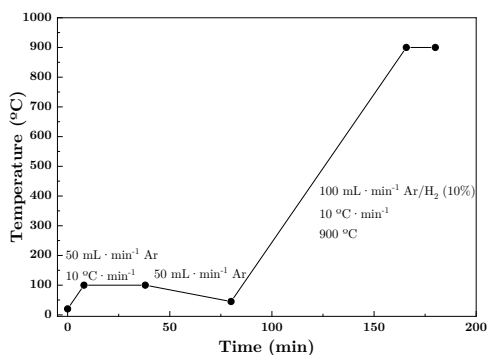


Figure 3.5: Hydrogen thermoprogrammed reduction scheme

3.3.5. X-Ray Photoelectron Spectroscopy (XPS)

Thanks to its versatility, high superficial sensitivity and applicability, XPS is one of the most used techniques in catalysis and materials science, since not only is it possible to qualitatively identify the elements present on the surface of a material, but also it provides information about their oxidation state and their chemical environment. Moreover, semiquantitative analysis can be performed.

The physical principle of XPS technique is the photoelectric effect (**Figure 3.6 (a)**). When a sample is bumped with a monochromatic X-ray beam with an energy higher than the binding energy of the sample atoms, the electrons of these atoms are ejected from the sample with a kinetic energy that is characteristic of each element, and its value is the one obtained from (Eq. 3.16), i.e., the difference between the photon energy, the binding energy (characteristic of the element) and the work function of the spectrometer, ϕ , that can be approximated as a constant specific for each equipment.

$$E_c = h\nu - BE - \phi \quad (\text{Eq. 3.16})$$

In addition to this process, another phenomenon can take place, called Auger emission (**Figure 3.6 (b)**), that implies the emission of a second electron (Auger electron) as a consequence of the relaxation of

another electron from superior to inferior layers, releasing the excess energy through the emission of this Auger electron.

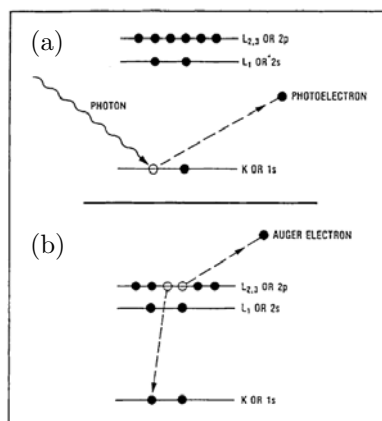


Figure 3.6: (a) Photoelectric effect (XPS emission) and (b) Auger emission process [24]

XPS spectrum is the graphical representation of the number of electron counts versus the binding energy of inner levels of the atoms present in the sample. The analysis of the spectral peaks obtained with the XPS spectra allows elemental identification and provides information about both the oxidation state of the elements and the chemical environment, since the interactions between the different elements that exist in the sample as well as charge transfer provoke changes in the kinetic energy with which electrons are emitted, thus modifying the binding energy observed in the XPS spectra. In some cases, it is even possible to study the coordination state of some elements [1]. Also, it is possible to do a semiquantitative analysis considering the spectral peaks' areas, that are related to the amount of element present in the sample.

XPS measurements were carried out in a PHI 5700 Physical Electronics spectrometer, with non-monochromatic Mg K α radiation ($h\nu=1253.6$ eV) equipped with a hemispheric multichannel electron detector Electronics 80-365b. High resolution spectra were collected with PHI ACCESS ESCA-V6.0 F software and a constant step mode of 29.35 eV with an analysis area of 720 μm diameter. Binding energy values were referred

to C 1s peak of adventitious carbon contamination layer (284.4 eV) and the error in binding energy values was estimated to be ± 0.1 eV. The chamber pressure was kept under $5 \cdot 10^{-6}$ Pa. Data were analysed with Multipak v8.2b software considering Gauss-Lorentz type curves.

3.3.6. Scanning Electron Microscopy (SEM)

In Scanning Electron Microscopy (SEM), an electron beam falls upon the sample and allows to study it locally through the formation of a high-resolution image that provides information on its chemical, textural and morphologic properties.

In a SEM equipment, the electrons emitted by the tungsten filament are conducted through a column that operates at high vacuum thanks to electromagnetics lenses (condenser and objective lenses) and apertures that decrease the electron beam diameter up to a spot beam (**Figure 3.7**). This spot beam scans the surface of the sample and interacts with it producing, among other effects such as X-Ray and Auger electrons, secondary and backscattered electrons that can be collected by an appropriate detector in order to create an image that reflects the superficial properties of the sample.

Secondary electrons are those emitted by the sample due to inelastic collisions of electrons in the inner orbitals of the atoms in the sample. As these electrons are superficial, their energy is very low, thus they provide information about the sample's topology. On the other hand, backscattered electrons are those electrons from the incident beam that are elastically scattered. As this scattering depends on the atomic number of the atoms in the sample, these electrons are used to obtain a superficial composition mapping of the sample [25].

SEM images were obtained with a scanning electron microscope TESCAN MIRA3 LMU at 10 kV

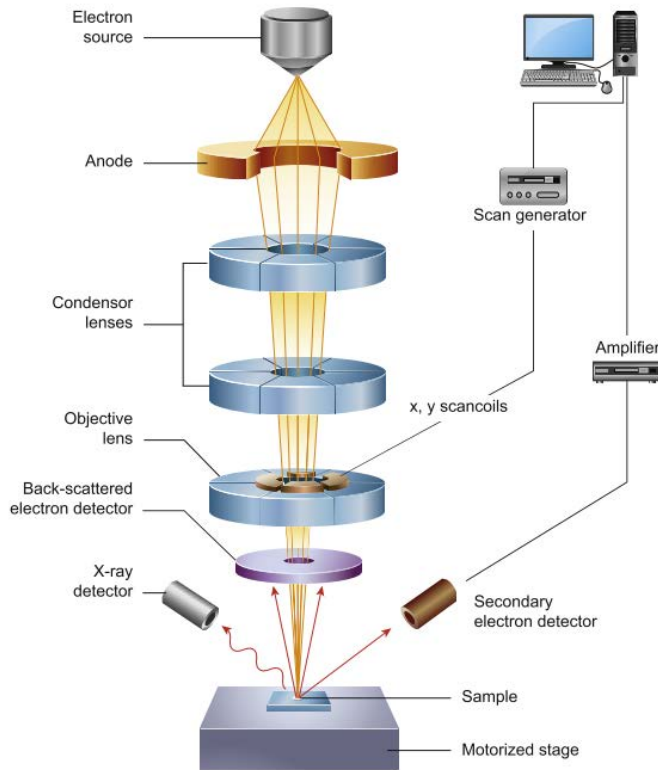


Figure 3.7: Conventional SEM optics [26]

3.3.7. Transmission Electron Microscopy (TEM)

Transmission electron microscopy technique is based on the physical-atomic phenomena that occurs when an accelerated electrons beam under high voltage (20-200 kV) collides with a sample. This electron beam is produced in an electron gun that can be thermionic (filaments made of tungsten or lanthanum hexaboride) or field emission [19]. High vacuum is required in order to avoid the dispersion of the electron beam, which is oriented by means of electromagnetic condenser lenses in order to attain optimal coherence (see **Figure 3.8**).

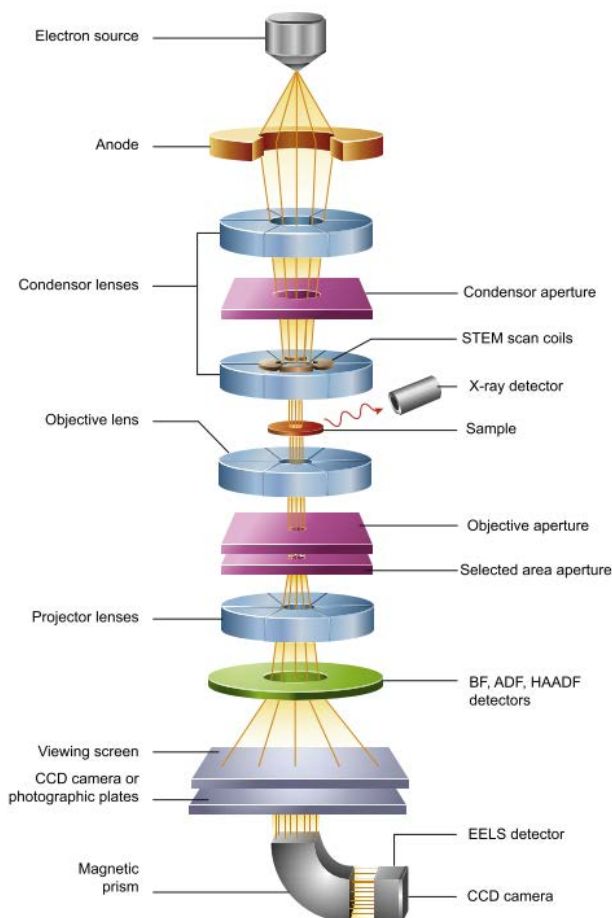


Figure 3.8: Schematic of core composition of a TEM microscope [26]

When electrons interact with the atoms in the sample, different processes occur, generating signals directly related with the atomic structure of the sample (see **Figure 3.9**). Elastic interactions are those in which the electron beam's path is altered but not its kinetic energy. Contrary, inelastic processes change the electrons beam direction and part of its energy is transferred to the sample, exciting its atoms to higher energy levels. Lastly, radioactive processes occur when incident electrons are slowed down by electrical repulsion and energy is loss as radiation (photons). Several techniques can be extracted of these interactions, as shown in **Figure 3.9**, which allows the study of morphology, dispersion, composition, inner structure, crystalline interfaces and even local defects in the atomic net.

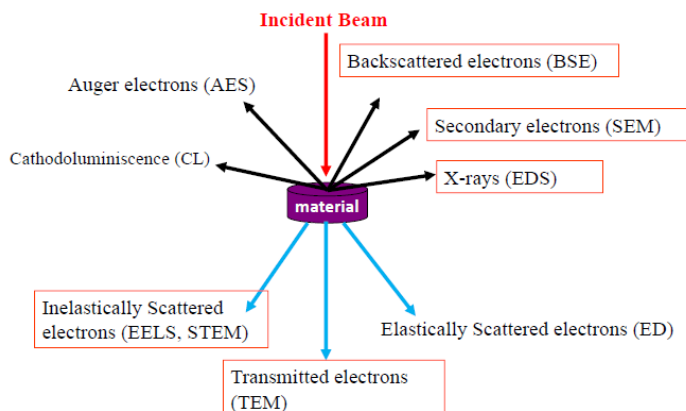


Figure 3.9: Radiation-matter interactions

A TALOS F200x transmission electron microscope was used to obtain high resolution micrographs of the prepared materials. TEM analyses were performed at 200 kV and 5.5 A and STEM ones with a HAAD detector working at 200 kV and 200 nA. EDX Super-X system with four X ray detectors and a X-FEG beam was used for microanalysis in order to study the local composition of the samples. For the sample preparation, a small amount of material was put on a lacey carbon-coated Cu grid. ImageJ software was used for particle size measurements.

3.3.8. X-Ray Fluorescence Spectroscopy (XRF)

X ray fluorescence spectroscopy was used to determine the chemical composition of the prepared catalysts. The fundamentals of this technique are based on the fact that, when a sample is excited using an X-ray beam, the electrons bounded to the innermost orbitals can be ejected from the atom, leaving it in an instable energetic situation. In order to stabilize the atom, electrons from the outer orbitals occupy the generated vacancies, and the excess energy resulted from this transaction is dissipated as a photon with a wavelength equal to the energy difference between the two involved orbitals. This radiating secondary emission is called X-Ray fluorescence, and each element is characterized by a unique set of absorption and emission

energies (Moseley's law), thus elemental analysis both qualitative and quantitative can be obtained with this technique [27].

Elemental analysis of the catalysts was performed in an X-Ray fluorescence microscope Shimadzu EDX-720 (ADXP Rh 60kV LiF200 PET AX03 LiF220).

3.3.9. Differential Thermal / Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used to study the mass gains or losses of a sample as a function of temperature, so information about the thermal stability, composition of the sample and final residue can be obtained. On the other hand, differential thermal analysis consists of comparing the sample's temperature with the one of a reference material like Al_2O_3 , in order to detect changes in thermal capacity, which are associated to phase transitions as well as to endothermic or exothermic thermal processes [19].

Thermogravimetric experiments were carried out in a Perkin Elmer STA 6000 equipment, from 30 to 800 °C at a rate of $10\text{ °C} \cdot \text{min}^{-1}$ and a flow of $20\text{ mL} \cdot \text{min}^{-1}$ of synthetic air.

3.3.10. Gas chromatography (GC)

Gas chromatography was used to analyse the reaction products obtained by comparison of the chromatograms obtained in each reaction time with those of the calibrated expected compounds. It is based on the separation of the components of a sample, allowing their identification through their retention time given certain heating conditions and quantification thanks to the peak areas in the chromatogram. When the sample is injected in the GC equipment, it volatilizes and enters the capillary column. The different components of the sample are then swept around by a carrier inert gas (He, Ar or N_2 usually) and they interact with the stationary phase. These interactions give rise to the separation of the components that exit the column at different and characteristic times that depends both on the column type and the heating rate [19].

A Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a TRB-14 capillary column was used to analyse liquid samples from HDO catalytic tests. Typically, the sample was diluted in the reaction solvent and 2 μL were injected. Injection port and detector temperature was 250 $^{\circ}\text{C}$.

3.3.11. Diffuse Reflectance UV-Vis (DRUV-Vis) spectroscopy

A reflectance spectrum is obtained by the collection and analysis of surface-reflected electromagnetic radiation as a function of frequency or wavelength. Considering textured surfaces like powders, diffuse reflection occurs, which implies the scattering of the incoming radiation due to the irregular surface [28]. Thus, if the material presents electronic energy levels separated by energy in the visible light scope, when irradiated, it may absorb that specific energy, causing the migration of electrons from the conduction to the valence band, which eventually causes a decrease of light at that particular energy.

The technique was used to determine the band gap of the prepared photocatalysts by collecting DRUV-Vis spectra with a Perkin Lambda 35 UV-Vis spectrophotometer equipped with Labsphere RSA-P3-20 integrating sphere accessory. Wavelength ranged from 200 to 800 nm using a mercury lamp for UV radiation and a tungsten one to cover up the visible light scope. The absorption coefficient α was calculated using Eq. 3.17, where T is the measured transmittance and d is the optical path length. Band gap energy (E_g) was calculated from the intercept of the tangent to the absorption curves in the graphical representation of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$), where h stands for Planck's constant and ν is the frequency (s^{-1}).

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} \quad (\text{Eq. 3.17})$$

Measures were performed in the Research laboratories of the Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, Italia.

3.3.12. Raman Spectroscopy

Raman spectroscopy is a non-destructive technique that provides a unique spectrum for each molecular system which gives detailed information about chemical structure, structural changes like conformation or orientation, as well as intermolecular interactions.

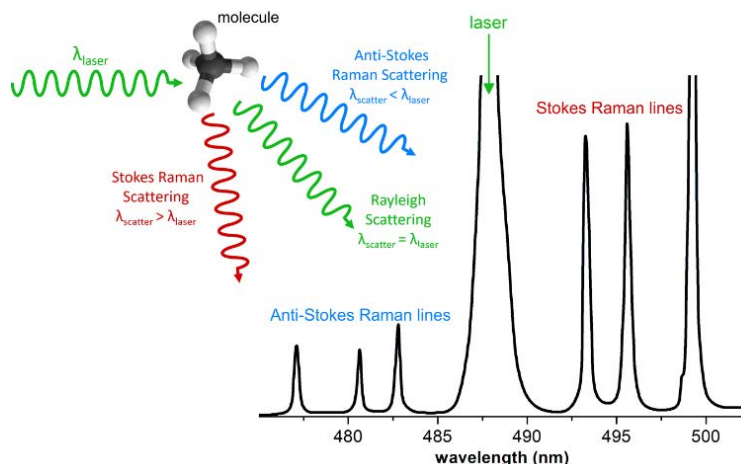


Figure 3.10: Stokes, Rayleigh and anti-Stokes Raman scattering

This characterization technique is based on the interaction between photons in the incident radiation and chemical bonds in the sample. When light falls upon the sample, the atoms or molecules conforming the sample elastically scatter this incident light at the same wavelength as the light source, which is called Rayleigh scattering (see **Figure 3.10**). However, a considerably small amount of this incident light is scattered at different wavelength (one dispersed photon for every 10^6 - 10^8 incident ones), which depends on the chemical structure of the atoms or molecules in the sample

[29]. This effect is known as Raman scattering, which in turn, as depicted in **Figure 3.10**, can be divided into Raman Stokes, when the released energy is less than the absorbed one thus wavelength is increased and radiation frequency is decreased; or Raman anti-Stokes when more energy is released than absorbed, which results in a diminishing in wavelength and conversely in radiation frequency [19].

Thus, the Raman spectrum in **Figure 3.10** represents these phenomena plotting the scattered optical intensity as a function of the wave number (cm^{-1}), obtaining a main band, called Rayleigh band, and two series of secondary bands, symmetrically positioned, corresponding to Raman Stokes and anti-Stokes.

Raman spectra were recorded using a WiTec CRM-200 microRaman system equipped with an Olympus LMPlanFL 20x/0.40 objective. The excitation laser wavelength was 633 nm and the laser power on the samples was kept at 1 mW.

3.3.13. Time resolved Photoluminescence Spectroscopy (TRPL)

Time-resolved photoluminescence (TRPL) spectroscopy is a powerful technique to study excited charge carrier recombination phenomena in bulk semiconductors or photo-active molecular systems. After illuminating a sample with a pulsed light source, the emission process involves both non-radiative and radiative decays from excited to basal states of the studied system. This decay in photoluminescence can take from picoseconds to microseconds, depending on the nature of the excited state (singlet or triplet states), which would eventually give rise to fluorescence or phosphorescence, respectively, thus, interesting information about chemical changes affecting the emitters can be obtained. The main advantage of time-resolved photoluminescence in contrast to spectrally resolved photoluminescence is that the former is insensitive to ambient light, since any continuous light gives a insignificant contribution to the signal as it is uncorrelated with the excitation pulse [30].

TRPL experiments were recorded using an FLS980 photoluminescence spectrometer from Edinburgh Instruments, which is equipped with a high-speed photomultiplier tube. The samples were excited with 250 nm UV light from a microsecond Xe flashlamp and the decay spectra of sample emission at 400 nm were collected in CeTNTx–water dispersion both before and after mixing with MB.

3.3.14. Solid state nuclear magnetic resonance (ss-NMR)

Solid-state nuclear magnetic resonance is one of the most powerful, non-destructive characterization techniques that provides qualitative and quantitative information of solid materials, in terms of structural resolution, composition and chemical environment, characterized by the presence of anisotropic interactions.

Nuclear magnetic resonance phenomenon can be exclusively observed in samples containing elements with non-zero overall spin value ($\vec{S}$), which is associated with a non-zero nuclear magnetic dipole moment ($\vec{\mu}$) via the relation in Eq. 3.18, in which γ is the gyromagnetic value, characteristic of the different types of nuclei:

$$\vec{\mu} = \gamma \vec{S} \quad (\text{Eq. 3.18})$$

The observation of ss-NMR phenomenon is related to the interactions between an external magnetic field and the nuclei magnetic moments that, according to the different possible orientations, give rise to transitions between nuclear spin levels, so-called Zeeman effect. In the case of a single atom, one could consider a nuclei with spin $\frac{1}{2}$, for which the quantum number m can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. Under the influence of an external magnetic field ($\vec{B}_{ext}$), the spins can get aligned in favour or against it, as shown in **Figure 3.11**. As the energy difference ΔE is quite small, nuclei magnetic moments tend to align with the external magnetic field occupying the minimum energy level and, as the transitions take place in the radiofrequency scope of the spectrum, this energy difference is determined

by Boltzmann distribution. Another consequence of this small ΔE is that thermal agitation tends to equilibrate occupancies in different energy levels, resulting in an occupied superior energy level [31]. Therefore, energy variation and hence radiation frequency are proportional to the external magnetic field, so radiation with a quantized energy equal to ΔE leads to spin inversion (spin relaxation), then resonance condition is attained (Eq. 3.19, where h is Planck's constant) at a certain frequency known as Larmor frequency [32]:

$$h\nu = \Delta E = \gamma \frac{h}{2\pi} \overrightarrow{B_{ext}} \quad (\text{Eq. 3.19})$$

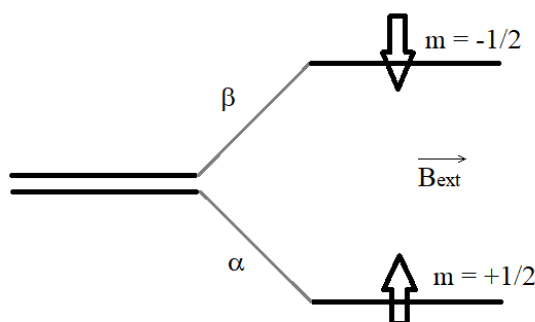


Figure 3.11: Nuclear spin energy levels diagram for a nuclei with spin $\frac{1}{2}$ and positive gyromagnetic value when subjected to an external magnetic field

Likewise, the presence of different nuclei produces a modification in energy levels that leads in position changes in the NMR spectrum, called chemical shift (δ , ppm). It can be generally assumed that an increase in coordination number tends to shift NMR signal to lower values. This fact results specially interesting in the case of silicates, since it has been demonstrated that this chemical shift can be related to tetrahedral coordination density [33].

^{29}Si and ^{13}C solid state nuclear magnetic resonance (NMR) analyses were carried out using the Hpdcc (cw decoupling sequence) and CP-MAS technique, respectively, at a rotation speed of 15 kHz on a DVT probe of

2.5 mm of triple resonance and double wideband range and registered. ^{29}Si spectra were measured with 4000 scans, $D1 = 5$ s and $P15 = 2$ ms. ^{13}C spectra with an excitation pulse of 4.0 μs and a recycling time of 50 s and 2.500 scans.

3.3.15. Fourier Transform infrared (FTIR)

Infrared spectroscopy studies the interaction between matter and infrared radiation, which encompass wavelengths between 0.7 and 1000 μm . IR spectroscopy is sensitive to the presence of functional groups in a molecule, allowing the identification of chemical species through the determination of the frequency at which functional groups present absorption bands in the IR spectrum. Moreover, the intensity of these bands can be used to determine the concentration of the chemical species.

It has been reported that there is a correlation between the presence of a certain type of chemical bond (O-H, N-H, C=O, etc.) and the presence of absorption bands at positions that just slightly vary from a compound to another. This is due to the fact that chemical bonds have a strong essence, thus its electronic structure is similar from one molecule to another owning the same type of chemical bond. In addition, in some vibration modes, vibration movements are located in a specific bond. Thus, the rest of the molecule has negligible influence and vibration frequency will be determined by the bond force constant and its reduced mass, hence the similarity among different molecules [19]. Particularly, Fourier Transform Infrared spectroscopy (FTIR) presents an interesting property: for the same acquisition time, the obtained signal-to-noise (S/N) ratio is quite superior, thus, the interferometer allows the acquisition of the spectrum in a shorter time than in a dispersive equipment for the same S/N ratio, since the interferometer receives all wavelengths simultaneously. Moreover, in FTIR spectrometer has a greater beam intensity that also improves S/N ratio and also presents a constant resolution in all the spectrum without light polarization effects, characteristic of diffraction arrays [19].

Infrared FTIR spectra were obtained using Bruker tensor 27 equipment, with ATR module (Attenuated Total Reflectance), in the range of 4000 to 500 cm^{-1} , performing 30 scans per sample.

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4. **Bimetallic Nb-based catalysts for anisole HDO**

Summary

The role of iron, cobalt and nickel doping in supported niobium catalysts in the hydrodeoxygenation reaction of anisole, chosen as a model molecule present in lignocellulosic biomass derived bio-oil, has been evaluated. Catalysts containing a total metal loading of 12 wt.% were prepared and reduced following the procedure in section 3.2.2. of *Materials and Methods* chapter and were named FeNb, CoNb and NiNb.

4.1. Catalytic test

Hydrodeoxygenation reaction (HDO) of anisole was performed as described in Materials and Methods chapter. Prior to the catalytic reaction, the catalysts were reduced in situ at 450 °C for 2 hours with a heating rate of 10 °C · min⁻¹. HDO conversion on stream and total and HDO conversion at 5 hours of reaction are compiled in **Figure 4.1**. Likewise, selectivity on stream and products distribution at 5 hours are collected in **Figure 4.2**.

Although no conclusions about the stability of the catalysts can be suggested with only 5 hours on stream, it is easily noticed that the NiNb catalyst presented higher stability in HDO conversion in comparison with its CoNb counterpart (FeNb is not plotted because no HDO conversion was attained over this catalyst). that seemed to deactivate during the reaction. The CNH elemental analysis was carried out after the catalytic test, evidencing that the catalyst with nickel presented less coke deposition than the cobalt one (4.1 wt.% vs 6.7 wt.%). Therefore, the deactivation of CoNb catalyst could be related to coke formation, that blocks the reaction active sites on the catalyst surface.

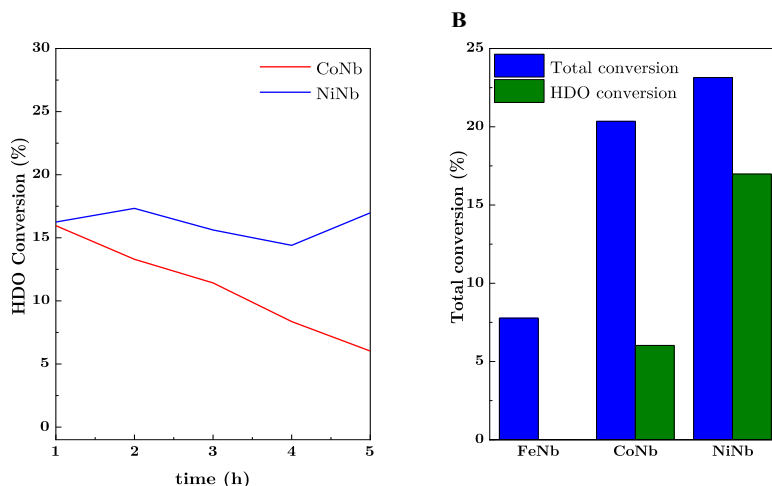


Figure 4.1: (A) HDO conversion on stream and (B) Total and HDO conversions at 5 hours of reaction

The same trend is also observed in products distribution in **Figure 4.2 A**, where nickel presented the highest selectivity to deoxygenated products and a higher hydrogenating capability. The main reaction products were cyclohexane and benzene in CoNb and NiNb catalysts, while the iron-based catalyst could just eliminate the methyl group from anisole, therefore forming phenol. The formation of aromatics such as cresol, toluene and xylenes was not detected, although some authors have reported the obtention of these compounds using similar catalysts [1]–[3].

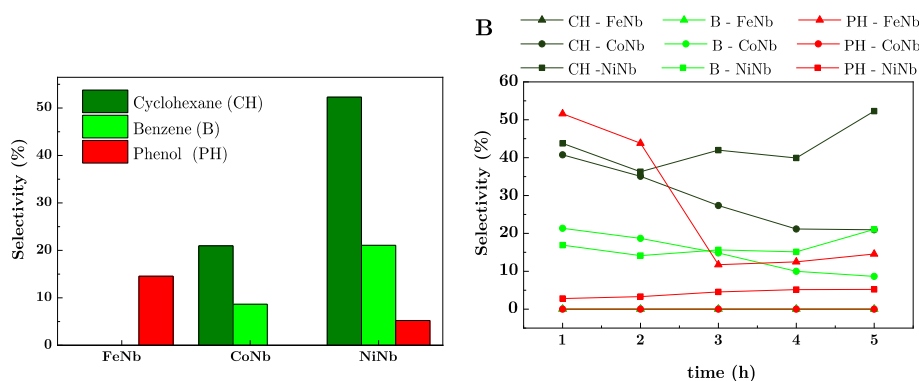


Figure 4.2: (A) Products distribution at 5 hours of reaction and (B) Selectivity on stream for cyclohexane (CH), benzene (B) and phenol (PH) over FeNb, CoNb and NiNb catalysts

To support the proposed reaction pathways included in **Figure 4.3**, the products evolution was monitored over time on stream. Two possible routes are suggested:

Route 1 involves demethylation (DM) of the methoxy O-CH₃ bond, forming phenol (1-a) that could be deoxygenated by C_{Ar}-OH bond breakage (1-b) [4] giving rise to benzene, that could eventually be hydrogenated to cyclohexane (1-c) [5]. Route 2 implies direct demethoxylation (simultaneous demethylation and hydrogenolysis reactions) forming benzene (2-d) that, via further hydrogenation, could be transformed into cyclohexane (2-e).

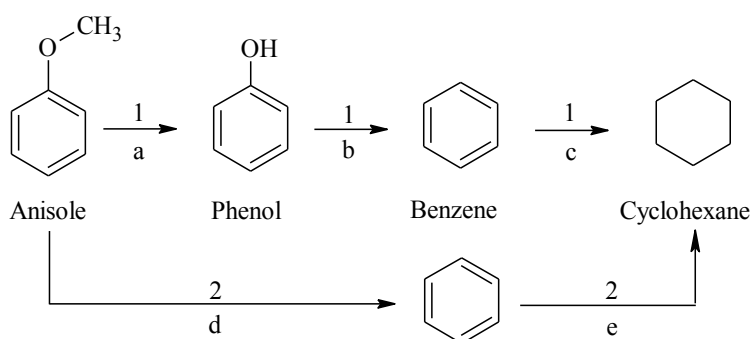


Figure 4.3: Proposed reaction pathways for anisole HDO

Several authors [6], [7] have already reported that niobium as is a promoter in the C-O bond cleavage (as will be evidenced by H₂-TPR results) which, together with the hydrogenating capability of nickel, led to the best catalytic performance and greatest deoxygenates selectivity for the NiNb catalyst. Considering the products distribution obtained, it is suggested that the Ni-containing catalyst followed Route 1 in **Figure 4.3**, with cyclohexane and benzene as main reaction products in 50% and 20%, respectively, and just 5% selectivity to oxygenated product phenol. Conversely, the Co-based catalyst did not show any selectivity for oxygenates, which suggests that when the reaction is carried out with CoNb catalyst, Route 2 in **Figure 4.3** is preferred. Lastly, FeNb had the worst catalytic performance with negligible HDO conversion. Therefore, it could

be concluded that even though hydrogen activation seems to take place on metal sites, the acid sites of the supports are responsible for the hydrogenation of the aromatic ring. In fact, according to Hewer et al. [1], the anisole molecule may interact with silanol (Si-OH) groups and eventually undergo hydrogenation of the aromatic ring on metal active sites.

4.2. Characterization results

4.2.1. X-Ray Diffraction (XRD)

The crystalline phases and the degree of ordering of the catalysts were studied by means of high-angle and low-angle X-Ray powder diffraction. Regarding the latter, the intense peak at $2\theta = 1^\circ$ in **Figure 4.4 A** for bare SBA-15 indicates that the prepared support maintained the characteristic hexagonal order of these amorphous materials [8]–[10]. When the metal species were incorporated, a decrease in the intensity of this peak is noticeable, suggesting a more disordered porous structure due to pore blockage by metals.

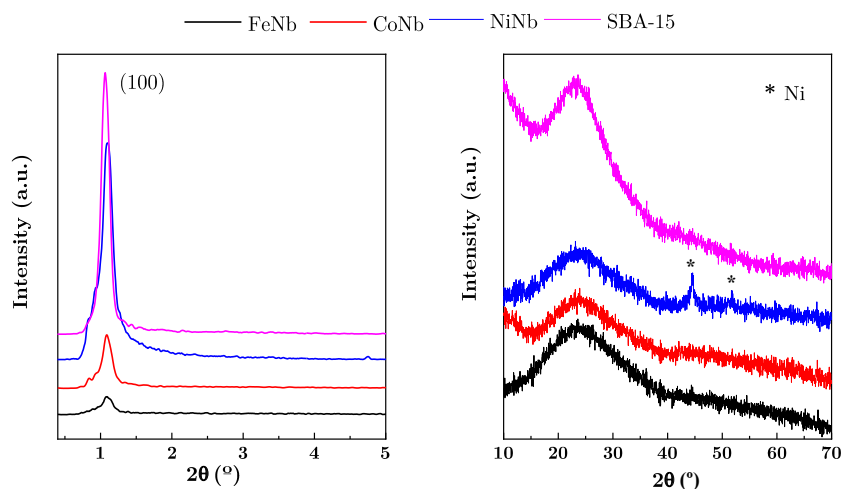


Figure 4.4: XRD patterns at (A) low and (B) high angles for FeNb, CoNb and NiNb catalysts as well as for bare SBA-15 support

The high angle diffractograms plotted in **Figure 4.4 B** present a broad shoulder between 20° and 30° , which is characteristic of amorphous

mesoporous materials [11]. Neither niobium segregated phases nor iron nor cobalt crystalline phases were detected, suggesting that the metallic phases are highly dispersed on the support's surface. On the other hand, just two nickel signals are detected in NiNb catalyst, which are found at $2\theta = 44.5$ and 51.7° (PDF No.: 03-065-2865), evidencing the presence of metallic nickel species [12]. The noise in the signals together with the absence or little presence of metallic reflections may suggest that the particles are present in a very small particle size, located either inside SBA-15 porous channels or on the surface of the channels' walls [13], as will be evidenced by HR-TEM images.

4.2.2. Nitrogen adsorption-desorption isotherms

The textural properties were determined by N_2 adsorption-desorption at -196°C and the obtained isotherms and the pore size distribution are compiled in **Figure 4.5 A** and **B**, respectively. As expected, all the prepared samples presented a type IV isotherm according to the IUPAC classification [14], with a non-closed H2 hysteresis loop, characteristic of ordered mesoporous SBA-like materials in which percolation occurs due to interconnection in the pore network.

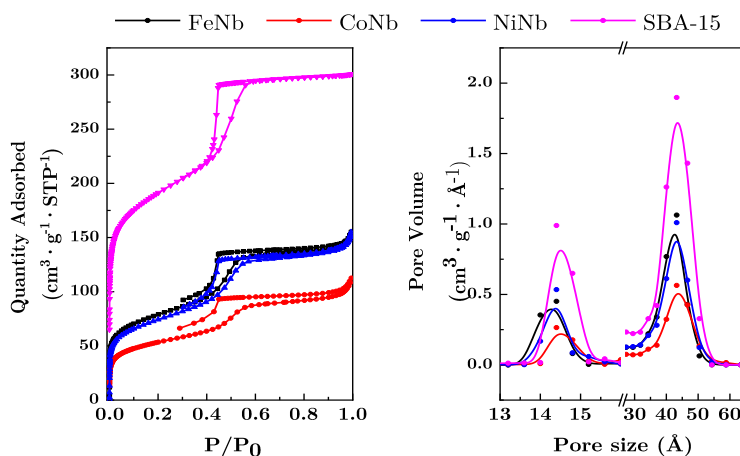


Figure 4.5: (A) N_2 adsorption-desorption isotherms and (B) micro- and mesopore size distribution by MP and DFT methods, respectively, of bare support and FeNb, CoNb and NiNb catalysts

The abrupt increase in N_2 adsorbed volume at low relative pressures indicates that the samples contain, as well as mesopores, a significant microporous contribution, suggesting that mesopores are interconnected to each other by micropores as previously reported [15], [16]. Micropores presence is also evidenced in the hysteresis behaviour, since the desorption branch of the isotherms does not completely close the hysteresis loop due to the confinement of nitrogen molecules inside the micropores that cannot be desorbed at a relative pressure close to 0.30 due to the sinuous nature of the micropores that are in turn filled with the metallic particles incorporated. Likewise, observing **Figure 4.5 B** it could be said that the samples present large micropores and small mesopores, the latter also evidenced by the step at relative pressures over 0.45 due to capillary condensation within these structures. Lastly, the presence of large mesopores between particles is also supported by the narrow hysteresis loop extending to relative pressures close to 0.99.

The SBA-15 prepared support presented a high specific surface area of $693 \text{ m}^2 \cdot \text{g}^{-1}$ (see **Table 4.1**) that was decreased after metals incorporation, as evidenced by the increase in disorder degree by XRD analysis. Nonetheless, the catalysts still showed a relatively high specific surface area, suggesting that metallic particles are well dispersed into SBA-15 pore channels. This decrease is also observed in micro- and mesopore volumes, which suggests pore blockage by metallic particles, especially in the case of cobalt. Regarding pore size distribution, the average values for micro- and mesopore widths are hardly modified, indicating that metallic particles are quite small. However, larger particles or metallic agglomerates could be blocking the entrance of nitrogen into some pores, hence diminishing pore volume (see **Figure 4.6**), as previously reported by Hewer et al.[1] for nickel- and molybdenum-based SBA-15 catalysts.

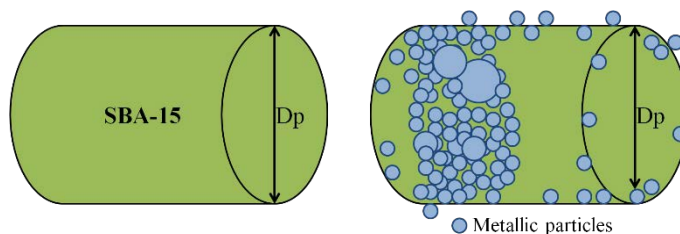


Figure 4.6: Proposed deposition mechanism of the metallic particles into the pores of SBA-15 prepared support

Finally, it is noticed that NiNb catalyst presents one of the highest BET surface values which, together with the well-known hydrogenating capability of Ni, is in accordance with the better catalytic activity of this sample, since Ni could be better dispersed onto the surface of the support.

Table 4.1: Textural properties of SBA-15 support and FeNb, CoNb and NiNb catalysts

Sample	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$) ^a	V_{meso} ($\text{cm}^3\cdot\text{g}^{-1}$) ^b	V_{micro} ($\text{cm}^3\cdot\text{g}^{-1}$) ^c	D_{meso} (nm) ^d	D_{micro} (nm) ^e
<i>SBA-15</i>	693	0.50	0.081	4.34	1.41
<i>FeNb</i>	272	0.21	0.030	4.32	1.39
<i>CoNb</i>	188	0.13	0.019	4.32	1.40
<i>NiNb</i>	261	0.19	0.027	4.34	1.38

^aBrunauer-Emmet-Teller specific surface area. ^bMesopore volume calculated by DFT method. ^cMicropore volume calculated by MP method. ^dAverage mesopore width (DFT method). ^eAverage micropore width (MP method)

4.2.3. High Resolution Transmission Electron Microscopy (HR-TEM)

Morphology and metallic particles dispersion of the as-prepared samples were studied by means of HR-TEM images and EDX-STEM mapping, and selected images are displayed in **Figure 4.7**.

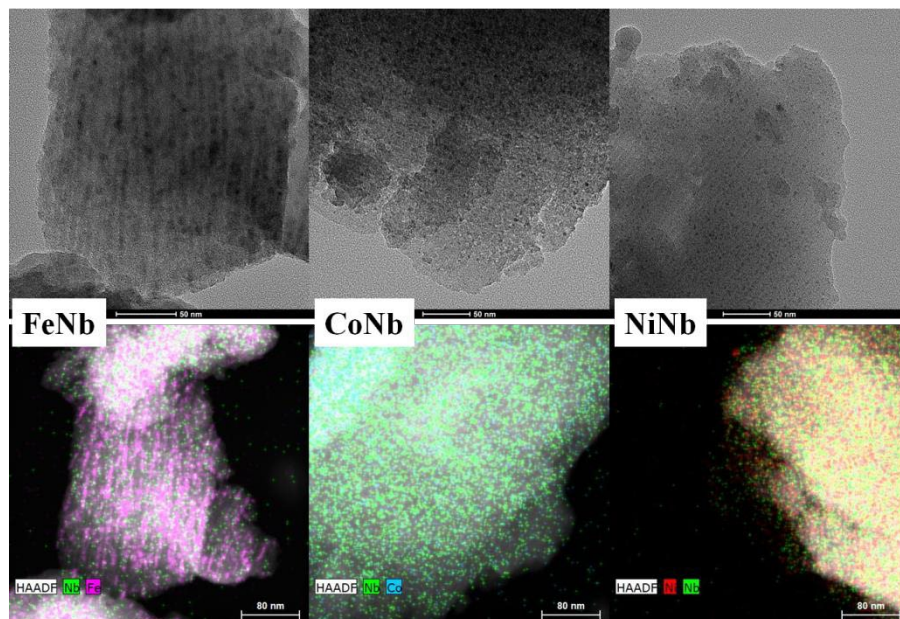


Figure 4.7: HR-TEM micrographs and mapping results corresponding to FeNb, CoNb and NiNb catalysts.

HR-TEM micrographs confirmed what XRPD and N_2 adsorption-desorption analysis suggested: all samples presented highly dispersed metallic particles of very small sizes placed inside the SBA-15 pore channels. In the case of the FeNb catalyst, iron particles are easily observed inside the support channels, but no interaction could be observed between Nb and Fe by EDX-STEM mapping. On the contrary, cobalt and nickel seemed to interact more closely with niobium species, since a more homogeneous distribution of both metallic phases is easily seen in EDX-STEM images. Together with the relatively high specific surface area in this catalyst, the close interaction of nickel and niobium and their high dispersion on the catalyst's surface could explain its higher catalytic activity in anisole hydrodeoxygenation.

4.2.4. X-Ray Photoelectron Spectroscopy (XPS)

So as to investigate the chemical environment and chemical surface composition of the prepared catalysts, XPS analysis was performed. **Figure**

4.8 shows Fe 2*p*, Co 2*p* and Ni 2*p* core level spectra of FeNb, CoNb and NiNb catalysts.

Table 4.2: Surface composition and Nb binding energies for FeNb, CoNb and NiNb catalysts

Catalyst	NbO ₂ / Nb ₂ O ₅	Nb/ Si	M _x O _y	Binding energy (eV)	
				Nb 3 <i>d</i> _{5/2}	
				NbO ₂	Nb ₂ O ₅
<i>FeNb</i>	1.02	0.026	710.8 ^a (Fe ₂ O ₃)	206.6 (51)	208.0 (49)
<i>CoNb</i>	0.57	0.026	781.2 ^b (CoO)	206.5 (36)	207.8 (64)
<i>NiNb</i>	1.22	0.034	852.5 ^c (Ni)	206.6 (55)	208.2 (45)
			854.3 ^c (NiO)		

^aRelative % of each species, ^aFe 2*p*_{3/2}, ^bCo 2*p*_{3/2}, ^cNi 2*p*_{3/2}

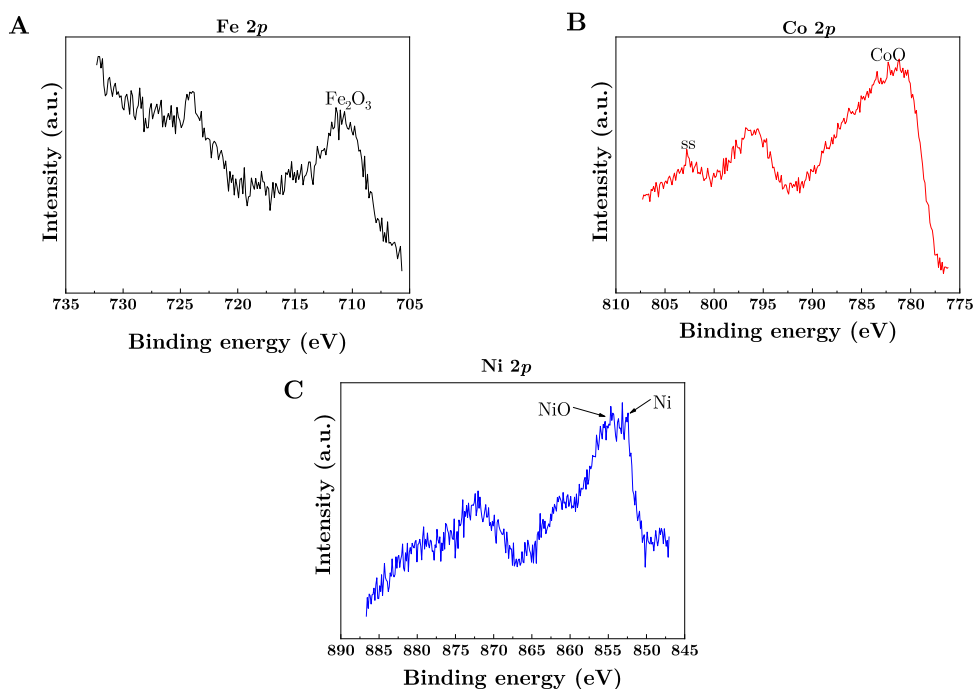


Figure 4.8: (A) Fe 2*p*, (B) Co 2*p* and (C) Ni 2*p* core level spectra for the prepared catalysts

In Fe- and Co-based catalysts, the presence of superficial oxidized iron and cobalt species can be evidenced by signals at *ca.* 710.8 eV (Fe_2O_3) and 781.2 eV (CoO) in **Figure 4.8 A** and **B**, respectively. In NiNb catalyst, two contributions can be distinguished in the Ni $2p_{3/2}$ signal, at *ca.* 852.5 eV and *ca.* 854.3 eV, corresponding to metallic Ni^0 and NiO, respectively, the former also evidenced in XRD patterns [17].

Regarding the Nb $3d$ core level spectra in **Figure 4.9**, the signals have been deconvoluted, giving rise to two contributions present in all catalysts, ascribed to Nb_2O_5 and NbO_2 , whose binding energies and relative percentages for each catalyst are collected in **Table 4.2**. Nb/Si ratios indicate that niobium is more superficially exposed in the most active sample, NiNb, in which NbO_2 species are predominant.

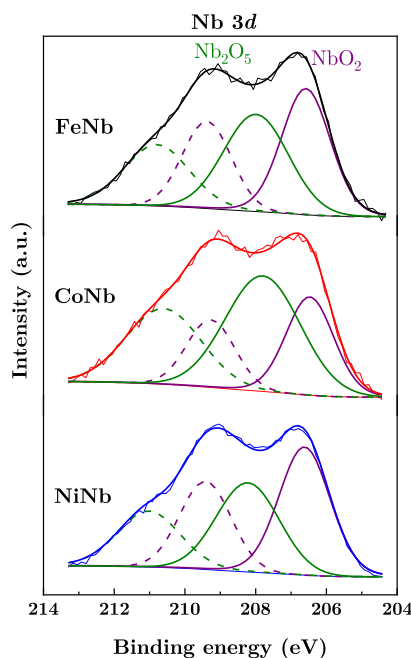


Figure 4.9: Nb $3d$ core level spectra for FeNb, CoNb and NiNb catalysts

4.2.5. Hydrogen thermoprogrammed reduction (H_2 -TPR)

The reducibility of the prepared catalysts was studied by hydrogen thermoprogrammed reduction (H_2 -TPR). All samples presented a main peak

in **Figure 4.10** localized at *ca.* 584 °C for FeNb and CoNb and at around 607 °C for their nickel counterpart. As already reported, this hydrogen consumption is related to the reversible reduction of Nb₂O₅ species to NbO₂ [3], [4], [18].

Less noticeable contributions also occurs between 250 and 450 °C, related to the reduction of superficial NbOx oxides [18] as well as to nickel [19], iron [20] and cobalt [21] oxidized species. These contributions are more pronounced in the FeNb catalyst, probably due to the weaker interaction between Fe and Nb that leads to higher hydrogen consumption. On the contrary, the greater interaction between Ni and Nb leaves fewer niobium species susceptible of to consume hydrogen for their reduction [22], [23]. The stronger interaction of Ni and Nb would also support the better catalytic performance of NiNb catalyst followed by CoNb and lastly FeNb. Therefore, from these results, it could be suggested that nickel and niobium interaction results beneficial for hydrodeoxygenation reaction, since hydrogen consumption could be decreased without compromising the activity.

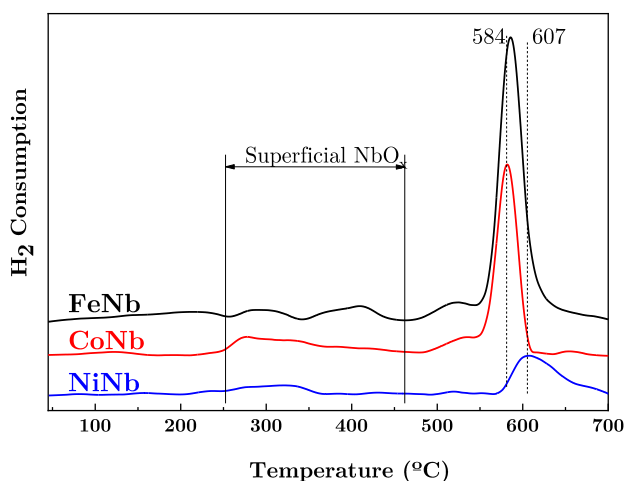


Figure 4.10: H₂-TPR profiles for FeNb, CoNb and NiNb catalysts

4.2.6. NH_3 thermoprogrammed desorption (NH_3 -TPD)

The nature of the acid sites present in the prepared catalysts was studied by NH_3 thermoprogrammed desorption and their desorption profiles are displayed in **Figure 4.11**. Ammonia desorption was completed at 450 °C, indicating the weak and medium acidity nature of the three samples, as reported in **Table 4.3**. The main contribution for all catalysts was located at *ca.* 175 °C, revealing that the catalysts' acidity was predominantly weak. According to consolidated research [24], this acidity is associated with Lewis acid sites related to NbO_2 species, whose presence has been confirmed by XPS analysis. In addition, the presence of stronger acid sites (ammonia desorption taking place at temperatures between 300 °C and 450 °C) in Co-based catalyst could be related to a greater contribution of Nb_2O_5 species in this catalyst (see **Table 4.2**). Moreover, the catalytic behaviour of the catalysts can also be justified in terms of acidity, since bimetallic silica-supported catalysts containing nickel or copper have been reported to be more selective towards benzene rings thanks to active sites with weak acidity [5]. Likewise, from data in **Table 4.3** it could be concluded that a high acidity leads to a detriment in catalytic activity.

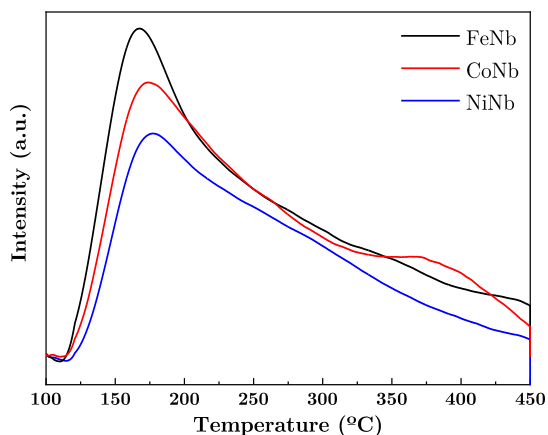


Figure 4.11: NH_3 thermoprogrammed desorption for FeNb, CoNb and NiNb catalysts

Table 4.3: Acidic properties of FeNb, CoNb and NiNb catalysts

Catalyst	Acidity ($\mu\text{mol NH}_3 \cdot \text{g}^{-1}$)		Total
	Weak ^a	Medium ^b	
<i>FeNb</i>	56.7	11.5	68.1
<i>CoNb</i>	51.4	15.4	66.8
<i>NiNb</i>	44.9	10.7	55.6

^aNH₃ desorbed between 100 and 300 °C. ^bNH₃ desorbed between 300 and 450°C

4.3. Discussion

In this chapter, bimetallic FeNb, CoNb and NiNb supported on non-commercial SBA-15 catalysts were prepared by the incipient wetness impregnation synthesis method and tested in the hydrodeoxygenation reaction of anisole at 275 °C and 15 bar of hydrogen pressure. The NiNb catalyst presented the best catalytic performance, followed by CoNb and FeNb, the latter without any hydrodeoxygenation conversion. This trend in the catalytic behaviour is supported by the data interpretation of the different characterization techniques used.

Considering the XRD results, even though the SBA-15 hexagonal mesoporous structure is maintained after metals incorporation, a greater disorder degree is observed, especially after Fe and Co incorporation, due to the larger ionic radius of these elements, as previously reported by Kilos et al. [25]. The high-angle patterns suggest that metal particles are small and highly dispersed on the SBA-15 surface, since no signals related to oxidized metallic phases are detected, except for the NiNb catalyst, indicating a greater interaction between Nb and Ni.

The presence of small particles has also been confirmed by HR-TEM images and textural properties calculated from N₂ adsorption-desorption

isotherms, the latter showing that the support presents both micropores and mesopores and the former showing quite small particles are found in all samples, with remarkable dispersion inside the SBA channels and pores. Additionally, close contact between niobium and cobalt and nickel is observed in EDX-STEM images. In the case of iron, this interaction is weaker, which supports the negligible hydrodeoxygenation capability of this catalyst, which was also support by H_2 -TPR measurements.

The catalytic behaviour of the prepared catalyst could also be understood from the characterization results of ~~by~~ XPS and NH_3 -TPD. The XPS analysis shows that all catalysts present two main oxidized niobium species, Nb_2O_5 and NbO_2 , the latter being responsible for a higher Lewis acidity, especially in CoNb catalyst, which has been demonstrated to be detrimental to the catalytic performance, therefore, moderate weak acidity is preferred. The XPS analysis also shows that the Nb species are more superficially exposed in Ni-containing sample, thus confirming the greater interaction between these elements, and justifying the better catalytic performance of this sample.

4.4. Conclusions

Iron, cobalt and nickel were incorporated by incipient wetness impregnation to a niobium-based catalyst, supported on a low-cost SBA-15 support. The prepared catalysts were tested in the hydrodeoxygenation reaction of anisole at 275 °C and 15 bar of hydrogen pressure.

All samples presented well-dispersed metal particles located inside the pore channels of the prepared SBA-15 support, that maintained its characteristic hexagonal structure although with a lower specific surface area due to pore blockage after metal incorporation. The results of HR-TEM, EDX-STEM and H_2 -TPR show a close contact between niobium and the second metal, greater in the NiNb catalyst than in the rest of the prepared catalysts, suggesting that the interaction between nickel and

niobium is stronger, leading to a better catalytic performance. The remarkable catalytic activity of NiNb compared to CoNb and FeNb counterparts is due to both the hydrogenating capacity of nickel and the acidity provided with oxidized niobium species, Nb_2O_5 and NbO_2 , whose presence was demonstrated by XPS analysis.

To sum up, it can be concluded from this study that the presence of nickel and niobium in a catalyst supported on a mesoporous and neutral solid like SBA-15 results beneficial for the anisole HDO process, since this catalyst presents the needed bifunctionality for this reaction: on the one hand, nickel activates hydrogen molecule; on the other hand, the acid sites supplied by niobium oxidized species promote the elimination of oxy-groups, allowing the obtention of deoxygenated compounds with high added value.

4.5. References

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**5. NiAlCe mixed oxides derived
from layered double hydroxides for
anisole HDO**

Summary

In this chapter, the role of the redox pair $\text{Ce}^{3+}/\text{Ce}^{4+}$ in mixed oxides derived from layered double hydroxides (LDHs) containing Ni, Al and Ce in the hydrodeoxygenation reaction of anisole as a model lignocellulosic biomass-derived bio-oil compound has been studied. Five LDHs were prepared following the procedure described in section 3.2.3. in Materials and Methods section using terephthalic acid as compensation anion, with a Ni/(Al+Ce) molar ratio of 1, and with a partial replacement of Al^{3+} by Ce^{3+} and/or Ce^{4+} , in molar percentages of 10% and 50% were synthesized and named LDH-NAC-y,z, where N = nickel, A = aluminium and C = cerium, y stands for cerium species ($y = 3$ for Ce^{3+} and $y = 4$ for Ce^{4+}) and z indicates the molar percentage of Ce species added ($z = 10\%$ or 50%). Thus, the LDHs obtained will be referred hereafter as LDH-NAC-3,10 (Ce^{3+} , 10%), LDH-NAC-3,50 (Ce^{3+} , 50%), LDH-NAC-4,10 (Ce^{4+} , 10%), LDH-NAC-4,50 (Ce^{4+} , 50%) and LDH-NAC-3-4,50 (Ce^{3+} and Ce^{4+} , 50%). The mixed oxides were obtained from the thermal decomposition of these hydroxides, and were named c-NAC-3,10; c-NAC-3,50; c-NAC-4,10; c-NAC-4,50 and c-NAC-3-4,50, where c- indicates that samples have been calcined as detailed in Materials and Methods section 3.2.3. Lastly, the samples reduced in hydrogen flow under conditions detailed in the abovementioned section were named NAC-3,10; NAC-3,50; NAC-4,10; NAC-4,50 and NAC-3-4,50.

5.1. Catalytic test

The activity of reduced mixed oxides (NAC-y,z set) was tested in the hydrodeoxygenation (HDO) reaction of anisole at 15 bar hydrogen pressure and 275 °C and total and HDO conversions after six hours of reaction are displayed in **Figure 5.1**. All the catalysts presented a remarkable catalytic performance with conversions over 50% in all cases, the catalytic activity followed the trend $\text{NAC-4,10} > \text{NAC-4,50} > \text{NAC-3-4,50} > \text{NAC-3,50} > \text{NAC-3,10}$, with total conversion values of 93.7%, 72.5%,

66.6%, 60.5% and 55.1%. Paying attention to **Figure 5.1**, it is easily noticed that the samples prepared from Ce^{4+} species showed a better catalytic activity than those from Ce^{3+} , being the catalyst NAC-4,10 the most active one with 93.7% total conversion and 89.3% HDO conversion suggesting that, as will be evidenced by the characterization results shown below, the nickel active sites, as well as the cerium oxide species, are highly dispersed on the catalyst surface, allowing the creation of new active sites at the interphase between surface Ce species and metal particles as previously reported by Yang et al. [1].

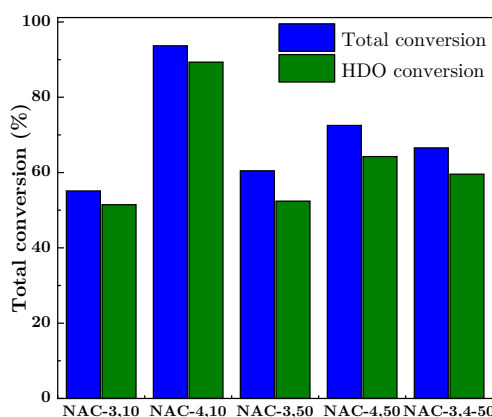


Figure 5.1: Total and HDO conversions after six hours on stream

The worsening of the catalytic performance in samples with higher Ce content could be due to pore blockage, as evidenced by BET values (see **Table 5.4**) and to surface coverage by cerium oxide species that hinders the access of the reagent molecule to nickel active sites.

Although a stability study must consider an appropriate number of hours of reaction on stream, the conversion evolution profile was studied in the six hours of reaction performed, with a remarkable stability in conversion values during the period studied for all catalysts. **Figure 5.2** shows that in NAC-4,10 and NAC-4,50 the conversion was over 60% after just one hour of reaction, and around 50% for the rest of the prepared samples. Noteworthy is the fact that the activity of the catalyst prepared

from Ce^{3+} and Ce^{4+} species got stabilized after three hours of reaction, probably due to the transformation of the redox pair Ce^{3+} - Ce^{4+} in the presence of hydrogen.

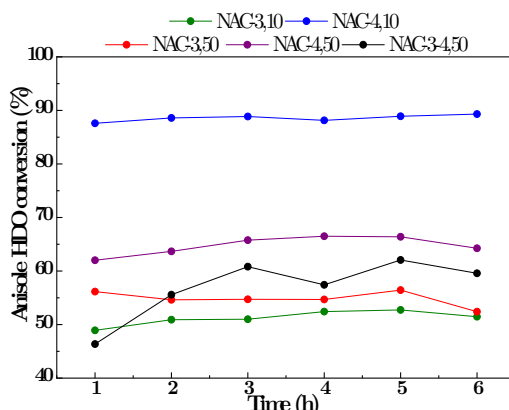


Figure 5.2: Anisole conversion profile during six hours on stream

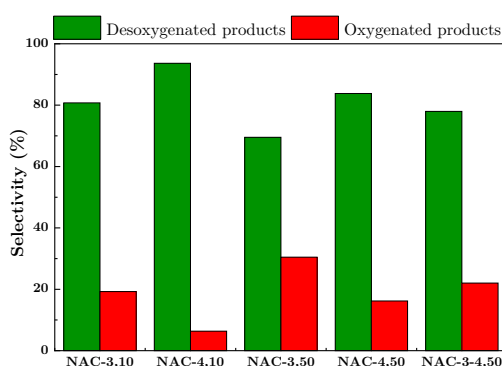


Figure 5.3: Deoxygenated and oxygenated products selectivity at 6h of reaction

Regarding product selectivity in **Figure 5.3**, all the catalysts presented higher selectivity to deoxygenated products than to oxygenated ones, over 70%, and no changes were observed in the initial trend after six hours of reaction. In fact, **Figure 5.4** illustrates the products distribution on stream, showing that all catalyst showed outstanding hydrogenating and deoxygenating capabilities, hence cyclohexane (CH) remained the main deoxygenated product in all cases, followed by benzene (B), toluene (T) in less than 0.5% and lastly cyclohexyl methyl ether (CHME) as hydrogenated oxygenated product.

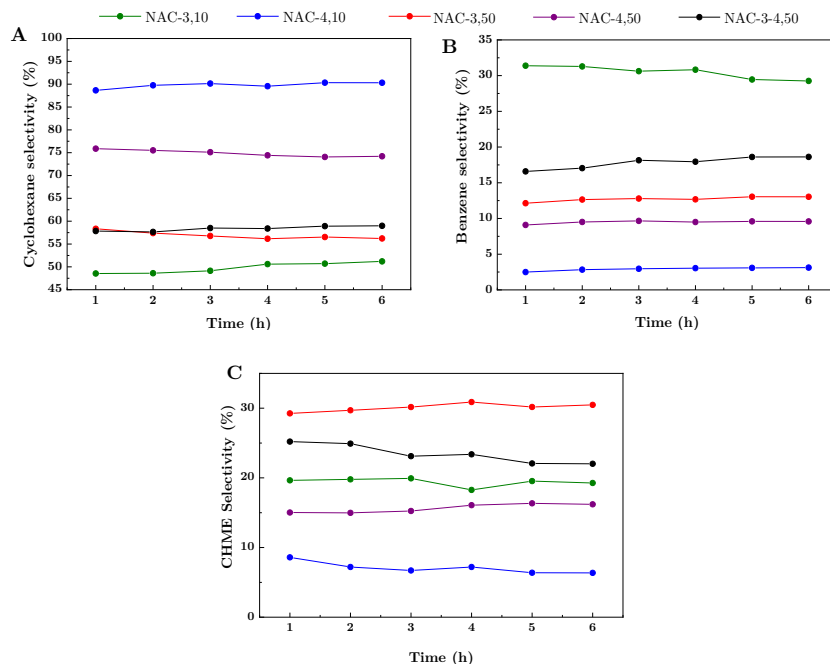


Figure 5.4: Selectivity on stream for (A) cyclohexane, (B) benzene and (C) cyclohexyl methyl ether for all studied catalysts

The product distribution is justified taking into consideration the product selectivity profiles in **Figure 5.4** and the main reaction pathways proposed for the anisole hydrodeoxygenation collected in **Figure 5.5**.

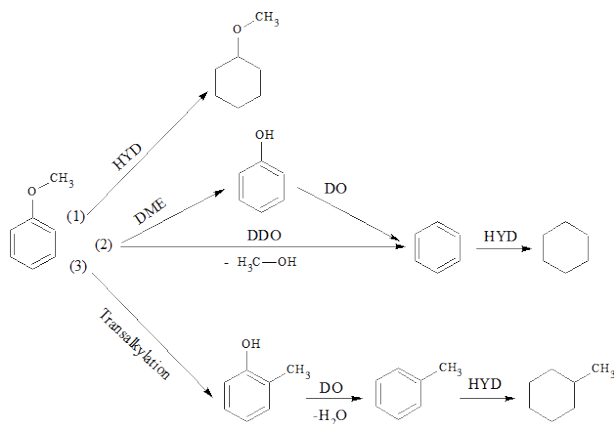


Figure 5.5: Anisole conversion routes: direct hydrogenation (1), direct deoxygenation (2) and transalkylation (3)

Three predominant routes for anisole hydrodeoxygenation have been thoroughly studied [2]–[5]. Route 1 involves the direct hydrogenation

(HYD) of aromatic ring to give rise to oxygenated compounds such as cyclohexyl methyl ether or cyclohexanol. Conversely, route 2 implies direct deoxygenation (DDO) breaking $C_{Ar}-O$ bond forming benzene (with methanol as by-product) that may eventually undergo hydrogenation to form cyclohexane. Likewise, this step could take place in two consecutive steps: firstly, demethylation (DME) to form phenol and deoxygenation (DO) to obtain benzene or cyclohexane with further hydrogenation of the latter, releasing water and methane. Likewise, a third route is considered, in which the anisole could suffer transalkylation (TK) and be transformed into cresol, that in turn could undergo deoxygenation and dehydration reactions to form toluene or methylcyclohexane if it is subsequently hydrogenated.

The highest selectivity for cyclohexane was found for the NAC-4,10 catalyst, with values over 90% in all the reaction period studied. This fact indicates that over this catalyst, the DME+DO or direct DDO route is preferred, and that the catalyst is strongly hydrogenating, since just 3.1% of benzene formed remained unhydrogenated. According to Li et al. [4], the DDO route is favoured thanks to the $C_{Ar}-O-CH_3$ bond dissociation energy (339 kJ/mol) in comparison to that of $C_{Ar}-OH$ one (468 kJ/mol), thus, for anisole, it seems more difficult, in energetic terms, to dehydroxylate phenol than to dissociate to benzene. A less favoured route over NAC-4,10 is direct HYD, with CHME selectivity under 10%.

Worth mentioning is that, although NAC-3,10 presented the lowest total and HDO conversions (55% and 51.5%, respectively), the highest selectivity to benzene, close to 30%, was found over this catalyst. NAC-4,50 and NAC-3-4,50 also showed an increase in benzene with respect to the most active catalyst, with a selectivity of 9.6% and 18.7%, respectively, with a consequent decrease in the cyclohexane selectivity (74.2% and 59%, respectively), which supports the assumption that these materials undergo hydrodeoxygenation reaction mainly through route 2. **Table 5.1** collects

the catalysts' selectivity for each proposed HDO reaction pathways. For route 1, cyclohexyl methyl ether is the only oxygenated product considered. For route 2, both benzene and cyclohexane are taken into account to the reached percentage. Lastly, route 3 just considered the obtention of toluene.

Table 5.1: Catalysts' selectivity (%) to proposed HDO reaction pathways displayed in **Figure 5.5**

Catalyst	Route 1	Route 2		Route 3
	HYD	DDO	DDO	TK
			+	+
			HYD	DO
<i>NAC-3,10</i>	19.3	29.2	51.2	0.3
<i>NAC-4,10</i>	6.4	3.1	90.3	0.2
<i>NAC-3,50</i>	30.5	13.0	56.2	0.3
<i>NAC-4,50</i>	16.2	9.6	74.2	0
<i>NAC-3-4,50</i>	22.0	18.6	59.0	0.4

Regarding the cerium precursor, it is also noticed that NAC-3,10 and NAC-3,50 catalysts showed a lower anisole conversion, as well as reduced selectivity for cyclohexane formation, suggesting that with these catalysts, benzene, a high value-added product, is less hydrogenated to cyclohexane.

5.2. Characterization results

5.2.1. LDHs precursors

5.2.1.1. X-Ray Diffraction (XRD)

The effect of Ce^{3+} and Ce^{4+} incorporation in the crystalline structure was studied by X-Ray powder diffraction, and XRD patterns for all prepared LDH precursors are displayed in **Figure 5.6**. Characteristic peaks ascribed to layered double hydroxides are found at $2\theta = 6.3, 12, 18, 25$ and

62°. The reflection at the lowest angle, 6.3°, is ascribed to (003) basal reflection and corresponds to an interplanar distance of *ca.* 14 Å for all LDHs (see **Table 5.2**) [6], considering the lamellar thickness of the brucite layer, 4.8 Å [7], and the interlayer region of around 9.2 Å related to the size of the terephthalate ion [8], [9]. The reflection at the highest angle corresponds to (110) crystallographic plane, ascribed to layer structure. This reflection is highly influenced by the cationic radius regardless of the layer stacking sequence [10]. The abovementioned reflections at the lowest and highest angles were used to calculate unit cell parameters *c* and *a*, respectively, following the corresponding formulas in Eq. 5.1 and Eq. 5.2, and calculated values are collected in Table 5.2.

$$c = 3 \cdot d_{003} \quad (\text{Eq. 5.1})$$

$$a = 2 \cdot d_{110} \quad (\text{Eq. 5.2})$$

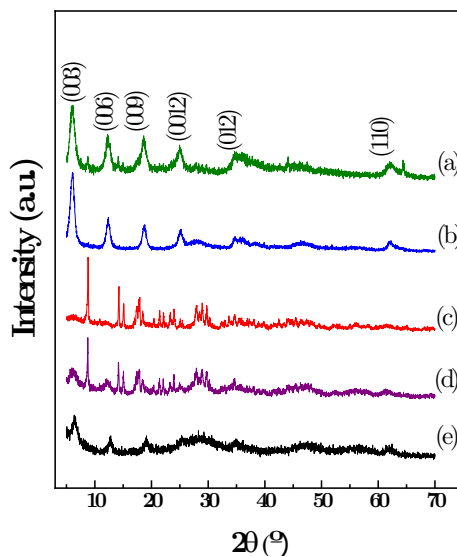


Figure 5.6: High-angle X-Ray diffraction patterns of LDH precursors: (a) LDH-NAC-3,10; (b) LDH-NAC-4,10; (c) LDH-NAC-3,50; (d) LDH-NAC-4,50 and (e) LDH-NAC-3-4,50

It is observed in **Figure 5.6** (d) and (e) that the samples prepared with a higher proportion of Ce^{4+} showed a lower crystallinity compared to the 10% counterparts, which indicates that the incorporation of high ionic radius cations provoke a greater repulsion and distortion of the layer structure. Moreover, an increase in the calculated unit cell parameter a is observed in samples prepared from Ce^{3+} , confirming the incorporation of the Ce^{3+} cation, with a larger ionic radius (1.07 Å) in comparison to Al^{3+} (0.54 Å) or its Ce^{4+} counterpart (0.87 Å), into the LDH structure [11], [12].

Finally, noteworthy is the fact that no characteristic LDHs reflections were found in samples prepared with a higher Ce proportion, but some reflection related to Ce segregated phases were found. Unexpectedly, the diffractions peaks at $2\theta = 8.7, 14$ and 21.5° are associated with cerium in a coordination state similar to that of $\text{Ce}_2(\text{CO}_4)_3 \cdot 10\text{H}_2\text{O}$ (ICDS-109637), which suggests that, due to the higher ionic radii of Ce species with respect to ideal range reported for trivalent cations (0.50-0.69 Å [13]), there is a limiting Ce amount that can be incorporated into the structure without compromising the octahedral coordination and symmetry of the LDH structure.

Table 5.2: LDHs unit cell parameters

LDH	d_{003} (Å)	c (Å)	d_{110} (Å)	a (Å)
<i>LDH-NAC-3,10</i>	14.78	44.31	1.50	2.99
<i>LDH-NAC-4,10</i>	14.43	43.30	1.49	2.98
<i>LDH-NAC-3,50</i>	10.04	30.13	1.50	3.01
<i>LDH-NAC-4,50</i>	10.09	30.27	1.51	3.02
<i>LDH-NAC-3-4,50</i>	13.89	41.67	1.50	2.99

5.2.1.2. Fourier Transform Infrared (FTIR)

To study the chemical nature of the bond in LDHs, FTIR analyses of LDH precursors were performed and spectra are collected in **Figure 5.7**.

All the LDHs presented a wide band associated with the stretching vibrations of hydroxyl groups around $3600\text{--}3200\text{ cm}^{-1}$. These -OH groups are related to interlayer water as well as to layer-forming hydroxyls. Likewise, the band at *ca.* 1600 cm^{-1} is attributed to the deformation of adsorbed and interlayered water molecules [11], [12], [14].

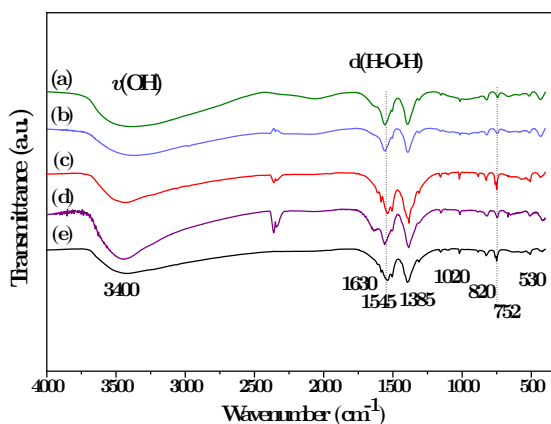


Figure 5.7: FTIR spectra of LDHs: (a) LDH-NAC-3,10; (b) LDH-NAC-4,10; (c) LDH-NAC-3,50; (d) LDH-NAC-4,50; (e) LDH-NAC-3-4,50

M-O interactions are evidenced at lower wavenumbers: $980\text{--}1020\text{ cm}^{-1}$ and 530 cm^{-1} are associated with the stretching of Al-O in octahedral coordination. These bands were slightly shifted and reduced in samples containing higher Ce loadings due to the decrease in Al^{3+} concentration [9], [15].

Terephthalate ion presence is confirmed by the symmetric and anti-symmetric vibrations modes of carboxylate group at 1545 and 1385 cm^{-1} . Likewise, bands around 820 and 752 cm^{-1} were associated with vibrations of benzene ring [9], [16]. As already suggested by the XRD and TGA results, the LDH-NAC-3,50 sample showed bands close to 1545 cm^{-1} and 1385 cm^{-1} referring to the presence of carboxylate groups, confirming the formation of

the segregated phase $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (ICSD-109367). Thus, it can be concluded that, due to Ce^{3+} has a larger ionic radius and lower solubility compared to Ce^{4+} counterpart, Ce cannot be fully incorporated into de LDH structure, so it precipitates in segregated phases coordinated with the oxygen of the carboxylate groups, present in the terephthalate ion.

5.2.1.3. Thermogravimetric analysis (TGA)

Hydrotalcite-type compounds have been reported to undergo two characteristic transitions, both strongly dependent on the type and the ratio of the metal cations used; firstly, the loss of the interlayer water and, secondly, the loss of hydroxyl groups and anions in the brucite-type layer [8]–[10], [15], [16].

As depicted in **Figure 5.8**, three main mass loss events of endothermic nature can be distinguished: the loss up to 200 °C is related to physically adsorbed water molecules loss on the surface and in the interlamellar region; the one between 200 °C and 350 °C is assigned to hydroxyl groups coordinated with metal ions; and the main event at 350 °C–450 °C corresponds to the decomposition of the terephthalate anion in LDH containing Ni^{2+} , Al^{3+} or Zr^{4+} anions [17]–[20].

Regardless of the Ce oxidation state, samples containing greater amount of Ce species presented the first event of water loss at lower temperature, i.e., as found by Das et al. [21], the higher the Ce content, the lower the temperature of the first event of water loss, i.e., water removal is eased with high Ce loadings [21].

Conversely, samples prepared with Ce^{4+} species (see **Figure 5.8 B and D**) showed higher thermal stability than those with Ce^{3+} species. In fact, the most active catalyst, NAC-4,10, was also the most stable on stream. In the case of the sample with Ce^{3+} 50%, a different profile with five peaks of an endothermic nature was obtained, that suggests that, as

previously thought with the XRPD analyses, the typical structure of the LDH was not formed. Likewise, the sample prepared with both Ce^{3+} and Ce^{4+} species presented two events, endothermic and exothermic, taking place simultaneously at temperature between 360 °C and 420 °C. Daza et al. [22] reported that this behaviour is likely due to defects or even collapse of the LDH crystalline structure.

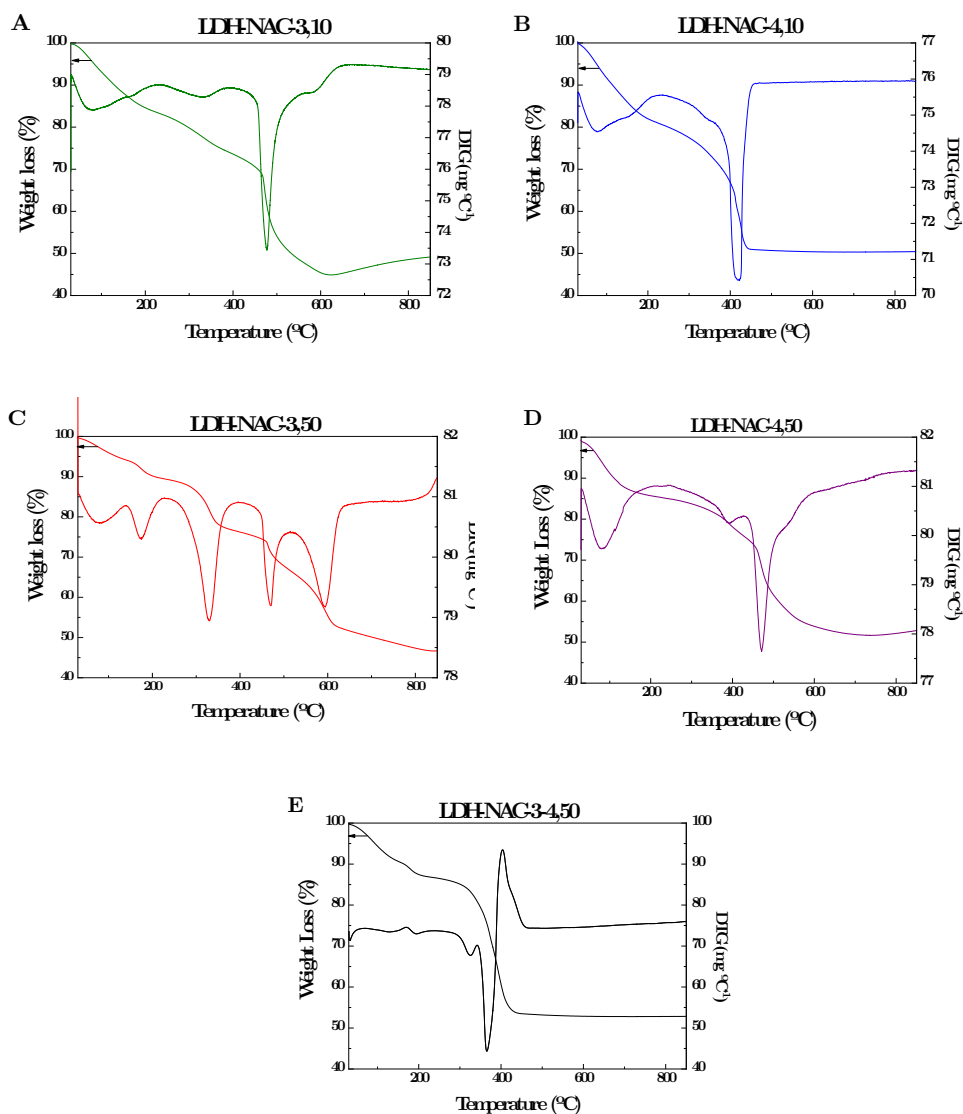


Figure 5.8: Thermogravimetric curves of LDHs: (A) LDH-NAC-3,10; (B) LDH-NAC-4,10; (C) LDH-NAC-3,50; (D) LDH-NAC-4,50 and (E) LDH-NAC-3,4,50

5.2.1.4. Scanning Electron Microscopy (SEM)

SEM analysis was performed to study the morphology of the prepared LDH precursors and selected images are collected in **Figure 5.9**. All the samples presented a typical morphology of materials prone to particle agglomeration [23], [24], with some roughness especially in the samples synthesized with the Ce^{3+} precursor. Moreover, it has been reported that the water existence in the structure favours the agglomeration into larger particles [25]. In samples containing higher cerium content (see **Figure 5.9 c**), **d**) and **e**)), agglomerates and an irregular lamellar morphology are noticed. What's more, in the LDH-NAC-3,50 sample, a unique plaque-like morphology with aggregates on the edges is observed, which could be indicative of non-formed LDH. These results, together with TGA and XRD analysis, suggest that metal ratios are crucial factors influencing not only the morphology but also the crystallinity of the prepared LDHs.

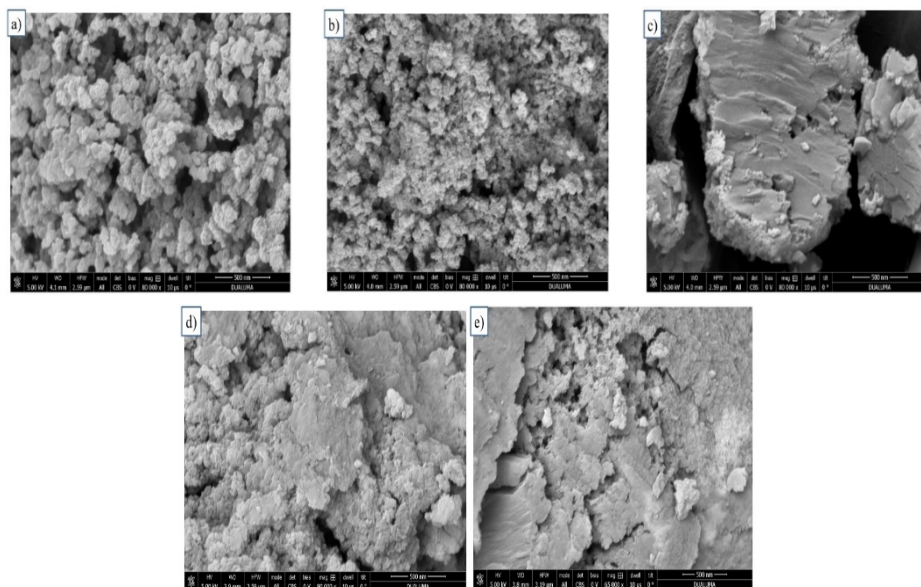


Figure 5.9: SEM images of LDH precursors: (A) LDH-NAC-3,10; (B) LDH-NAC-4,10; (C) LDH-NAC-3,50; (D) LDH-NAC-4,50 and (E) LDH-NAC-3-4,50

5.2.2. Mixed oxides

5.2.2.1. X-Ray Diffraction (XRD)

Figure 5.10 displays high-angle diffractograms for calcined mixed oxides derived from LDH precursors. The presence of CeO_2 (ICSD-88752), NiO (ICSD-87108) and NiAl_2O_4 spinel (ICSD-72067) phases was observed for all catalysts after calcination, the latter with less intensity. Conversely, the formation of aluminium oxide was not detected, suggesting that either it is amorphous or that Al^{3+} ions have successfully entered into the NiO network, forming a solid solution [16], [20].

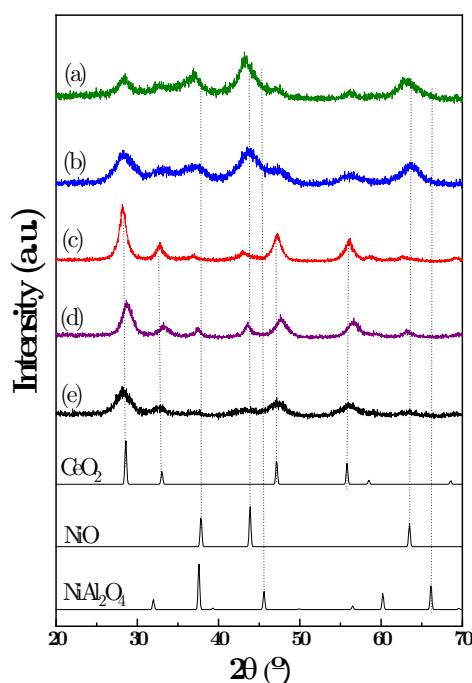


Figure 5.10: High-angle X-Ray diffraction patterns of mixed oxides: (a) c-NAC-3,10; (b) c-NAC-4,10; (c) c-NAC-3,50; (d) c-NAC-4,50 and (e) c-NAC-3-4,50

The widening of the CeO_2 peak at *ca.* $2\theta = 30^\circ$ for samples with low Ce content indicates that this phase is well-dispersed in the mixed oxides. Likewise, in samples with 50% Ce, NiO reflections were diminished whereas those of CeO_2 and NiAl_2O_4 were increased, suggesting that at higher cerium content, Ni tends to form the NiAl_2O_4 spinel phase.

Noteworthy is the fact that NiO reflections are slightly shifted in the diffractograms of the samples derived from the Ce³⁺ precursor, which may be due to the alteration of the crystal structure of NiO because of the larger ionic radius of Ce³⁺ in comparison to the Ce⁴⁺ counterpart.

Therefore, these results indicate that, as already suggested by XRD results of the LDH precursors, the Ce loading is a limiting factor to keep the crystalline structure of not only LDH but also mixed oxides.

5.2.2.2. X-Ray Fluorescence (XRF)

The presence and contribution of Ni, Al and Ce in calcined mixed oxides were determined by X-Ray Fluorescence, and weight percentages, as well as molar ratios, are displayed in **Table 5.3**.

Table 5.3: Metal content (wt.%) and molar relationships in NiAlCe oxides

Mixed oxide	Ni ^a (%)	Al ^a (%)	Ce ^a (%)	^b Theor. Al/Ce ratio	^c Exp. Al/Ce ratio	^d Exp. Molar ratio, x
<i>c-NAC-3,10</i>	46	15	10	9	7.78	0.45
<i>c-NAC-4,10</i>	48	14	10	9	7.26	0.42
<i>c-NAC-3,50</i>	31	6	38	1	0.82	0.48
<i>c-NAC-4,50</i>	32	8	36	1	1.15	0.51
<i>c-NAC-3-4,50</i>	32	7	37	1	0.98	0.49

^aXRF results of nickel, aluminium and cerium in mixed oxides; ^bTheoretical molar ratio Al/Ce of mixed oxide; ^cExperimental molar ratio Al/Ce of mixed oxide, ^dMolar ratio (Al+Ce)/(Al+Ce+Ni) of mixed oxide (theoretical value: 0.5)

Sublimation of metals during the calcination process [20] was ruled out considering that the experimental molar ratio in the mixed oxides is quite similar to that of the LDH precursors in all samples ($x = 0.5$). However, the Al/Ce ratio in samples with lower Ce content, *c-NAC-3,10* and *c-NAC-4,10*, is lower than the theoretical one, which could be justified

considering that aluminium could be incorporated both in the LDH structure and as aluminate species occupying interlayer spaces [26].

5.2.2.3. Nitrogen adsorption-desorption isotherms

Porous nature of the prepared mixed oxides was studied by means of N_2 adsorption-desorption isotherms, plotted in **Figure 5.11**. Additionally, the textural properties, such specific surface area calculated by BET method or pore volume, are collected in **Table 5.4**.

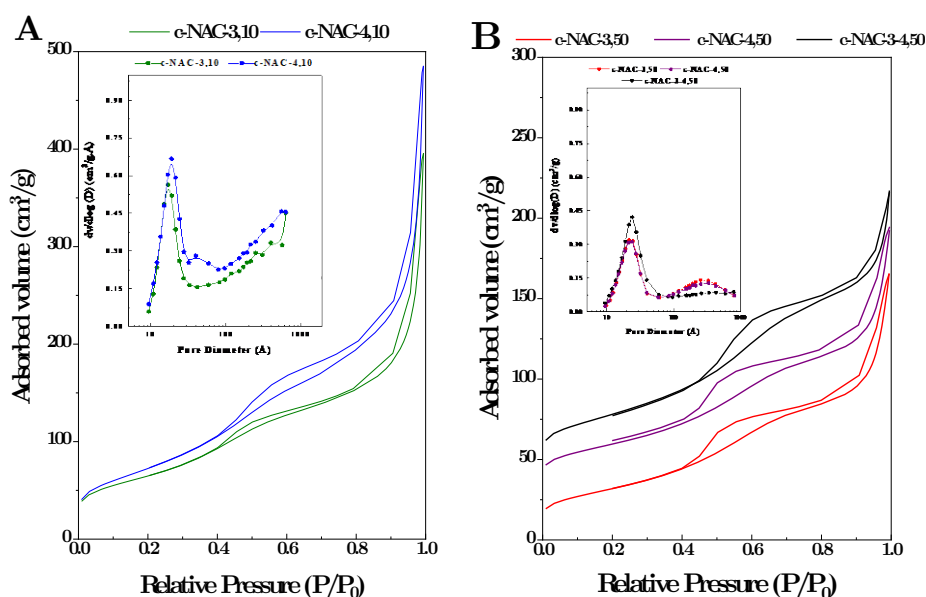


Figure 5.11: N_2 adsorption-desorption isotherms of calcined mixed oxides with with (A) 10% Ce and (B) 50% Ce

All mixed oxides presented type IV isotherms according to the IUPAC classification [27], with H3 hysteresis loop, proof of the mesoporous nature of these materials [21]. The asymptotic approach to relative pressures close to 1 is indicative of capillary condensation in the interplanar space due to slit-like pores generated by particle aggregation forming plaques, as already inferred in SEM images [27], [28].

Table 5.4: Textural properties of calcined mixed oxides

Mixed oxide	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore vol. ($\text{cm}^3 \cdot \text{g}^{-1}$)	Mesopore average size ($\text{\AA}$)	Macropore size distribution ($\text{\AA}$)
<i>c-NAC-3,10</i>	233	0.61	18	100-630
<i>c-NAC-4,10</i>	265	0.75	19	100-630
<i>c-NAC-3,50</i>	115	0.25	24	150-480
<i>c-NAC-4,50</i>	119	0.25	24	150-480
<i>c-NAC-3,4-50</i>	136	0.27	24	150-480

Regarding BET surface values, *c-NAC-3,10* and *c-NAC-4,10* presented the highest values: 233 and 265 $\text{m}^2 \cdot \text{g}^{-1}$, respectively. Predictably, in the samples containing a higher Ce proportion, adsorbed volume was diminished, which is also revealed in the decrease in BET surface values of almost 50% with respect to the 10% Ce counterparts. Considering that CeO_2 is non-porous, it could be suggested that the CeO_2 phase caused a significant pore blockage on the catalyst surface [22], [29].

Plots regarding pore size distribution are depicted in the inset of **Figure 5.11**, showing that samples presented a bimodal distribution, indicating, as previously reported for hydrotalcite-like systems [21], a pore network with mesopores and macropores in these materials, with a greater contribution of the former. In the case of *c-NAC-3,10* and *c-NAC-4,10* samples, one small mesopores region was around 10-100 $\text{\AA}$, with an average mesopore size of 18 $\text{\AA}$, and another mesoporous region ranging 100-630 $\text{\AA}$. For 50% Ce samples, the average mesopore size was 24 $\text{\AA}$ and large mesopores presented a narrower mesopore size distribution, between 150 and 480 $\text{\AA}$.

5.2.2.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS measurements of Ni $2p_{3/2}$, O $1s$ and Ce $3d$ core level spectra were collected to obtain information on the chemical environment as well as the chemical oxidation state of the elements on the catalysts surface. Since Ce $3d$ and Ni $2p_{1/2}$ signals overlap, the identification of Ce species at low binding energy was hindered.

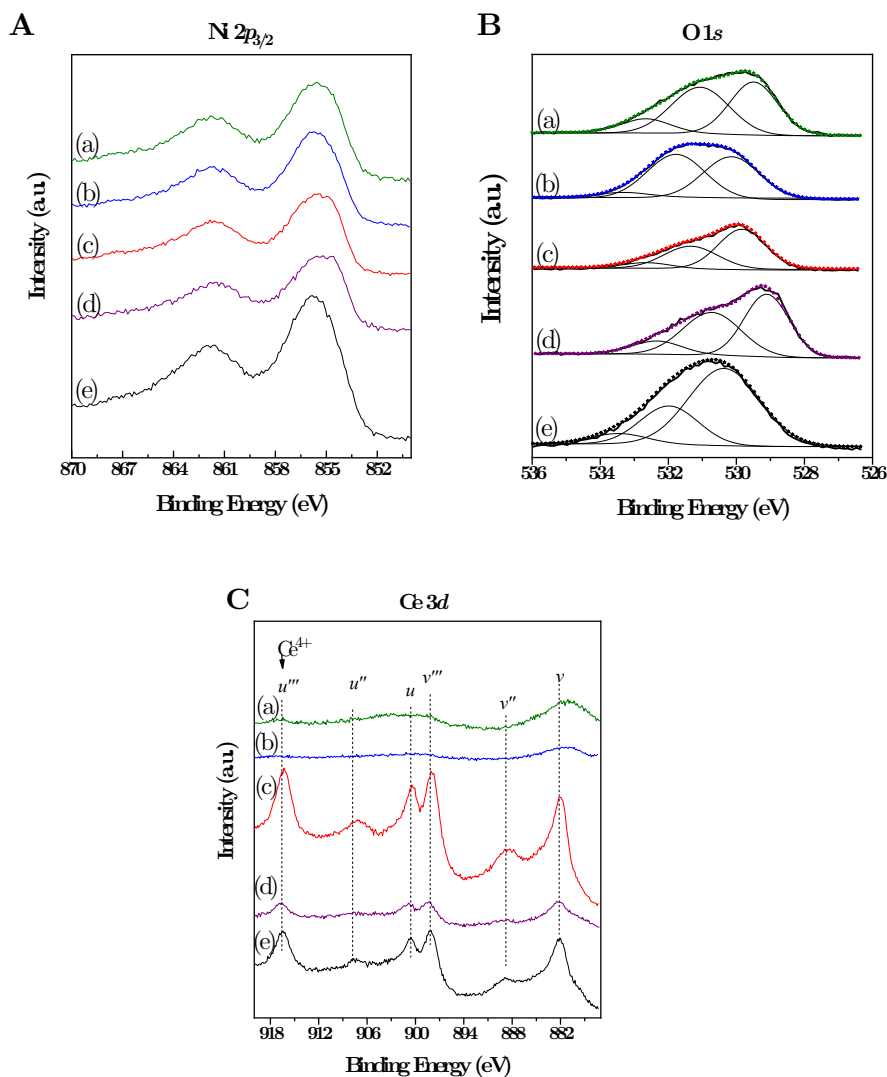


Figure 5.12: Ni $2p_{3/2}$, O $1s$ and Ce $3d$ core level spectra of calcined mixed oxides: (a) c-NAC-3,10; (b) c-NAC-4,10; (c) c-NAC-3,50; (d) c-NAC-4,50 and (e) c-NAC-3-4,50

Ni $2p_{3/2}$ core level spectra (**Figure 5.12 A**) showed a main contribution at *ca.* 855.5 eV (together with the shake-up satellite around 861.7 eV) associated with Ni^{2+} species [30]. No shifts in binding energies of the main signal nor in its intensity are noticed, indicating that the Ni presence in mixed oxides was not altered by cerium incorporation, irrespective of the Ce^{3+} or Ce^{4+} cations and proportion. Nevertheless, attention should also be drawn to the decrease in the Ni $2p_{3/2}$ signals at higher Ce contents, that could explain the worsening in the catalytic activity, since Ni active sites are less superficially exposed in these samples.

Conversely, the O $1s$ core level spectra (**Figure 5.12 B**) signals showed significant differences according to both the oxidation state and the proportion of Ce. In all cases, given the broadness of the registered signals, these have been decomposed in three contributions. In samples containing low Ce content, these contributions are located at *ca.* 530.0, 531.8 and 533.3 eV (see **Table 5.5**), assigned to lattice oxygen in Al_2O_3 oxides [31] and surface oxygen species and superficially adsorbed H_2O [32]. It has been reported that the lattice oxygen in NiO and CeO_2 is centred at *ca.* 529 [31] which could be evolve-at the first signal. In the case of the samples with highest concentration of cerium, the contribution due to ceria at *ca.* 529 eV appeared, being consistent with XRD where the diffraction peaks of this compound were evident at higher Ce incorporation degrees.

Noteworthy is the fact that the proportion of hydroxyl groups contribution in c-NAC-4,10 sample is the highest one, 50% (see **Table 5.5**), suggesting a significant proportion of acid sites on this catalyst's surface that could explain its better catalytic performance. Likewise, in the samples with 50% Ce, the contribution at lowest binding energy could also be related to CeO_2 lattice oxygen, as indicated by XRD results.

Table 5.5: Binding energy values of each contribution corresponding to O 1s core level signal in mixed oxides. Values in parenthesis indicate % of each contribution

Mixed oxide	Binding Energy (eV)			
	CeO ₂ -NiO	Me-O	Oxygen vacancies	H ₂ O _{adsorbed}
<i>c-NAC-3,10</i>	-	530.0 (66)	532.0 (27)	533.5 (7)
<i>c-NAC-4,10</i>	-	530.2 (46)	531.8 (50)	533.3 (4)
<i>c-NAC-3,50</i>	529.1 (47)	530.7 (41)	532.3 (12)	-
<i>c-NAC-4,50</i>	529.8 (56)	531.3 (35)	532.7 (9)	-
<i>c-NAC-3-4,50</i>	529.5 (43)	531.1 (44)	532.6 (13)	-

Lastly, Ce 3d core level spectra-are plotted in **Figure 5.12 C**. Given the low Ce loading in c-NAC-3,10 and c-NAC-4,10 samples, neither Ce³⁺ nor Ce⁴⁺ contributions are appreciated. Nonetheless, in the samples with 50% of Ce species, signals associated with Ce⁴⁺ Ce 3d_{3/2} and Ce 3d_{5/2} were identified at *v* (~882.8 eV) and *u* (~ 901.3 eV); *v*'' (~888.9 eV) and *u*'' (~ 907.6 eV); *v*''' (~898.5 eV), *u*''' (~917.0 eV) [33]. The presence of Ce³⁺ could not been clearly distinguished, these species should present two doublets: *v*₀ (~881.2 eV) and *u*₀ (~900 eV); *v*' (~885.3) and *u*' (~ 903.7 eV), which were not obvious for these samples. To avoid overlapping signals, the presence of Ce⁴⁺ species has been elucidated from the contribution at 916.5 eV, characteristic of this species that are present in the samples with higher cerium content (**Figure 5.12 C** (c), (d) and (e)). Anyhow, after calcination, oxidation of Ce³⁺ to Ce⁴⁺ species is expected. The shape of the spectra also

changed depending on the oxidation state of the Ce incorporated. In this way, the sample with 50% Ce^{3+} c-NAC-3,50, **Figure 5.12 C (c)**, presented the highest intensity signal, followed by c-NAC-3-4,50 and c-NAC-4,50, which could be related to the location of Ce specie. XRD results indicated that the dispersion was better for the Ce^{4+} sample and the incorporation of Ce^{3+} leads to the formation of agglomerates that can be located on the external surface. Moreover, SEM images of the LDH precursors also showed that this sample presented a distinct morphology with larger particle aggregates and a unique TGA decomposition profile.

5.2.3. Reduced mixed oxides

5.2.3.1. X-Ray Diffraction (XRD)

XRD diffractograms of reduced mixed oxides (**Figure 5.13**) indicated that Ni was successfully reduced from Ni^{2+} to Ni^0 , especially in samples with higher Ce content, with two characteristic reflections of metallic nickel at $2\theta = 44.3^\circ$ and 51.7° (ICSD-260169), assigned to (111) and (200) planes, respectively. Additionally, some reflections belonging to the NiAl_2O_4 spinel phase (ICSD-72067) were observed, as well as those related to CeO_2 , since the reduction temperature used (500°C) is not sufficient to achieve the Ce reduction [34]. Aluminium was neither reduced, thus Al^{3+} spinel is expected [29], [35].

Thus, it can be concluded that higher temperatures are needed to achieve complete Al or Ce reduction. Nonetheless, nickel was successfully reduced, and the presence of Ce^{3+} and Ce^{4+} has been reported to enhance catalytic activity [1].

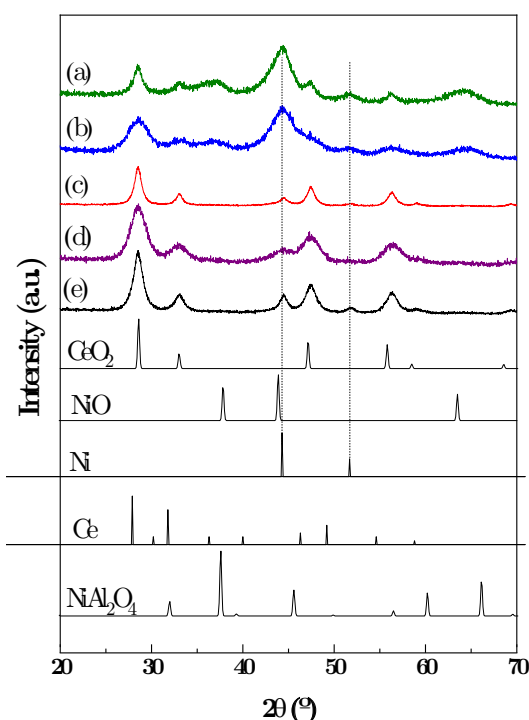


Figure 5.13: High-angle X-Ray diffractograms for reduced mixed oxides: (a) NAC-3,10; (b) NAC-4,10; (c) NAC-3,50; (d) NAC-4,50 and (e) NAC-3-4,50

5.2.3.2. X-Ray Photoelectron Spectroscopy (XPS)

To study the surface composition of the catalysts under operating conditions, XPS analyses of reduced mixed oxides were performed, and recorded spectra are collected in **Figure 5.14**.

Ni $2p_{3/2}$ was not altered neither by Ce content nor by its oxidation state, suggesting that the Ce species are not covering Ni ones. As a consequence of the passivation layer, Ni^{2+} is still present, but a new contribution at lower binding energy is observed by the widening of the main peak, which is attributed to metallic Ni as already suggested by XRD analysis.

Table 5.6: Binding energy values of each contribution corresponding to O 1s core level signal in reduced samples. Values in parenthesis indicate % contribution

Catalyst	Binding Energy (eV)			
	CeO ₂ -NiO	Me-O	Oxygen vacancies	H ₂ O _{adsorbed}
<i>NAC-3,10</i>	-	530.0	531.3	532.6
		(46.8)	(40.5)	(12.7)
<i>NAC-4,10</i>	-	529.9	531.2	532.4
		(36)	(45)	(19)
<i>NAC-3,50</i>	529.2	531.0	532.4	-
	(56)	(35)	(91)	
<i>NAC-4,50</i>	529.5	531.2	532.6	-
	(42)	(44)	(14)	
<i>NAC-3-4,50</i>	529.5	531.2	532.7	-
	(42)	(41)	(17)	

Regarding the O 1s core level spectra, comparing the data in **Table 5.5** and **Table 5.6**, it is easily noticed that hydroxyl groups contribution is higher in the reduced samples but followed the same trend as in the mixed oxides, with the greatest contribution in the most active sample NAC-4,10. Also, the presence of lattice oxygen from NiO and CeO₂ is observed in samples with 50% Ce.

Although, as above mentioned, the overlapping of Ce 3d and Ni 2p_{1/2} signals diffculted the identification of these species, the presence of Ce³⁺ species can be observed in reduced samples with v_0 , u_0 , v' and u' Ce³⁺ signals, pointed out in **Figure 5.14 C**. As expected, Ce⁴⁺ species contributions are present, especially in samples with higher Ce content because of the passivation layer.

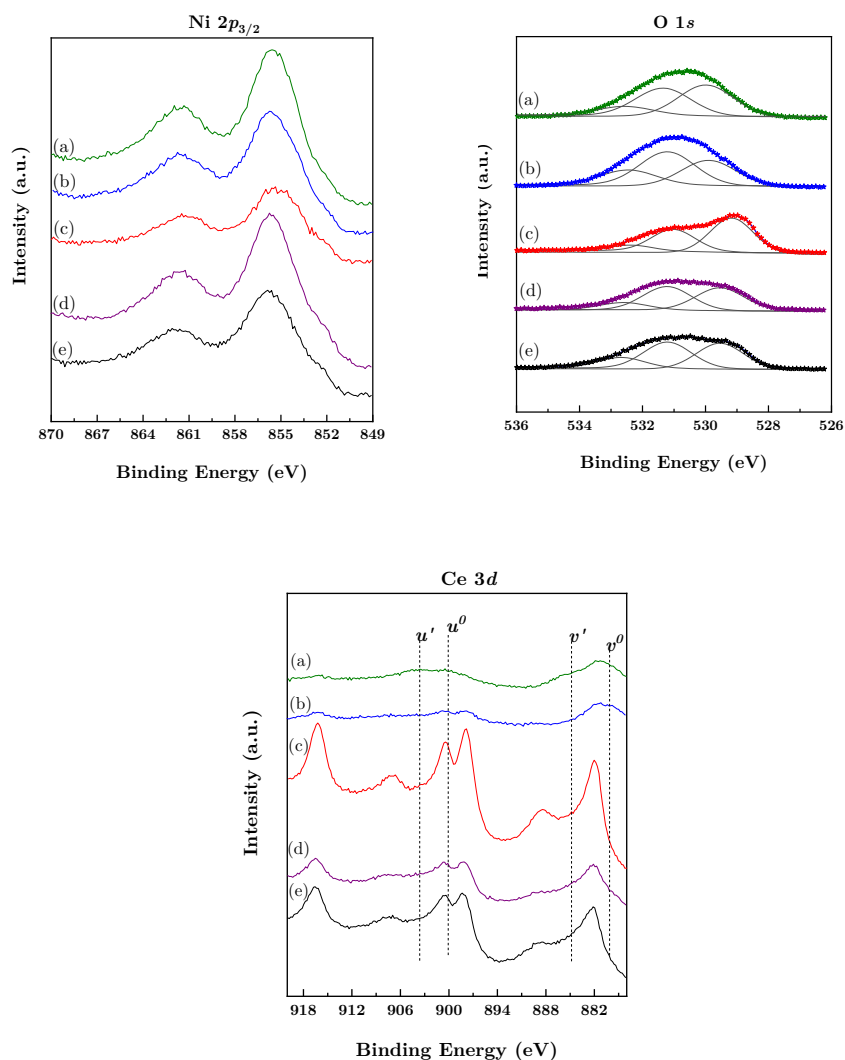


Figure 5.14: Ni $2p_{3/2}$, O $1s$ and Ce $3d$ core level spectra of reduced mixed oxides: (a) NAC-3,10; (b) NAC-4,10; (c) NAC-3,50; (d) NAC-4,50 and (e) NAC-3-4,50

5.2.3.3. Ammonia thermoprogrammed desorption (NH_3 -TPD)

The acidic properties of the samples were evaluated by ammonia thermoprogrammed desorption. Prior to ammonia adsorption, samples were reduced following the procedure described in the Materials and Methods section for these catalysts. **Figure 5.15** shows the desorption curves for

reduced samples, and the amount of NH_3 desorbed in each temperature range is collected in

Table 5.7. It is reported that the NH_3 desorbed between 100 and 300 °C is due to acid sites of weak nature, whereas the NH_3 desorbed between 300 and 500 °C represents medium acidity sites.

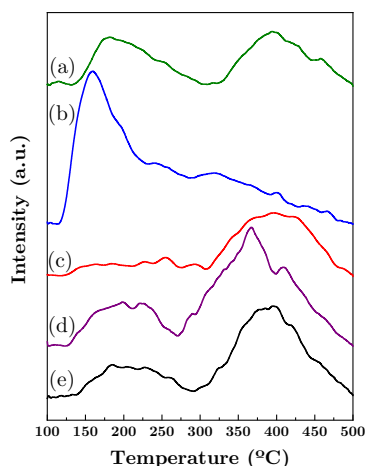


Figure 5.15: Ammonia desorption curves of reduced samples: (a) NAC-3,10; (b) NAC-4,10; (c) NAC-3,50; (d) NAC-4,50 and (e) NAC-3-4,50

Except for NAC-4,10 sample that showed a single desorption peak at around 160 °C, corresponding to weak acidity, all the reduced mixed oxides presented the same trend towards weak to medium acidity. Samples containing higher contents of Ce presented a higher proportion of medium acidity, which could be explained considering that surface Ce supplies oxygen vacancies, therefore promoting Ce^{4+} reduction to Ce^{3+} [36] and increasing the number of Lewis acid sites that are responsible for medium acidity, as reported by Pan et al. [37]. The higher acidity, mainly of weak nature in the NAC-4,10 sample, suggests that this kind of acidity favours a better catalytic performance in the hydrodeoxygenation reaction of anisole.

Table 5.7 data reveal that samples synthesized from Ce^{4+} species showed higher total acidity as a result of larger amount of ammonia desorbed at low temperatures, while NAC-3-4,50 sample prepared from both Ce^{3+} and Ce^{4+} showed an intermediate behaviour.

Table 5.7: μgram of NH_3 desorbed per gram of reduced catalyst

Catalyst	Acidity ($\text{mol NH}_3 \cdot \text{g}^{-1}$)		
	Weak ^a	Medium ^b	Total
<i>NAC-3,10</i>	122.3	106.8	229.1
<i>NAC-4,10</i>	338.7	96.5	435.3
<i>NAC-3,50</i>	97.3	151.6	248.9
<i>NAC-4,50</i>	221.8	220.2	442.0
<i>NAC-3-4,50</i>	137.8	181.9	319.7

^a NH_3 desorbed between 100 and 300 °C. ^b NH_3 desorbed between 300 and 500 °C

5.2.3.4. Hydrogen chemisorption

Nickel dispersion in reduced mixed oxides was studied by H_2 chemisorption at 35 °C. The apparent metallic dispersion was calculated by the double isotherm method of irreversible hydrogen chemisorption and is reported in **Table 5.8**. Despite the high theoretical nickel content in all samples, its dispersion was quite low in terms of accessibility. Samples derived from the Ce^{3+} precursor presented the lowest Ni dispersion, which is in good agreement with the XPS results for reduced samples that showed a decrease in the Ni $2p_{3/2}$ signal intensity in these samples, which is probably due to the larger ionic radius of Ce^{3+} in comparison to its Ce^{4+} counterpart. Thus, as evidenced by the SEM images, the sample is more prone to particle agglomeration that hinder hydrogen access to nickel active sites. Lastly, it is worth mentioning that the most active sample, NAC-4,10, also presented

the highest nickel dispersion, which is in accordance with BET surface values. Moreover, all samples followed a similar trend in nickel dispersion to that in catalytic activity.

Table 5.8: Metallic properties of reduced mixed oxides

Catalyst	Ni dispersion (%)
<i>NAC-3,10</i>	2.77
<i>NAC-4,10</i>	4.04
<i>NAC-3,50</i>	1.28
<i>NAC-4,50</i>	2.77
<i>NAC-3-4,50</i>	1.66

5.3. Discussion

This chapter shows that mixed oxides containing nickel, aluminium and different cerium species derived from hydrotalcite-like compounds are active catalysts in the anisole hydrodeoxygenation and selective towards high value-added products like cyclohexane and benzene. The high catalytic activity of these materials can be justified taking into consideration the characterization results obtained for layered double hydroxides precursors, as well as those of calcined and reduced mixed oxides, which are summarized below:

The LDH precursors characterization by XRD, TGA, SEM and FTIR techniques revealed that there is a limiting cerium amount that can be incorporated into the structure so that, it is maintained regardless the distortion and repulsion of the layer structure. Furthermore, this maximum loading is also related to the Ce species, Ce^{3+} or Ce^{4+} , because of their different ionic radius ($\text{Ce}^{3+} > \text{Ce}^{4+}$). By the SEM images, it was evidenced that the samples LDH-NAC-3,50 and LDH-NAC-4,50 showed different morphologies (see **Figure 5.9** c) and d), plaque-like and aggregates morphologies, respectively). Moreover, the thermal decomposition profiles differed from each other (see **Figure 5.8** c) and d)), showing in LDH-NAC-3,50 that the LDH structure was not attained, as XRD analysis also

suggested by the decrease in crystallinity. On the rest of the samples, the formation of the LDHs was confirmed by XRD results by characteristic reflections of LDH at $2\theta = 6.3^\circ$ and 62° , corresponding to d (003) and d (110) planes, the latter related to an increase in the unit cell parameter a in samples with 50% Ce: c-NAC-3,50, c-NAC-4,50 and c-NAC-3-4,50. Noteworthy is the fact that some segregate phases related to cerium and carboxylate derived from terephthalate ion were evidenced by the XRD and FTIR analyses, which also supports that indeed there is a limiting amount of cerium that can be incorporated into the structure without compromising the octahedral coordination and the symmetry of the structure.

Regarding calcined mixed oxides, the presence of NiO, CeO₂ and NiAl₂O₄ spinel phases was confirmed by XRD analysis. No phases related to aluminium oxide were detected, which indicates that Al³⁺ could be either present as an amorphous phase or that it is incorporated into NiO matrix. In addition, it was observed that in samples prepared from Ce³⁺, the reflections were slightly shifted from expected positions, which suggests that NiO crystalline structure could be distorted by the incorporation of Ce³⁺ ions. The BET surface area values indicated that, as expected, higher cerium loadings led to pore blockage by a non-porous CeO₂ phase. Nevertheless, all samples presented relatively high specific surface area over $110 \text{ m}^2 \cdot \text{g}^{-1}$, with bimodal porosity. XPS measurements exposed that Ce was mainly present as Ce⁴⁺, which endorses XRD results, and that Ni surface presence in calcined mixed oxides did not get altered by cerium incorporation. Also, it was found that samples prepared from Ce³⁺ showed greater intensity, which could be justified taking into consideration that this sample presented particle aggregates on the surface, as seen by SEM images of the LDH precursors. Lastly, elemental analysis by XRF confirmed the presence of these, obtaining metal ratios close to theoretical values.

In reduced mixed oxides, the presence of NiO and metallic Ni was confirmed by XRD analysis, especially in samples with 50% Ce species.

Given the low reduction temperature (500 °C), cerium and aluminium were present in their oxide phases. XPS results also confirmed that nickel is not covered by cerium on the catalyst surface and that it is present as Ni^{2+} due to the passivation layer, but also Ni presence was suggested. The greater contribution of hydroxyl groups in reduced mixed oxides was evidenced in O 1s core level spectra in comparison to calcined counterparts, indicating the higher acidity of samples in operating conditions. In fact, the most active sample, NAC-4,10, was the one showing the greatest -OH contribution. Moreover, NH_3 -TPD results indicated that the samples prepared from Ce^{4+} were the ones with highest acidity, with especial contribution of weak acid sites in NAC-4,10. XPS studies also confirmed that, due to the reduction process and the passivation layer, both Ce^{3+} and Ce^{4+} species are present on the catalysts surface, especially in samples with higher cerium content.

The catalytic activity followed the trend: NAC-4,10 > NAC-4,50 > NAC-3-4,50 > NAC-3,50 > NAC-3,10. The catalysts with higher Ce contents showed worse catalytic performance probably due to pore blockage by CeO_2 non-porous particles, as suggested by BET area values and N_2 adsorption/desorption isotherms, thus hindering the access of reactants molecules to Ni active sites. This fact was also supported by H_2 chemisorption results, indicating that NAC-4,10 was the sample with the highest Ni dispersion.

The main products obtained in the HDO of anisol with these catalysts were cyclohexane and benzene, which indicates that the reaction was carried out via the direct deoxygenation and further hydrogenation route (route 2 in **Figure 5.5**).

The better catalytic performance of NAC-4,10 (*ca.* 90% HDO conversion) could be attributed to several features: its thermal stability, evidenced by TGA analysis, its weak yet significant acidity, a high specific

surface area of mesoporous nature ($265 \text{ m}^2 \cdot \text{g}^{-1}$) and a good dispersion of the NiO phase.

Yang et al. [38], studied Ni- and Ce-containing catalysts in the anisole hydrodeoxygenation under 3 bar and temperatures in the range of 290-310 °C, and they reported conversions around 90% which suggests that the presence of either Ce^{3+} or Ce^{4+} influences the catalytic activity and selectivity. They also reported that the less hydrogenating capability of the prepared Ni supported on CeO_2 catalysts favoured oxygen adsorption and thus promoted demethylation via DDO route. Likewise, Phan et al. [39] reported the guaiacol hydrodeoxygenation using NiMo catalysts supported on different solids: alumina, ceria and SBA-15, at 50 bar and 250 °C, demonstrating the greater interaction between ceria and molybdenum and also the synergistic effect between ceria and nickel in terms of hydrogenating capability. Moreover, the low acidity of cerium oxides helped to inhibit coke deposition.

Table 5.9 resumes several works using nickel- and cerium-based catalysts in the hydrodeoxygenation reaction of model compounds that can be found in lignocellulosic biomass-derived bio-oil, such as anisole, guaiacol or phenol. From the reported data, it can be said that the prepared catalysts in this work successfully met the conversions and selectivities found in the literature. Additionally, noteworthy mentioning is the the study carried out by Aysu et al. [40], testing ceria-based catalysts supported on alumina and zirconia and adding a second metal like Mg or Ni in the hydrodeoxygenation reaction of pyrolyzed algae. Among all the catalysts, those containing both nickel and ceria resulted the most actives ones, especially those supported on an acidic support with a high specific surface area like Al_2O_3 , on which decarboxylation was favoured. This can be understood taking into consideration that these metal oxides are rich in defects that can increase oxygen vacancies, thus promoting adsorption and C-O bond cleavage [41].

Table 5.9: Ni- and Ce-based catalysts in hydrodeoxygenation reaction of model compounds present in lignocellulosic biomass-derived bio-oil

Catalyst	Preparation method	Reaction	Conditions	Conversion	Ref.
<i>NAC-4,10</i>	Mixed NiAlCe oxides obtained from the thermal decomposition of layered double hydroxides.	Anisole HDO	Fixed bed reactor, at 275 °C and 15 bar. Prior reduction in situ: H ₂ at 500 °C.	93.7%, with greater selectivity for cyclohexane.	This work
<i>Ni/CeO₂</i>	Wet impregnation of Ni precursor in CeO ₂	Anisole HDO	Fixed bed reactor, at 290-310 °C and 3 bar. Prior reduction with H ₂ at 550 °C.	290°C: 88%, 310°C: 98%, with selectivity for benzene formation.	[38]
<i>Ni/Ce-SBA-15</i>	Wet impregnation of Ni precursor in Ce-SBA-15 (Ce added during SBA synthesis)	Anisole HDO	Fixed bed reactor, at 270-290 °C and 7 bar. Prior reduction at 550 °C.	25%, with greater selectivity for benzene and methoxycyclohexane.	[1]
<i>NiMoCe/γ-Al₂O₃</i>	Wet impregnation of Ni, Mo, Ce precursor in γ -Al ₂ O ₃ .	Guaiacol and bio-oil from cassava rhizomes HDO.	Reaction at 300 °C and 10 bar. Prior in situ reduction	Ce increased the conversion of guaiacol. For bio-oil, 4% Ce improved the efficiency of the NiMo catalyst.	[42]

Ni/CeO_2	Wet impregnation of Ni precursor in calcined CeO_2 prepared by precipitation of $(NH_4)_2Ce(NO_3)_6$ with NH_4OH .	Phenol HDO	Fixed bed reactor at 300 °C and 1 bar. Prior reduction in situ at 500 °C.	13.4%, with low selectivity for benzene formation, which was overcome with the addition of Nb in the support ($Ni / Ce_{1-x}Nb_xO_2$).	[43]
$Ni/La_{1-x}Ce_xNiO_3$	Reduction of nickel in the perovskite oxides $La_{1-x}Ce_xNiO_3$ ($0.0 \leq x \leq 0.9$).	Guaiacol HDO	Autoclave reactor at 300 °C and 50 bar. Perovskites were previously activated ex situ with H_2 at 500 °C.	80%, with greater selectivity for the formation of cyclohexanol.	[44]
$Cu-Ni/CeO_2$	Deposition method via coprecipitation.	Vanillin HDO	Stainless-steel autoclave at 150 °C and 25 bar.	68%, with selectivity for the formation of 2-methoxy-4-methylphenol and vanyl alcohol.	[45]

5.4. Conclusions

This study showed that mixed oxides composed of nickel, aluminium and cerium, obtained from hydrotalcite-like compounds, are active catalysts in the anisole conversion to deoxygenated products. The catalytic activity was governed by the cerium oxidation state used in the synthesis, as well as by the Al/Ce ratio. It was demonstrated that there is a limiting amount of Ce that can be incorporated into the LDH without compromising the layer structure and symmetry, and that this loading was also strongly influenced by the Ce oxidation state because of the larger ionic radius of Ce^{3+} in comparison to Ce^{4+} counterpart. In fact, the sample prepared from Ce^{3+} with a 50% loading did not present the characteristics of LDH material, as evidenced by the TGA, SEM and XRD characterization results, showing a unique decomposition profile, agglomerated phases on the surface and lower crystallinity, respectively.

The higher anisole conversion values were evidenced for catalysts derived from LDH precursors mainly prepared from Ce^{4+} , which also showed higher thermal stability and more dispersed NiO and CeO_2 phases. Particularly, the NAC-4,10 sample was the most active, with an anisole conversion close to 93.7% and 89.3% of HDO conversion mainly to cyclohexane deoxygenated product. This better catalytic performance could be justified considering the characterization results obtained for this sample: it was the one with the highest Ni dispersion as calculated by H_2 chemisorption, it presented one of the highest specific surface areas ($265 \text{ m}^2 \cdot \text{g}^{-1}$) and greatest contribution of surface hydroxyl groups.

Their remarkable catalytic performance can be summarized in their bifunctionality: nickel acts as hydrogenating active site and aluminium and cerium oxides are the acid counterpart, needed for oxy groups activation. Therefore, these materials arise as a feasible low-cost option as hydrodeoxygenation catalysts, thanks to their high activity and selectivity

to deoxygenated products with high added value like cyclohexane and benzene.

5.5. References

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6. PtFe-based catalysts for anisole HDO

Summary

A set of bifunctional catalysts based on platinum and iron was studied in this chapter. All catalysts containing 1 wt.% Pt and different proportions of Fe were supported on a non-commercial neutral mesoporous solid, SBA-15. The role of iron, as the acid oxophilic compound able to activate oxy groups was studied by changing Fe proportion in the prepared catalysts. The catalytic activity of the catalysts was evaluated in the hydrodeoxygenation reaction of anisole, as a model molecule present in lignocellulosic biomass derived bio-oil. The reaction conditions were 30 bar of hydrogen pressure and 275 °C. The most active catalysts were also tested at 15 bar and 300 °C, in order to find optimal reaction conditions.

The catalysts containing 1 wt.% Pt and 5, 15, and 30 wt.% Fe were prepared by incipient wetness impregnation method as detailed in Materials and Methods section, and named Pt5Fe, Pt15Fe and Pt30Fe. Monometallic counterparts were also prepared and named Pt and 5Fe, 15Fe and 30Fe for 5, 15 and 30 wt.% Fe, respectively.

6.1. Catalytic test

Anisole hydrodeoxygenation (HDO) reaction at 30 bar of hydrogen pressure and 275 °C was performed to evaluate the catalytic activity of Pt- and Fe-based supported on SBA-15 prepared catalysts. **Figure 6.1** shows total and HDO conversion for all prepared catalysts during 5 hours on stream, and **Figure 6.2** represents total and HDO conversion at 5 hours of reaction. Besides, selectivity bar plot for all catalysts is displayed in **Figure 6.3**.

Although Pt seemed the most active catalyst in **Figure 6.1 A**, if attention is paid to **Figure 6.1 B**, it is observed that this activity is related to total and not HDO conversion, i.e., over this catalyst anisole is not transformed into deoxygenated products. Therefore, from the comparison of

these plots it can be said that samples containing both Pt and Fe achieved greater total and HDO conversions than their monometallic counterparts, confirming that the required bifunctionality for HDO reaction is present in these catalysts: on the one hand, Pt acts activating the hydrogen molecule and hydrogenates the aromatic ring in anisole, and Fe acts as the oxophilic part eliminating methoxy group [1].

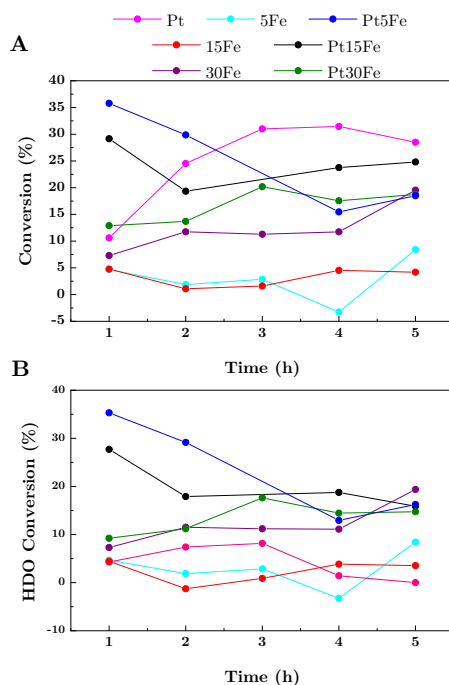


Figure 6.1: (A) Total conversion and (B) HDO conversion for all prepared Pt- and Fe- based catalysts during 5 hours on stream.

Regarding Pt-Fe samples, those containing 5 and 15 wt.% Fe, resulted the most active ones, which suggests that high Fe loadings cause blockage of Pt active sites.

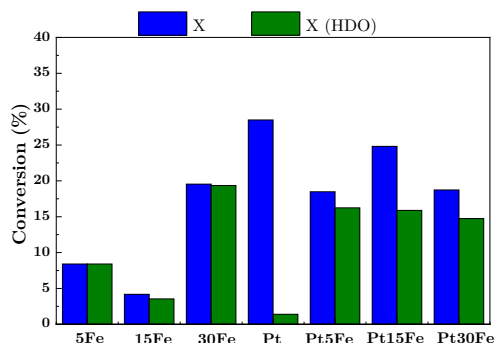


Figure 6.2: Total and HDO conversions at 5 hours of reaction.

As far as selectivity is concerned, except for Pt catalyst, all catalysts presented remarkable selectivity to deoxygenates (see **Figure 6.3 A**). Regarding product distribution in **Figure 6.3 B**, with Pt catalyst, the main product was cyclohexyl methyl ether, indicating that over this catalyst just hydrogenation of the aromatic ring of anisole was achieved. With the rest of the catalysts, the main product was cyclohexane. Noteworthy is that when Pt was added to the catalyst formulation, the selectivity to cyclohexane was doubled and hence benzene selectivity decreased, demonstrating the high hydrogenating activity of platinum.

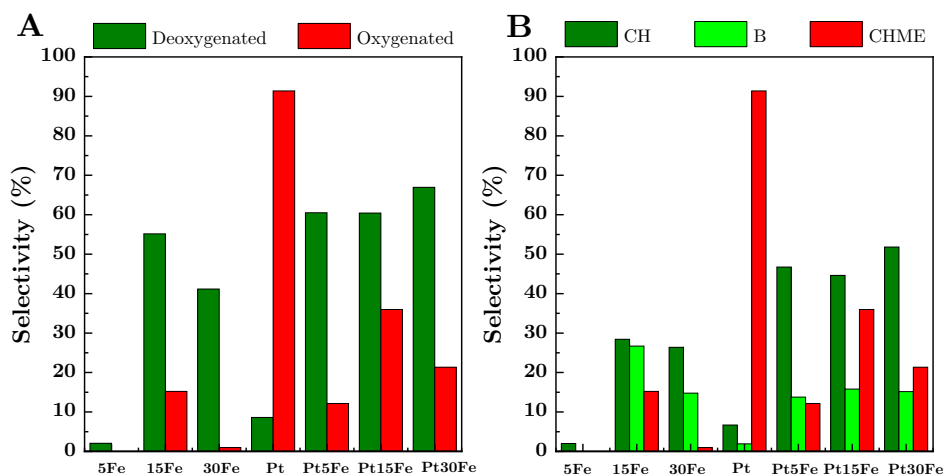


Figure 6.3: (A) Selectivity to deoxygenated and oxygenated products and (B) Product distribution after 5 hours of reaction.

Considering not only activity, but also stability and selectivity to deoxygenates in all catalysts, it was concluded that Pt5Fe and Pt15Fe were the catalysts showing the best catalytic performances. These catalysts were also tested in HDO of anisole reaction in the same conditions but were prior subjected to in-situ reduction at $350\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ for 1 hour, with a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ and the comparison of these reactions is included in **Figure 6.4**. It is observed that the reduction of the catalyst, not only favours HDO conversion, but also enhances catalytic activity, especially in Pt15Fe.

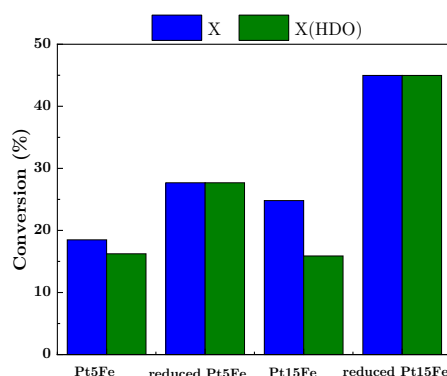


Figure 6.4: Conversion comparison over non-reduced and reduced Pt5Fe and Pt15Fe catalysts.

Additionally, Pt15Fe catalyst was tested under different reaction conditions in order to optimize anisole HDO. Thus, the comparison of catalytic activity and selectivity under 15 and 30 bar, as well as at $275\text{ }^{\circ}\text{C}$ and $300\text{ }^{\circ}\text{C}$ was studied and results are collected in **Figure 6.5 A** and **B**, respectively. Regarding pressure effect, it is observed that better conversions are obtained at 30 bar of hydrogen pressure, with more than doubled conversion. However, when it comes to temperature, negligible effect was noticed at $275\text{ }^{\circ}\text{C}$ or $300\text{ }^{\circ}\text{C}$, with even a detriment in HDO conversion at higher temperature. As for product distribution in **Figure 6.6 A** and **B**, it was also observed a worsening in deoxygenates selectivity when working at 15 bar or $300\text{ }^{\circ}\text{C}$, respectively, since the oxygenated product cyclohexyl methyl ether (CHME) was obtained.

Therefore, for this catalytic study it can be concluded that the optimal catalyst formulation was 1 wt.% Pt and 15 wt.% Fe, working at 30 bar of hydrogen pressure and 275 °C.

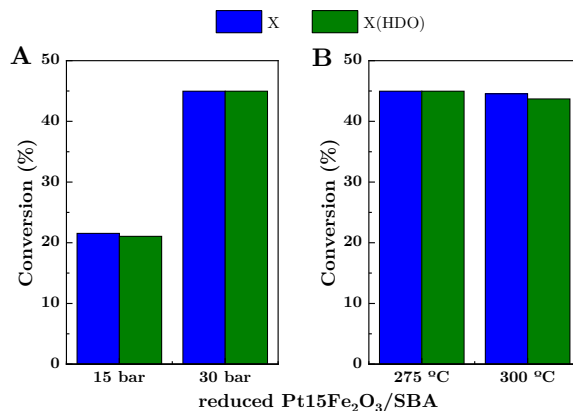


Figure 6.5: (A) Pressure and (B) Temperature conversion comparison for reduced Pt15Fe catalyst.

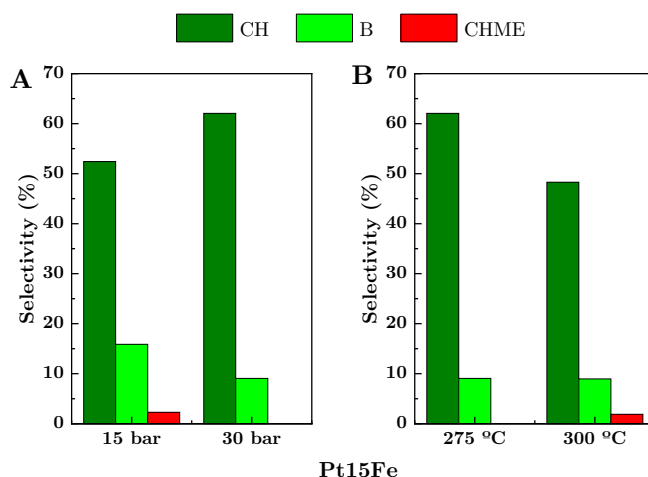


Figure 6.6: (A) Pressure and (B) Temperature products distribution comparison for reduced Pt15Fe catalyst.

6.2. Characterization results

6.2.1. X-Ray Diffraction (XRD)

The crystalline phases present in the samples were studied by means of X-Ray powder diffraction, and high-angle X-Ray diffractograms are displayed in **Figure 6.7**.

All samples presented a broad shoulder at 2θ angles between 20 and 30° , related to SBA-type amorphous materials [2]. Despite the low platinum loading (1 wt.%), reflections associated with this element in its metallic state were found at $2\theta = 39.8, 46.3$ and 67.5° (PDF No.: 96-101-1114) corresponding to (111) (200) and (220) crystallographic planes, respectively [3]. Regarding iron, in samples containing 15 and 30 wt.%, hematite formation was confirmed by reflection at $2\theta = 24.2, 33.2, 35.6, 40.9, 49.5, 54.1, 62.4$ and 66.0 (PDF No.: 96-901-5965). Moreover, the presence of Fe_3O_4 cannot be ruled out since the most intense diffraction peak is located at 35.6° and overlaps with the second diffraction peak of Fe_2O_3 and whose relative intensity is higher than that expected if only Fe_2O_3 phase were present. In fact, the samples are slightly magnetic. Noteworthy is the fact that the broad band related to amorphous materials got diminished after Fe incorporation, suggesting a high crystallinity in samples with iron oxide loadings over 15 wt.%. In samples with 5 wt.% no peaks were observed due to the low loading and probably also to the high dispersion onto SBA-15 surface.

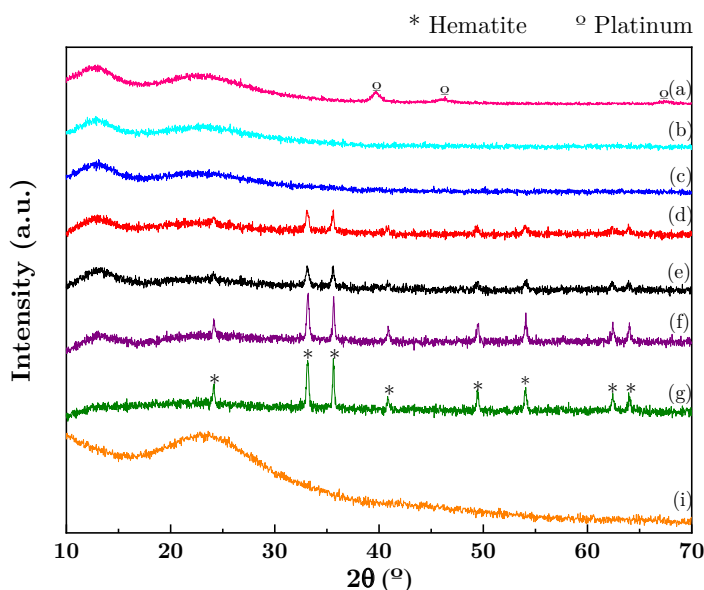


Figure 6.7:1 High-angle X-Ray diffraction patterns for (a) Pt, (b) 5Fe, (c) Pt5Fe, (d) 15Fe, (e) Pt15Fe, (f) 30Fe, (g)Pt30Fe and (i) bare SBA-15.

Considering the hematite particle size in samples with iron loadings over 5 wt.%, calculated from Scherrer equation, it raised with the iron loading but was unaltered under the presence of platinum (see **Table 6.1**).

6.2.2. Nitrogen adsorption-desorption isotherms

Textural properties displayed in **Table 6.1** of the prepared catalysts, as well as to bare SBA-15 support were calculated from N₂ adsorption-desorption isotherms at -196 °C, collected in **Figure 6.8**.

Table 6.1: Textural properties of prepared catalysts.

Catalyst	Particle size (nm)	S _{BET} (m ² .g ⁻¹) ^a	Pore volume (cm ³ .g ⁻¹) ^b	D _{meso} (nm) ^c
<i>SBA-15</i>	-	693	0.50	4.3
<i>Pt</i>	-	344	0.26	3.6
<i>5Fe</i>	-	366	0.26	3.7
<i>Pt5Fe</i>	-	276	0.21	3.4
<i>15Fe</i>	41	215	0.17	3.4
<i>Pt15Fe</i>	38	175	0.14	3.4
<i>30Fe</i>	69	277	0.19	3.6
<i>Pt30Fe</i>	71	219	0.17	3.7

^aBrunauer-Emmet-Teller specific surface area. ^bMesopore volume calculated by DFT method. ^cAverage mesopore size

All catalysts, as well as the bare support, presented type IV isotherms according to the IUPAC classification, which is characteristic of ordered mesoporous materials [4]. In addition, a clearly defined H2 hysteresis loop is found in all samples. This indicates that a more complex pore structure with significant network effects is present in these materials. The abrupt desorption branch suggests pore blockage and/or percolation due to bottle-neck pores. Also, the steep drop closing the loop at relative pressures around 0.42 corresponds to a large peak in pore size distribution at *ca.* 3.7 nm, as depicted in **Figure 6.9** and evidenced in **Table 6.1**, which

indicates the breakage of nitrogen meniscus at this relative pressure, typical when small mesopores are present in the catalyst [5].

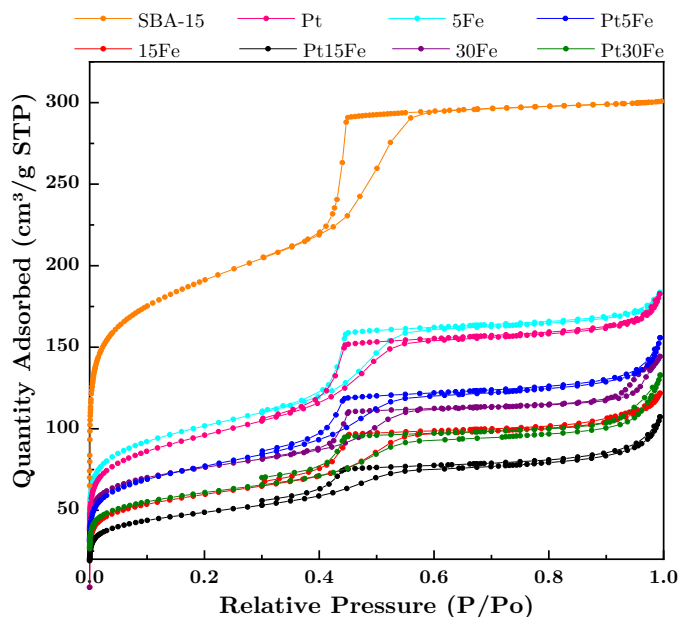


Figure 6.8: 2Nitrogen adsorption-desorption isotherms.

Regarding textural properties, in **Table 6.1** S_{BET} values and pore volumes are reported for all prepared samples. All samples presented relatively high specific surface area, especially in samples with lower metallic loadings. Predictably, a decrease in S_{BET} values was observed when Pt and Fe were incorporated into SBA-15 support. The diminishing was also noticed in pore volume values, which suggest that metallic particles could be hosted inside the SBA-15 pore channels but also on the surface, causing pore blockage and therefore decreasing specific surface area.

Therefore, from N_2 adsorption-desorption measurements it can be said that, although there is a considerable decrease in textural parameters (S_{BET} and pore volume), the SBA-15 mesoporous structure was maintained, which suggests that, as already evidenced by XRD results, Fe is successfully incorporated into SBA-15 porous structure despite the high loading applied.

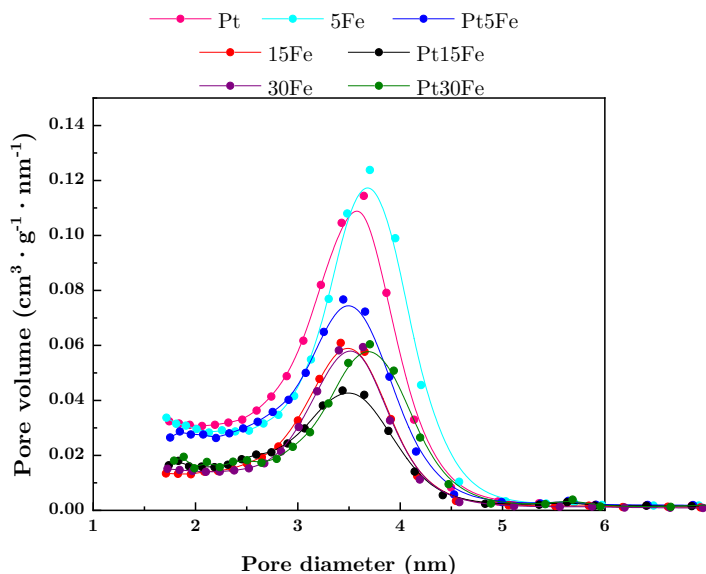


Figure 6.9: Pore size distribution of Pt- and Fe-based catalysts.

6.2.3. High Resolution Transmission Electron Microscopy (HR-TEM)

The dispersion of the metallic phases incorporated as well as the morphology of the samples was studied by means of HR-TEM and selected images are displayed in **Figure 6.10**.

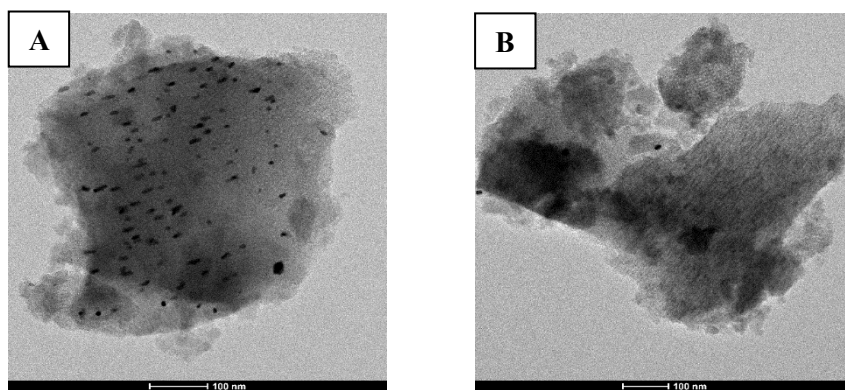


Figure 6.10: HR-TEM images for (A) Pt and (B) Pt5Fe catalysts.

In **Figure 6.10 A**, hexagonal ordered mesoporous structure of SBA is easily noticed, as well as dispersed platinum lengthened particles that seemed to be oriented in SBA-pore channels direction. ImageJ software was

used to measure particle size, resulting in an average length of 20 nm and 7 nm of diameter. When Fe was added, Pt particle size was greatly diminished, although some aggregates are still visible in **Figure 6.10 B**, also confirmed by EDX mapping, performed in STEM mode (see **Figure 6.11 B**). This fact suggests that there is a close interaction between Fe and Pt, as previously reported [6], [7]. Regarding Fe, **Figure 6.11 C** and **D** show that it is uniformly dispersed in SBA pore channels.

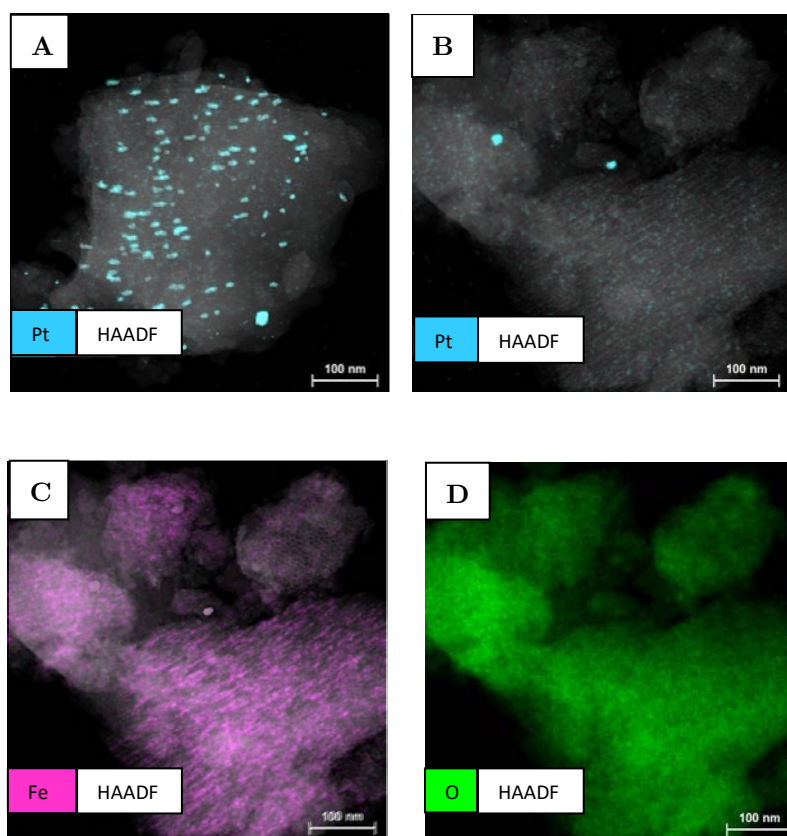


Figure 6.113: EDX-STEM mapping for (A) Pt and (B), (C) and (D) Pt₅Fe catalysts.

From this data it could be inferred that Fe is easily incorporated and greatly dispersed into SBA-15 matrix in the form of small Fe particles despite the high metal loadings used. Moreover, it was evidenced that Fe promotes the dispersion of Pt favouring the formation of smaller Pt particles when iron is present into the catalyst formulation.

HR-TEM images were also collected for Pt15Fe catalyst, before and after anisole HDO reaction, in order to study possible changes in morphology or Pt dispersion after the catalytic performance. **Figure 6.12 A** shows that fresh Pt15Fe presented highly dispersed Pt nanoparticles, with some Fe aggregates onto SBA matrix, probably due to the higher Fe loading in this sample compared to Pt5Fe in **Figure 6.11**. In **Figure 6.12 C** it is observed that, after reaction at 30 bar and 275 °C, some Pt agglomerates were found, indicating that this active phase may suffer from sintering. With respect to operating conditions at which anisole HDO was carried out, no significant changes were noticed in the catalyst neither working at 15 or 30 bar, nor at 275 or 300 °C.

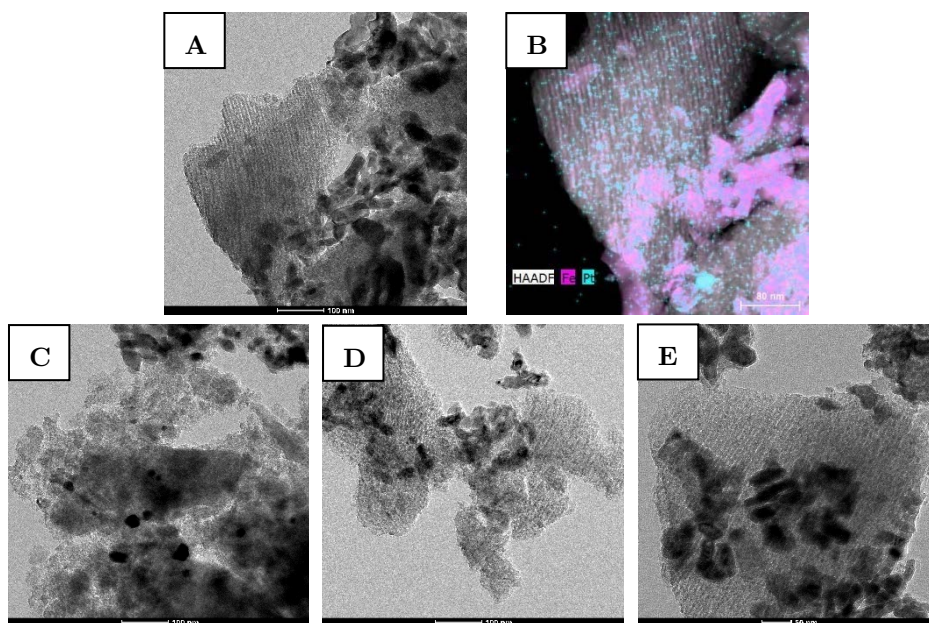


Figure 6.12: HR-TEM images: (A) fresh Pt15Fe, (B) EDX-STEM fresh Pt15Fe, (C) used Pt15Fe at 30 bar - 275 °C, (D) used Pt15Fe at 15 bar - 275 °C and (E) used Pt15Fe at 30 bar - 300 °C

6.2.4. X-Ray Photoelectron Spectroscopy (XPS)

Superficial composition and chemical environment were studied by XPS analyses. All signals were corrected with respect to Si 2p main peak at

103.4 eV attributed to oxygen in the lattice of SiO₂ [8]. Fe 2*p*, O 1*s* and Pt 4*f* core level spectra were registered and are displayed in **Figure 6.13**.

Table 6.2: Binding energy values for all prepared catalysts. Numbers in parenthesis indicate the % contribution.

Catalyst	Si 2 <i>p</i>	O 1 <i>s</i>			Fe 2 <i>p</i> _{3/2}	Pt 4 <i>f</i>
		Fe-O	Si-O	H ₂ O _{ads}		
<i>Pt</i>	103.4	-	531.0 (5.9)	532.7 (94.1)	-	71.4
<i>5Fe</i>	103.4	530.9 (7.9)	532.4 (68.8)	533.5 (23.3)	710.7	-
<i>Pt5Fe</i>	103.4	530.8 (8.9)	532.4 (68)	533.4 (23.1)	710.7	71.3
<i>15Fe</i>	103.4	529.9 (19.7)	532.4 (44.7)	533.4 (35.6)	710.5	-
<i>Pt15Fe</i>	103.4	529.7 (20)	532.1 (47.3)	533.1 (32.7)	710.6	71.3
<i>30Fe</i>	103.4	529.5 (28.7)	532.1 (34.1)	533.1 (37.2)	710.7	-
<i>Pt30Fe</i>	103.4	529.9 (32.4)	532.4 (31.3)	533.4 (36.3)	710.7	71.5 74.2

Regarding Fe 2*p* core level spectra in **Figure 6.13 A**, in samples with just 5 wt.%, Fe³⁺ presence is hardly distinguished because of the low metal loading. Conversely, in 15 and 30 wt.% samples, the peak at *ca.* 710.6 eV belonging to Fe 2*p*_{3/2} is clearly noticed, as well as its doublets for Fe 2*p*_{1/2} at *ca.* 724.3 eV [9]. The 13.6 eV separation between both doublets as well as the satellite peak at around 714.8 eV confirms the presence of Fe³⁺

ions in Fe_2O_3 [10] [11]. The greater width of Fe $2p_{1/2}$ peak could be associated with the presence of a second satellite peak at 729.5 eV [12].

Figure 6.13 B displays O $1s$ core level spectra present a similar trend to that of Si $2p$. Taking into account that Fe $2p_{3/2}$ signal did not suffer any shift when increasing the Fe loading in the sample, it could be said that Fe incorporation is somehow affecting SiO_2 structure. O $1s$ signals could be decomposed into several contributions, depending on the sample studied, and binding energies of each one are collected in **Table 6.2**. For Fe, three main contributions have been reported: the contribution at *ca.* 530 eV is associated with oxygen in the lattice of the oxide, the one at ~ 531.2 eV is attributed to hydroxide, hydrated or defective oxide sites and, lastly, the contribution at around 532.5 eV is related to adsorbed water or organic oxygen [13]. Considering that O $1s$ signal of silica gel materials appears at *ca.* 532 eV [8], it could be assumed that the signal at ~ 532 eV is related to oxygen in SiO_2 lattice and not to hydroxide species, although their presence cannot be disregarded. Expectedly, O $1s$ contribution related to metal oxide increased with Fe loading, but also there was an increase in contribution at ~ 533 eV, related to water adsorbed on the catalyst surface, probably due to the oxophilic nature of iron oxide.

Table 6.3: Atomic relative concentration for all samples.

Sample	Si/O	Fe/O	Si/Fe	Pt/Fe
<i>Pt</i>	0.43	0.00	-	-
<i>5Fe</i>	0.41	0.02	21.17	-
<i>Pt5Fe</i>	0.39	0.02	20.83	0.02
<i>15Fe</i>	0.37	0.12	3.10	-
<i>Pt15Fe</i>	0.33	0.13	2.59	0.03
<i>30Fe</i>	0.30	0.20	1.49	-
<i>Pt30Fe</i>	0.29	0.20	1.47	0.03

Lastly, **Figure 6.13 C** collects Pt 4*f* core level spectra of Pt-containing samples. Given the low Pt loading (1 wt.%), the signals are quite noisy thus it was difficult to distinguish Pt species. Nonetheless, in pure Pt sample, the presence of Pt as Pt²⁺ could be suggested by the contributions of Pt 4*f*_{7/2} at *ca.* 71.3 eV and its corresponding doublet of Pt 4*f*_{5/2} at 74.6 eV [8], [14]. In the sample with the highest Fe loading, it is also observed another contribution at higher BE values, finding a clearly defined Pt 4*f*_{7/2} at 74.7 eV, that has been related to PtO₂ [15].

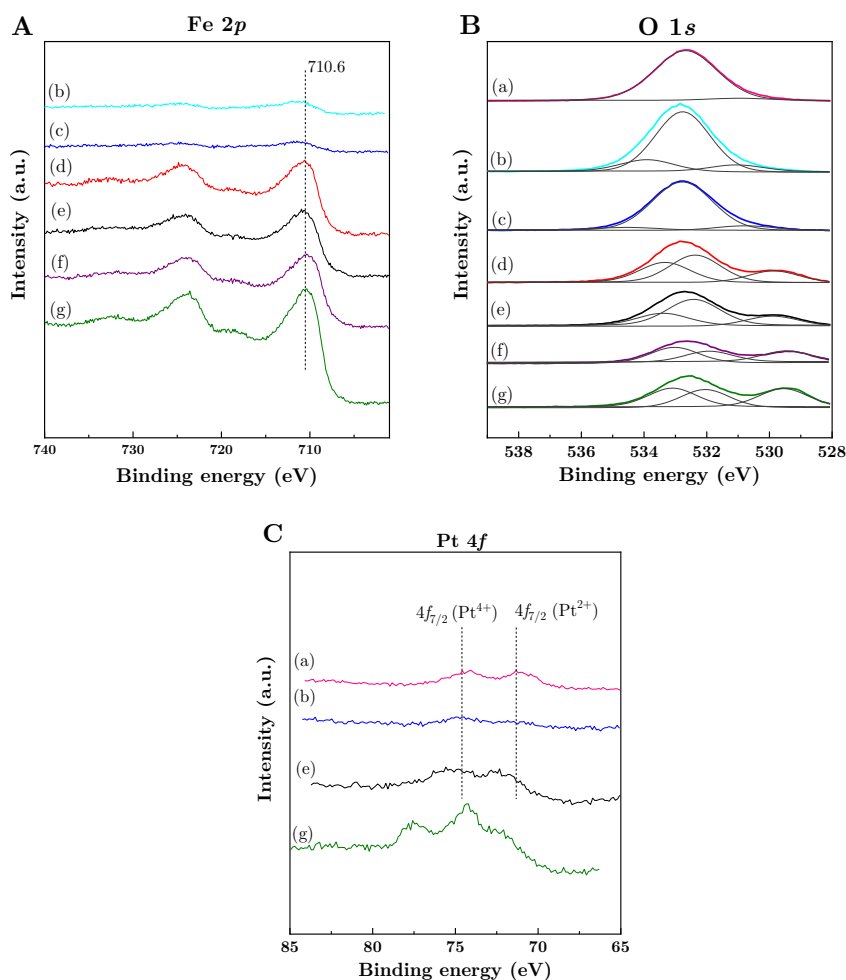


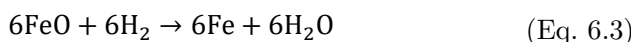
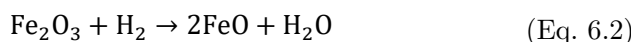
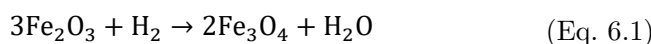
Figure 6.13: (A) Fe 2*p*, (B) O 1*s* and (C) Pt 4*f* core level spectra for (a) Pt, (b) 5Fe, (c) Pt5Fe, (d) 15Fe, (e) Pt15Fe, (f) 30Fe and (g) Pt30Fe catalysts.

Additionally, relative atomic concentrations have been calculated and are compiled in **Table 6.3**. It is observed that, predictably, when Fe was added to the SBA-15, Si/Fe ratio diminished, due to the covering of silica surface by iron and therefore hindering its detection by X-ray beam. Likewise, when Pt was added after Fe incorporation, apart from Si/Fe ratio Si/O one also decreased, which suggests that Pt also preferably stays on SBA-15 surface and not in the pores, as already evidenced by HR-TEM and EDX analysis, that showed Pt particles with a higher size than SBA-15 pore channels.

6.2.5. Hydrogen thermoprogrammed reduction (H_2 -TPR)

The reducibility of the species present in the catalysts were evaluated by means of hydrogen thermoprogrammed reduction, and H_2 consumption curves are collected in **Figure 6.14**.

Considering that iron can form different oxides, its reduction can be described in several steps, detailed in Eq. 6.1, Eq. 6.2 and Eq. 6.3 [16]:



H_2 consumption was significant for Fe loadings over 15 wt.%. Even though peaks are not well resolved due to the high heating rate ($10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$), several contributions could be distinguished. The first one at *ca.* $350\text{ }^\circ\text{C}$ is related to Fe_2O_3 reduction to Fe_3O_4 , whereas the second starting at around $550\text{ }^\circ\text{C}$ is attributed to Fe_3O_4 reduction to FeO , which is metastable and eventually gets reduced to Fe [17]. Regarding Pt reduction, it is reported to occur at $130\text{ }^\circ\text{C}$ and $365\text{ }^\circ\text{C}$ [8] for similar materials. The reduction of Pt species overlaps with those of iron, however, when Pt is added to Fe-containing catalysts, the peaks are shifted to lower temperature and therefore indicating that the reducibility is improved and therefore could be

another fact to justify the better catalytic results attained by the bimetallic catalysts.

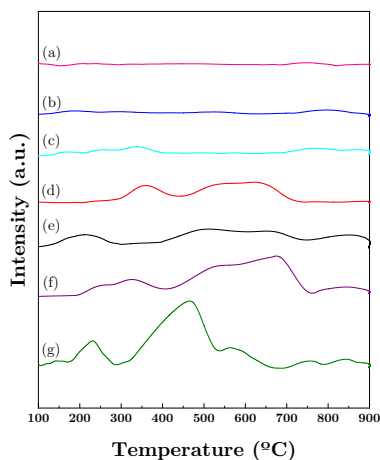


Figure 6.14: H_2 thermoprogrammed reduction profiles for (a) Pt, (b) 5Fe, (c) Pt5Fe, (d) 15Fe, (e) Pt15Fe, (f) 30Fe and (g)Pt30Fe catalysts.

6.3. Discussion

In this chapter, the synergistic effect between platinum and iron has been investigated in the hydrodeoxygenation reaction of anisole, resulting in active catalyst in the conversion of anisole to deoxygenated products cyclohexane and benzene. The catalytic activity of these materials has been associated with, on the one hand, the well-known remarkable hydrogenating capability of Pt and, on the other hand, the oxophilic and acid nature of Fe, as demonstrated by characterization results of the prepared catalysts:

Firstly, XRD analysis showed that iron oxide formed was hematite, Fe_2O_3 , with high crystallinity. Platinum presence was confirmed in monometallic sample, given the low metal loading and the high dispersion of this phase onto the catalyst surface. Moreover, HR-TEM and EDX-STEM images confirmed that Fe was highly dispersed into SBA pore channels, and that this phase enhanced the obtention of small Pt nanoparticles.

The mesoporous nature of these catalysts was evidenced by N₂ adsorption-desorption isotherms, showing that although Fe was partially blocking SBA-15 pore channels, the samples were still mesoporous, with S_{BET} values of *ca.* 200 m² · g⁻¹.

Surface analysis confirmed that Fe was successfully incorporated into SBA-15 porous structure, with a strong interaction between SiO₂ and Fe, given the shift in Si 2*p* core level spectra when iron oxide was incorporated, especially at high loadings. Also, the presence of a greater amount of adsorbed water on the catalyst surface was evidenced in samples with over 15 wt.% Fe, confirming the oxophilic nature of this compound. The reducibility of the catalysts improved under the presence of Pt.

Regarding the catalytic behaviour, the bimetallic samples were the ones with highest activity, following the trend Pt5Fe > Pt15Fe > Pt30Fe. However, the catalyst containing just 5 wt.% Fe suffered from deactivation during the reaction time on stream. Conversely, Pt15Fe resulted the most stable catalyst, with total and HDO conversions of *ca.* 30 % and 28 %, respectively during the whole reaction time studied (5h). Thus, this catalyst was chosen to study the influence of a hydrogen treatment prior to the anisole HDO reaction. It was observed that prior reduction had a significant beneficial effect in the catalytic behaviour, achieving 45% of total HDO conversion when reduced at 350 °C for 1 hour. In order to optimize operating conditions, the reduced Pt15Fe catalyst was studied at 15 and 30 bar, and 275 °C and 300 °C, demonstrating that the decrease in pressure had a detrimental effect not only in conversion, but also in products selectivity. Conversely, the temperature increase showed negligible effect and also an enhancement of selectivity to oxygenated product cyclohexyl methyl ether. To sum up, it can be concluded that the optimal operating conditions for this catalyst are 30 bar of hydrogen pressure and 275 °C.

6.4. Conclusions

This study shows that Pt-Fe supported catalysts are active in anisole conversion to deoxygenated products. The catalytic activity is influenced both by platinum presence as the hydrogenating part and by Fe loading, since it provides the oxophilic nature and the acidity needed in HDO bifunctional catalysts.

All catalysts maintained the mesoporous structure of SBA-type materials, presenting well-dispersed crystalline Fe particles in SBA-15 pore channels, with also highly dispersed Pt particles, whose size was influenced by Fe presence as evidenced by XRD and HR-TEM results. A close contact between Si and Fe was evidenced by XPS analysis, where a high superficial exposure of Pt was observed for samples with over 15 wt.% Fe.

Regarding the catalytic activity, Pt15Fe showed the best catalytic performance in terms of activity, stability and deoxygenates selectivity, with 28% anisole conversion mainly to cyclohexane (45%) and benzene (15%). This catalyst was also studied at different operating conditions under a hydrogen treatment, showing that the prior reduction of the catalyst had a beneficial effect, promoting HDO conversion up to 45%, and increasing cyclohexane selectivity (60%). Regarding pressure and temperature, it was observed that 30 bar and 275 °C resulted optimal conditions for anisole HDO reaction, since at lower pressure and higher temperature, detrimental effects in total and HDO conversion and an increase in oxygenates selectivity was noticed.

In conclusion, from this study it can be extracted that noble metal supported catalysts combined with a low-cost compound like 15Fe are good candidates for HDO reaction, since these catalysts present a bifunctional nature required for HDO reaction.

6.5. References

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7. AuCu-based supported catalysts for CO Photo-PROX and Methylene Blue photodegradation

Summary

The activity of supported gold and copper nanoparticles and their synergy in the photo-PROX of CO reaction as well as in the photodegradation of methylene blue dye are discussed in the present chapter. The photo-PROX catalytic tests were carried out in excess of hydrogen, at room temperature and atmospheric pressure both in dark and under simulated solar light. Methylene blue photodegradation tests were also performed at ambient conditions and under UV irradiation. The supports were synthesized as described in section 3.1.1. from *Materials and Methods* chapter. Likewise, gold and copper nanoparticles were incorporated by the deposition-reduction method detailed in section 3.2.1. thereof. In this sense, samples containing 1.5 wt.% Au, 2.0 wt.% of total metal loading and an Au/Cu molar ratio of 1 supported on pure SBA-15 and Ti-containing SBA were named AuCu/SBA and AuCu/Ti-SBA, respectively. The influence of hydrogen treatment in titania-containing sample was also studied using the non-reduced sample as reference, which was named Au-Cu/Ti-SBA. For comparison purposes, also Au/Ti-SBA and Au/SBA catalysts were studied in the photocatalytic reactions.

7.1. Catalytic test

The prepared mono and bimetallic catalysts, as well as bare supports were tested both in the preferential CO oxidation in excess of hydrogen and in methylene blue photodegradation under UV light at ambient conditions, using the experimental set up detailed in section 3.2.3 and 3.2.4. in *Materials and Methods* chapter, respectively.

7.1.1. CO Photo-PROX

Figure 7.1 displays CO conversions for titania containing support, Au and AuCu-based catalysts. Since copper monometallic counterpart as well as bare SBA-15 support did not show any catalytic activity neither in

dark nor under simulated solar light conditions their data has not been included. It can be observed that, although the Ti-SBA support had an insignificant photoactivity, an improvement is observed when gold nanoparticles were deposited on this support, attaining CO conversion values of 23.4%, compared to 1% for bare Ti-SBA under simulated solar light. Regarding photoactivity, all the catalysts presented an enhanced activity under simulated solar light, especially pronounced in samples containing both gold and copper. In bimetallic samples, CO conversion followed the trend $\text{AuCu}/\text{Ti-SBA} > \text{AuCu}/\text{SBA} > \text{Au-Cu}/\text{Ti-SBA}$, which suggests that copper, gold and titania present a synergistic effect, and that the hydrogen treatment to which the sample is subjected plays a crucial role in the photocatalytic activity.

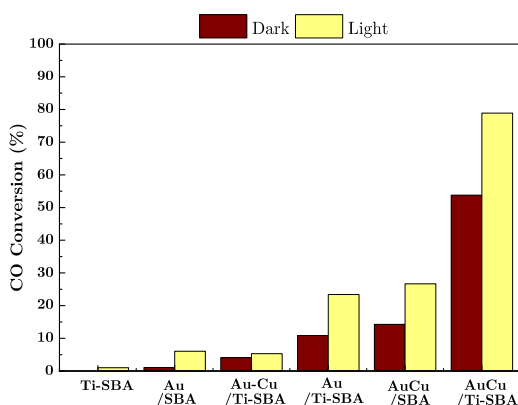


Figure 7.1: CO conversion for CO Photo-PROX reaction for Au and AuCu based catalysts

Focusing on **Figure 7.2** and **Figure 7.3**, it is easily observed that copper incorporation enhances not only conversion but also CO_2 selectivity. In fact, the most active and selective catalyst was $\text{AuCu}/\text{Ti-SBA}$, with 79% of CO conversion under simulated solar light and 81% CO_2 selectivity, which reinforces the fact that the hydrogen treatment influences the photoactivity of the catalysts.

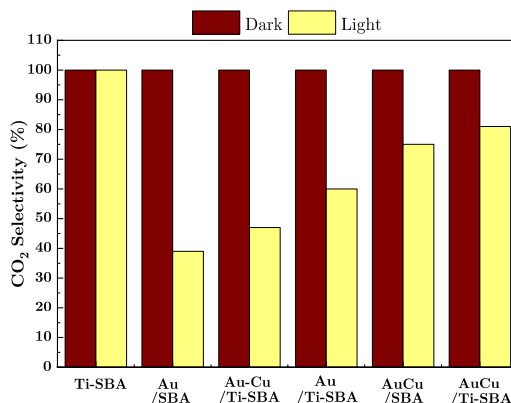


Figure 7.2: CO₂ selectivity for Ti-SBA, Au and AuCu-based catalysts

As previously mentioned in the Introduction chapter, two main interfacial phenomena can take place in compounds containing metal nanoparticles and a semiconductor like titania: Schottky barrier and Surface Plasmon Resonance (SPR), on which one could rely to understand the improvement in the photocatalytic activity when nanoparticles are incorporated to the mesoporous titania-containing support. When a Schottky barrier is formed between gold and copper nanoparticles and titania, electron states are created within titania's band gap that decrease its value [1], thus shifting the operating radiation to the visible light scope. Likewise, visible light irradiation induces localized surface plasmon resonance (LSPR) in metal nanoparticles, that act as electron harvesters [2] thus charge carriers (electron and holes) recombination rate is diminished and CO photo-oxidation by oxygen molecules is improved.

On the other hand, worth mentioning is the enhancement both in activity and selectivity when the catalysts were subjected to post-synthesis hydrogen treatment, which suggests that a close interaction, such as an alloy, is occurring between gold and copper nanoparticles. In the case of the non-hydrogen treated sample, Au-Cu/Ti-SBA, an abrupt decrease in photoactivity is observed, which could be related to the presence of partially oxidized copper species that could impede the electron transfer from gold to adsorbed oxygen molecules.

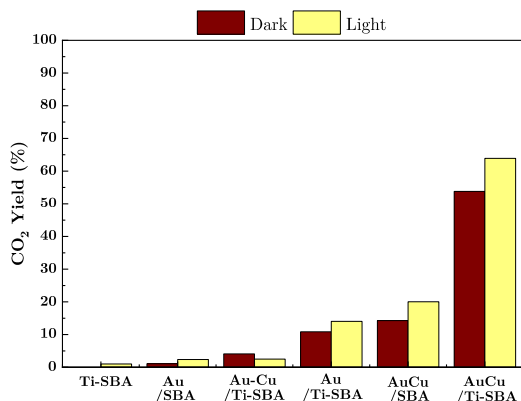


Figure 7.3: CO₂ yield for Ti-SBA, Au and AuCu-based catalysts

7.1.2. Methylene blue photodegradation

Photodegradation tests were also performed for Au and AuCu supported samples and also for both SBA and Ti-SBA supports. Since the latter presented negligible photoactivity, results have not been plotted in **Figure 7.4**. Prior to the catalytic test, the catalyst was suspended in MB aqueous solution for half an hour inside a dark box, so adsorption equilibrium was reached. The adsorption was less than 30% for all the studied samples, with the lowest values in Ti-containing samples, probably due to the diminishing in the support surface area after Ti incorporation, that partially blocked SBA mesoporous channels as well as to the pH adjustment described in section 3.2.4. of *Materials and Methods* chapter. Although all samples presented an exponential decrease of MB concentration after switching on the UV lamp, the best photocatalytic performance was obtained for the bimetallic sample supported on Ti-SBA, AuCu/Ti-SBA, with a total degradation of MB after two hours of reaction. This could be due to the simultaneity of the two previously mentioned phenomena occurring at the interface of the semiconductor and metal nanoparticle system: Schottky barrier formation and Localized Surface Plasmon Resonance (LSPR), that diminish the recombination rate of electron-hole pairs [2] as well as enhancing photocatalytic activity thanks to

metal nanoparticles' ability to act as electron reservoir, hindering electron backflowing to titania.

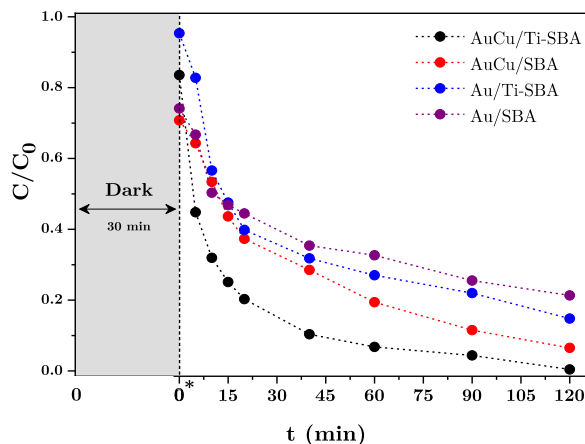


Figure 7.4: Methylene blue adsorption and photodegradation test

Methylene blue photodegradation kinetic constants have been calculated following equations Eq. 3.8 and Eq. 3.9 detailed in *Materials and Methods* section using the non-stationary state data and values have been collected in **Figure 7.5**. As expected, the highest value was obtained for the sample with titania and gold-copper alloy. This is due to the synergistic action of highly dispersed titania photoactive sites together with gold and copper NPs that absorb under UV light promoting the transition of electrons from $5d$ to $6sp$ band, which enhances the oxidation reaction of the dye [3].

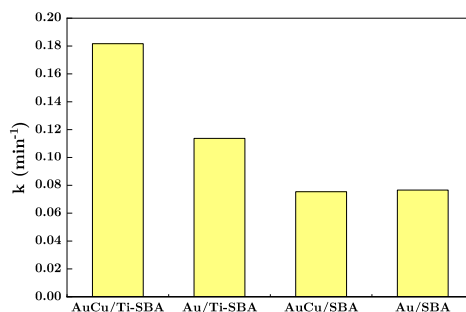


Figure 7.5: Kinetic constant for methylene blue photodegradation under UV light

7.2. Characterization results

7.2.1. X-Ray Diffraction (XRD)

X-Ray diffraction measurements were carried out to study the crystalline structure of bare supports and supported catalysts. **Figure 7.5 A** displays low angle diffractograms for all samples, showing d_{100} reflection characteristic of hexagonal symmetry in ordered mesoporous SBA-15 at $2\theta = 1.1^\circ$ [4]. It can be observed that in Ti-SBA support, the d_{100} reflection is shifted to lower angle, which suggests that titanium may have been incorporated into SBA-15 matrix and, consequently, the d_{100} is diminished from 8.74 to 8.57 nm, as reported in **Table 7.1**. Likewise, although Au and Cu incorporation also provoked a decrease in d_{100} values, the presence of a d_{100} reflection in mono and bimetallic samples indicates the maintenance of the typical SBA-15 mesoporous structure. In fact, the small decrease in d_{100} values suggests that both Au and Cu are preferentially incorporated inside SBA and Ti-SBA pore channels, as previously reported by Chen et al. [5].

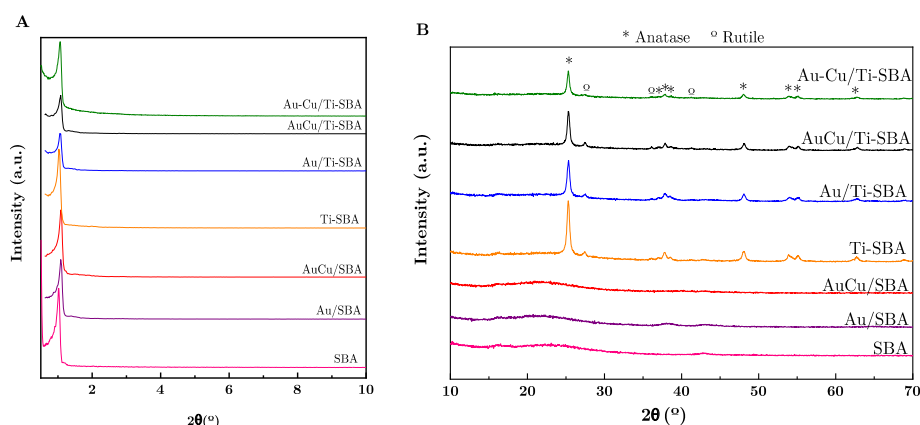


Figure 7.6: (A) low angle and (B) high angle diffractograms for bare supports and supported AuCu based catalysts

In addition, as reported in **Table 7.1**, d_{100} values after Au and Cu incorporation are higher in samples supported on Ti-SBA, since Ti is preferentially incorporated into SBA-15 inner porous structure, blocking

part of silica channels due to the high titania loading (30 wt. %). Lastly, noteworthy is that in the sample without hydrogen thermal treatment, Au-Cu/Ti-SBA, a greater d_{100} value is found in contrast to its treated counterpart AuCu/Ti-SBA, which may indicate that Au and Cu can form an alloy that helps to decrease particle size and ease nanoparticles incorporation into Ti-SBA pore channels.

Figure 7.5 B displays high angle diffractograms for all prepared samples. In all samples, a broad band typical of amorphous materials is observed at $ca. 2\theta = 22^\circ$, more accused in samples supported on SBA, since in the ones containing titania, this band is less noticeable due to diffraction peaks associate to titania crystalline phases. Regarding the presence of the latter, all samples containing titania presented both anatase and rutile crystalline phases, with diffraction peaks assigned to anatase (PDF No.: 01-089-4921) at $2\theta (^\circ) = 25.3, 37.3, 37.8, 38.6, 40.1, 53.9, 55.1$ and 62.8 , and to rutile (PDF No.: 01-072-1148) at $2\theta (^\circ) = 27.4, 36.0$ and 41.3 . The contribution of each crystalline phase was calculated using HighScore Plus software (P'Analytical, Almelo, The Netherlands) and was estimated to be *ca.* 86% for anatase and 14% for rutile, which are close to values found in commercial benchmark photocatalyst P25 titania. In addition, anatase mean crystal size calculated with the Scherrer equation was *ca.* 24 nm, which has been reported to be an optimal value for photocatalysis processes [6] [7].

Table 7.1: d_{100} parameter calculated by Bragg's equation

Catalyst	d_{100} (nm)
<i>SBA</i>	8.74
<i>Au/SBA</i>	8.10
<i>AuCu/SBA</i>	8.10
<i>Ti-SBA</i>	8.57
<i>Au/Ti-SBA</i>	8.17
<i>AuCu/Ti-SBA</i>	7.25
<i>Au-Cu/Ti-SBA</i>	8.33

7.2.2. Solid state nuclear magnetic resonance (ss-NMR)

In order to study titania's incorporation into the SBA-15 matrix and the influence of the APTES treatment, ^{29}Si and ^{13}C ss-NMR experiments were performed.

Structural studies of silicates by ss-NMR have been extensively studied by Lippmaa et al. [8], that reported that chemical shift is related to tetrahedral condensation, which gives rise to five distinguishable regions, from -60 to -120 ppm, in ^{29}Si spectrum (see **Figure 7.7**), conventionally named Q^n units where Q is referred to $[(\text{SiO})_n\text{Si}(\text{OX})_{4-n}]$, and n stands for bridging oxygen atoms surrounding the Si atom: Q^0 is associated with Si in isolated tetrahedrons, (monosilicates), Q^1 with disilicates and chain end groups, Q^2 with middle groups in chains (geminal silanols), Q^3 with planes and chain branching sites and lastly, Q^4 is assigned to three-dimensional cross-linked structures.

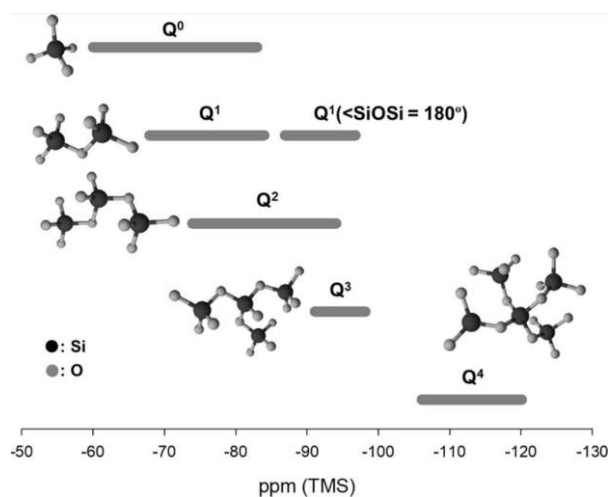


Figure 7.7: Typical ranges of ^{29}Si chemical shifts for silicates [9]

Other building units can also be described according to silicon functionality and are found in different regions of the ^{29}Si spectrum, which is especially interesting for polysilanes characterization. T^m region is associated with tri-functional silicon centres, where $\text{T}^m = [(\text{SiO})_m\text{RSi}(\text{OX})_3]$.

$m]$, being m the number of bridging oxygen atoms surrounding the central Si atom. These building units are schemed in **Figure 7.8**.

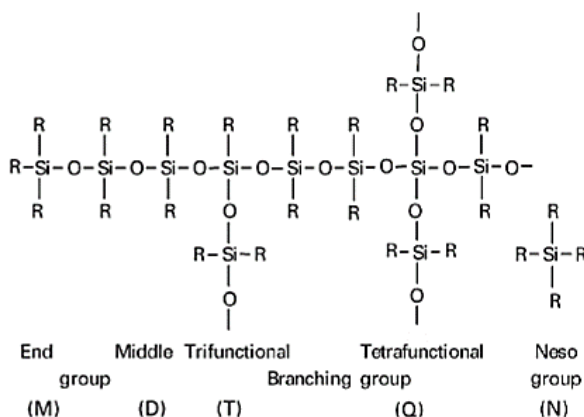


Figure 7.8: Building units in polysilanes [10]

Figure 7.9 A contains ^{29}Si spectra for SBA and Ti-SBA supports. It can be observed that three Q^n units are present in both supports: at $\delta = -91$ ppm Q^2 units corresponding to $[\text{Si}(\text{OSi})_2(\text{OH})_2]$ units, at $\delta = -100$ ppm Q^3 units assigned to $[\text{Si}(\text{OSi})_3\text{OH}]$ silicon units and, lastly, at $\delta = -110$ ppm, which is the major contribution, is related to Q^4 $[\text{Si}(\text{OSi})_4]$ units [11]. Nonetheless, when Ti is incorporated, Q^3 and Q^2 contributions decreased as shown in **Table 7.2**, which suggests that Ti preferentially interacts with OH^- groups on the silica surface and that Ti is successfully integrated in the SBA-15 matrix by means of covalent bonding, as already suggested by XRPD measurements.

SBA-15 and Ti-SBA supports were treated with 3-aminopropyltriethoxysilane, APTES, to ease nanoparticles incorporation since a previous work [12] has demonstrated that amino-silanes can form Si-O-Si bonds by means of grafting APTES to the silica surface. In this case, tri-functional silicon centres are also present, as observed in **Figure 7.9 B**, where T^2 and T^3 units are marked for both APTES-functionalized supports at -57 ppm and -67 ppm, respectively. T^2 units correspond to $[(\text{SiO})_2\text{RSiOH}]$

whereas T³ to [(SiO)₃R]. Analysing data exposed in **Table 7.2**, it is noted that T³ and T² units are created at the expense of Q³ and Q² units, which suggests that hydroxyl groups are the ones reacting with APTES in covalent bonding, as previously reported [13], [14].

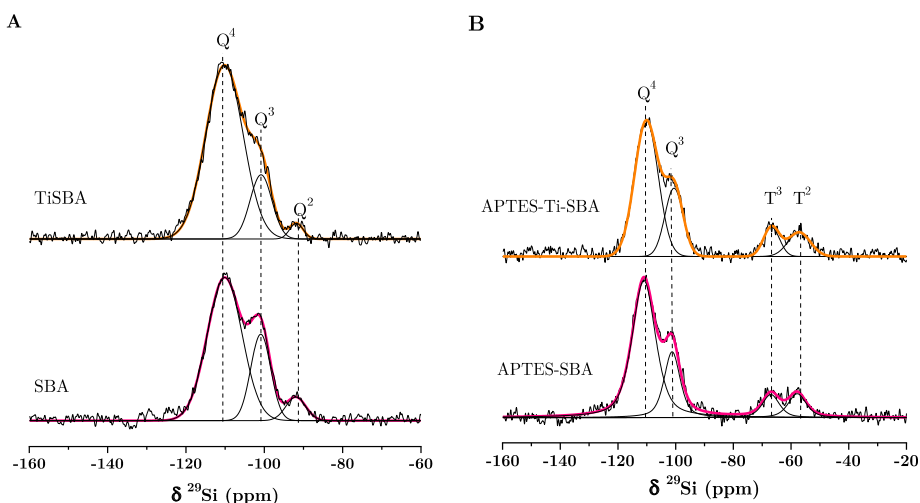


Figure 7.9: ²⁹Si nuclear magnetic resonance spectra of A: non-grafted Ti-SBA and SBA bare supports, B: APTES-functionalized Ti-SBA and SBA supports

Table 7.2: ²⁹Si ss-NMR band positions and contributions

	SBA		APTES-SBA		Ti-SBA		APTES-Ti-SBA	
	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%
Q ⁴	-110.1	69.4	-111.1	63.1	-110.2	80.1	-110.2	58.6
Q ³	-101.0	24.1	-101.2	20.7	-100.8	17.3	-100.6	22.8
Q ²	-91.9	6.5	-	-	-91.8	2.6	-	-
T ³	-	-	-67.0	7.7	-	-	-66.8	8.6
T ²	-	-	-57.8	8.5	-	-	-57.2	9.9

For a better understanding of APTES interaction with SBA and Ti-SBA, ¹³C NMR-ss was also performed and non-deconvoluted spectra are displayed in **Figure 7.10**. In both cases, three contributions associated with carbon atoms in the propyl chain: at 10.0 ppm, 24.1 ppm and 42.7 ppm,

which are related to $\text{CH}_3\text{-N}$, CH_2 and $\text{CH}_3\text{-Si}$, respectively, are observed [14], [15]. The negligible difference between APTES-SBA and APTES-Ti-SBA spectra led to the conclusion that Ti did not influence APTES functionalization.

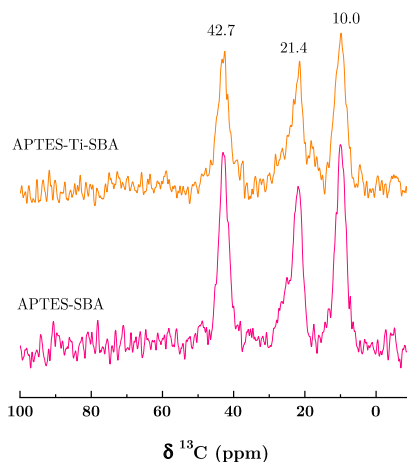


Figure 7.10: ^{13}C nuclear magnetic resonance of APTES-functionalized SBA and Ti-SBA supports

7.2.3. Nitrogen adsorption-desorption isotherms

Textural properties of the prepared supports and samples were studied by means of nitrogen adsorption-desorption isotherms at $-196\text{ }^{\circ}\text{C}$, which are displayed in **Figure 7.11**. The supports presented a type IV isotherm according to IUPAC classification [16] with a H1 hysteresis loop, due to capillary condensation, characteristic of SBA-like mesoporous materials. In titania containing support, the adsorbed volume is lower due to partial pore blocking due to titania incorporation inside SBA pore channels, which can be observed in the decrease in BET specific surface area (**Table 7.3**) from $654\text{ m}^2 \cdot \text{g}^{-1}$ in SBA to $393\text{ m}^2 \cdot \text{g}^{-1}$ in Ti-SBA. Likewise, pore volume is also diminished from $0.50\text{ cm}^3 \cdot \text{g}^{-1}$ to $0.32\text{ cm}^3 \cdot \text{g}^{-1}$. In mono and bimetallic samples, a decrease is also observed in BET values, due to partial blockage provoked by Au and Cu deposition.

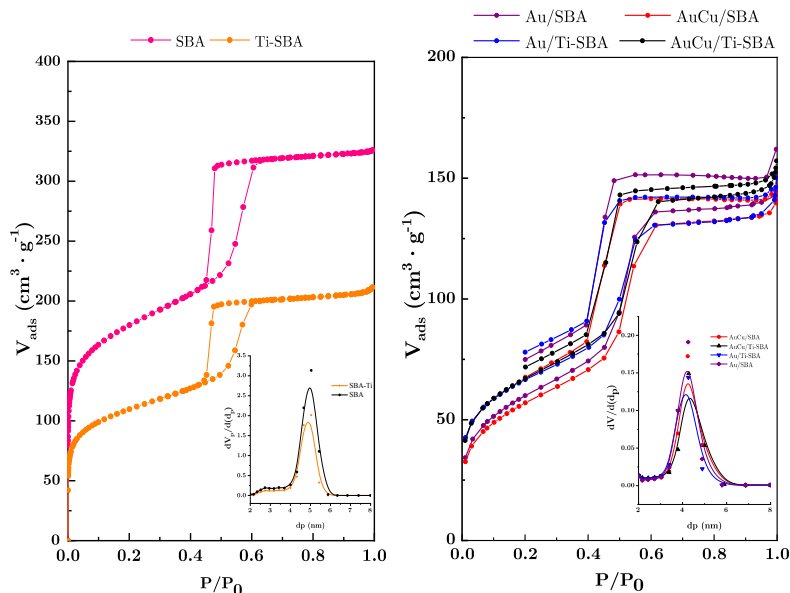


Figure 7.11: N₂ adsorption-desorption isotherms at T = -196 °C

Regarding pore size distribution, all samples presented unimodal profiles, with mean pore diameter ranging from 4.1 nm to 5.0 nm (see **Table 7.3**). The maintenance of mean pore diameter after titania incorporation indicates that wall thickness was not modified. Cumulative pore volume of SBA suggests a relatively large internal pore surface that is impoverished when titania and/or Au and Cu are deposited. This fact would also confirm that both titania and metallic nanoparticles are being incorporated inside the ordered SBA pore channels, which allows an effective control of nanoparticles size below silica pores diameter.

Table 7.3: Textural parameters of supports and as-prepared samples

Catalyst	S _{BET} (m ² · g ⁻¹)	V _p (cm ³ · g ⁻¹)	d _p (nm)
<i>SBA</i>	654	0.50	5.0
<i>Au/SBA</i>	213	0.21	4.2
<i>AuCu/SBA</i>	200	0.20	4.3
<i>Ti-SBA</i>	393	0.32	4.8
<i>Au/Ti-SBA</i>	236	0.18	4.1
<i>AuCu/Ti-SBA</i>	237	0.19	4.3
<i>Au-Cu/Ti-SBA</i>	240	0.21	4.3

7.2.4. High Resolution Transmission Electron Microscopy (HR-TEM)

To study the morphology and metal dispersion of as-prepared samples, HR-TEM analyses were performed, and representative images of them are displayed in **Figure 7.12**, **Figure 7.13** and **Figure 7.14**.

Figure 7.12 A shows that SBA-15 support maintains its mesoporous structure after titania or metals incorporation, as suggested by XRPD analyses and nitrogen isotherms. In addition, in EDX STEM image (**Figure 7.12 B**) it is observed that, although titania agglomerates are present around SBA surface, a considerable part of it is successfully incorporated inside SBA-15 pore channels as titania nanoparticles, which also supports the decrease in S_{BET} values in **Table 7.3**.

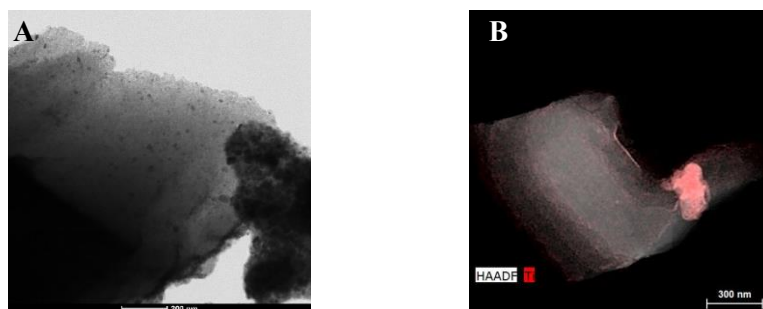


Figure 7.12: (A) HR-TEM image and (B) EDX-STEM mapping of Ti-SBA support

Regarding the gold-based samples, HR-TEM images show a high dispersion of uniform, circular-shaped gold nanoparticles (Au NPs) on both SBA and Ti-SBA supports, as observed in **Figure 7.13**. In addition, although titania seems not to affect the size of Au NPs, with an average size of 5 nm in monometallic samples, a preferential incorporation of gold onto titania rich agglomerates is suggested, hence a close contact between Ti and Au can be assumed, as supported by mapping analyses.

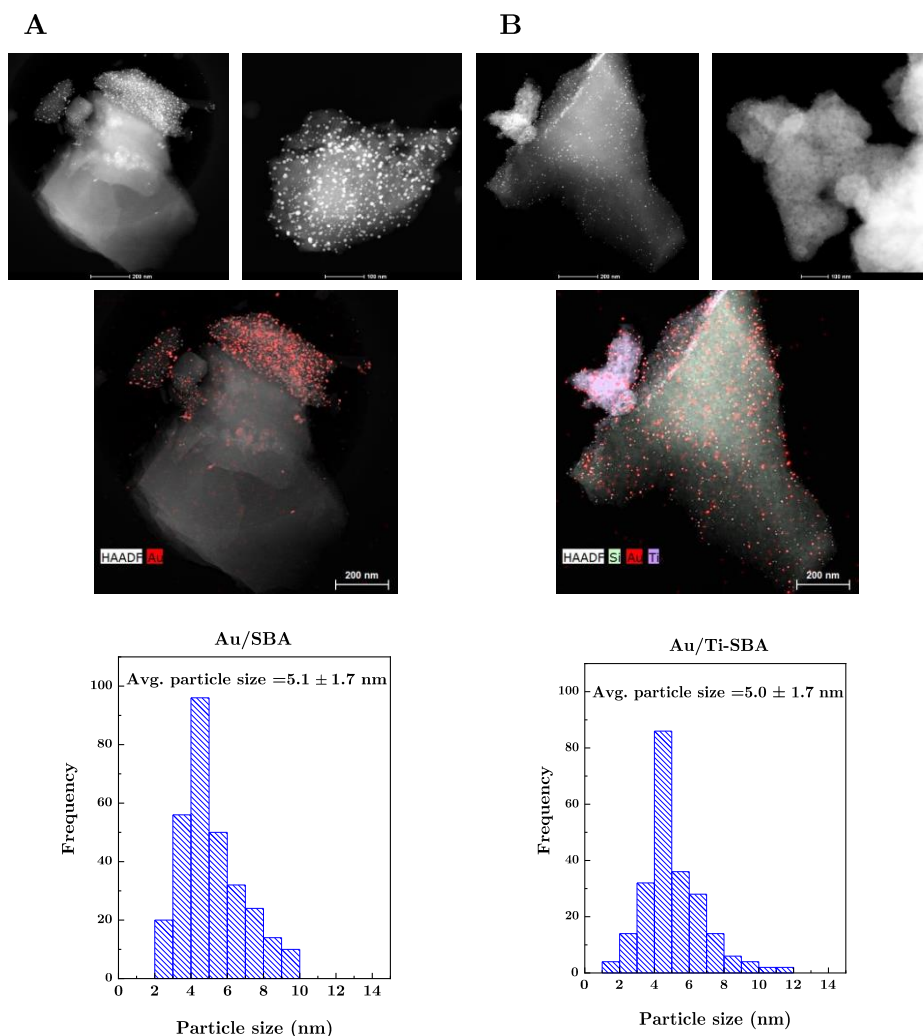
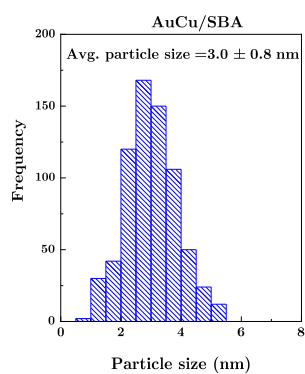
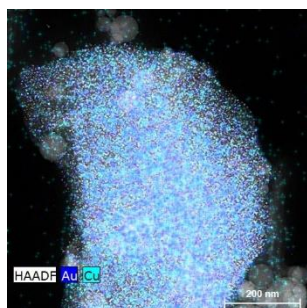
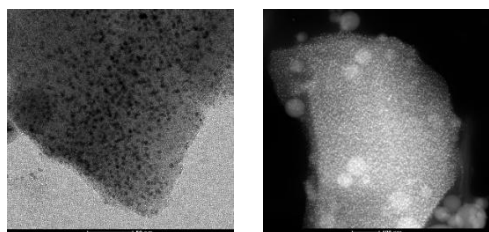


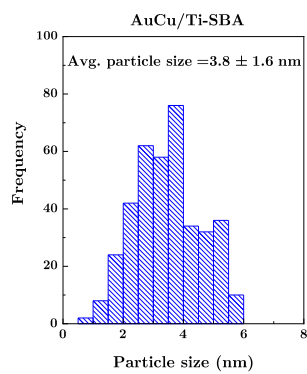
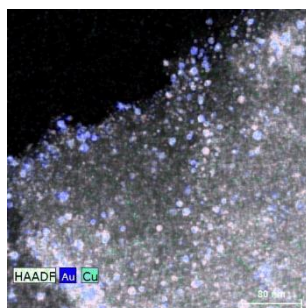
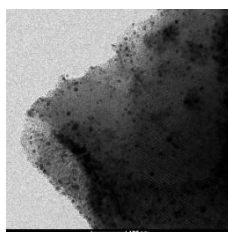
Figure 7.13: HR-TEM images, EDX-STEM mapping and particle size distribution of (A) Au/SBA and (B) Au/Ti-SBA catalysts

In the case of bimetallic catalysts, HR-TEM images in **Figure 7.14** indicate that the incorporation of a second metal has multiple beneficial effects as far as morphology is concerned: on the one hand, it enhances nanoparticles dispersion into the mesoporous support pore channels; and, on the other hand, it diminishes particle size. Likewise, although titania seems not to influence particle size, it does in its homogeneity, since from particle size histograms, it is easily observed that Ti-containing samples present a more uniform distribution.

A



B



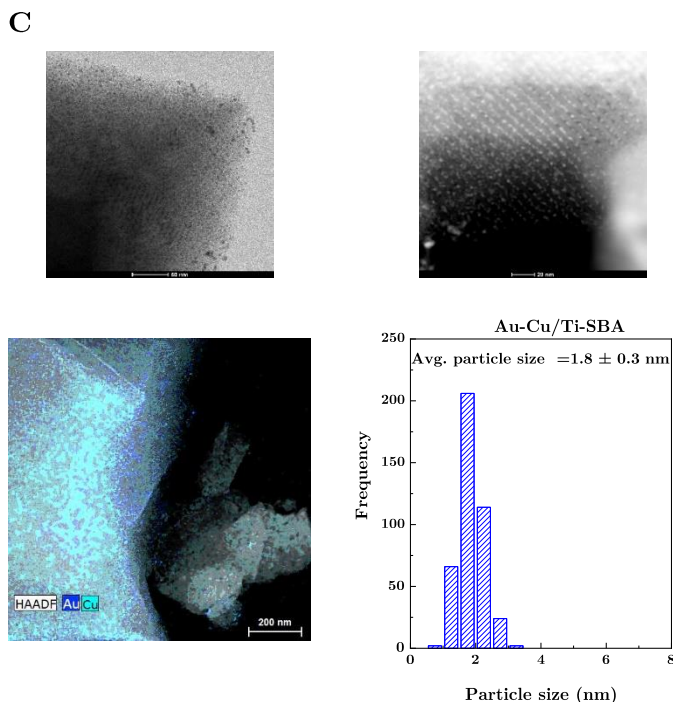


Figure 7.14: HR-TEM images, EDX-STEM mapping and particle size distribution of (A) AuCu/SBA, (B) AuCu/Ti-SBA and (C) Au-Cu/Ti-SBA catalysts

In addition, hydrogen treatment seems to also have an influence in particle size, since the smallest particles were obtained with the non-reduced bimetallic sample. It is widely accepted that gold can be regarded as one paradigmatic example of nanometric scale catalysis, since bulk gold (particles over 20 nm) is hardly reactive [17] but highly active when it is present as nanoparticles below 10 nm [18]. Particularly, gold nanoparticles sized around 3 to 5 nm have demonstrated remarkable activity when supported in relatively high surface area supports in low temperature reactions like CO oxidation or selective hydrogenation of nitroaromatic compounds [19]. In fact, the close contact in AuCu samples suggests the formation of an alloy between gold and copper after hydrogen treatment, as previously reported [20], [21].

7.2.5. X-Ray Photoelectron Spectroscopy (XPS)

The surface composition, possible chemical interactions and chemical environment at the catalyst's surface have been studied by means of XPS measurements.

The Si $2p$ core level spectra of the supports in **Figure 7.15** showed a main peak signal at ca. 103.1 eV, belonging to SiO_4 bond state in SiO_2 . In the case of Ti-containing support, the intensity of this peak is decreased, which is ascribed to Ti covering the support surface. Likewise, Ti $2p$ core level spectrum of Ti-SBA support shows a Ti $2p_{3/2}$ peak at ca. 458.1 eV (and its corresponding doublet), related to Ti^{4+} species in the TiO_2 matrix. In the case of the O $1s$ core level spectra, the peak at 532.5 eV corresponds to oxygen in SiO_2 . In the case of Ti-containing support, a second peak centred at 529.4 eV appeared, related to oxygen in the TiO_2 lattice [22]. These values are in good agreement with the theoretical ones reported in literature [23], with small deviations that can be related to the formation of Ti-O-Si, as elucidated from ss-NMR results and also reported elsewhere [24].

Regarding as-prepared catalysts, **Figure 7.16** displays the Cu $2p$ and Au $4f$ core level spectra for mono- and bimetallic samples. Au $4f$ core level spectra deconvoluted signals are depicted in **Figure 7.16**, being solid lines representative of Au $4f_{7/2}$ and dotted ones of Au $4f_{5/2}$. Two contributions can be distinguished: the one at ca. 83-84 eV, attributed to Au in metallic state Au^0 , and a second, smaller one, at ca. 84-85 eV, associated with $\text{Au}^{\delta+}$. The position of the first one, which is expected to be found at 84 eV, is strongly influenced by the catalyst formulation. In the case of monometallic samples, this peak is located at ca. 83.0 eV, indicating a strong interaction between gold and the support. On the other hand, bimetallic samples present this peak at 83.5, 83.8 and 83.6 eV for AuCu/SBA, AuCu/Ti-SBA and Au-Cu/Ti-SBA, respectively, indicating that copper also influences the position, suggesting an electron transfer from Au to Cu and the formation of a gold-copper alloy. This electron transfer,

although against Pauling's electronegativity table, the reverse electron transfer could be considered due to both electron deficiency in copper because of surface chemical interactions and to the greater work function of gold (5.10 eV) versus copper (4.65 eV) [25]. Regarding $\text{Au}^{\delta+}$ contribution, the greatest proportion found in samples without titania, suggests that Ti favours the presence of gold in its metallic state because of the electron transfer from the semiconductor to Au NPs together with the negative charging of Au [25].

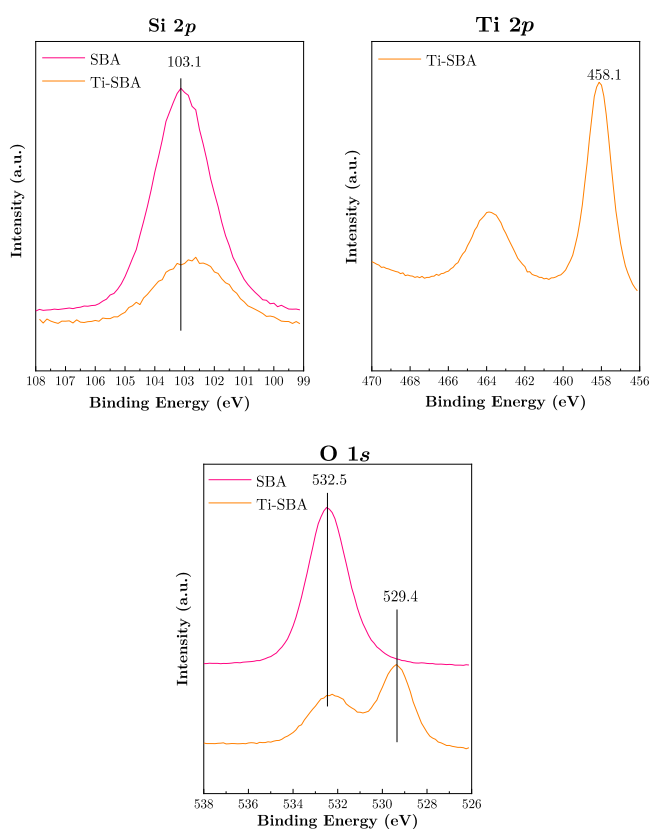


Figure 7.15: Si 2p, Ti 2p and O 1s core level spectra for SBA and Ti-SBA supports

The signals for Cu 2p were noisy due to the low copper loading, complicating their deconvolution. Nonetheless, it is clearly observed a main peak at *ca.* 932.3 eV attributed to Cu 2p_{3/2} and its correspondent doublet at 951.8 eV (Cu 2p_{1/2}), which is usually ascribed to Cu⁰ and Cu¹⁺ species

[26]. Contrary to gold, copper signal was not affected by titania's presence in the support, which reinforces the fact that Ti preferentially interacts with gold. The expected energy gap for these doublets is 20 eV, but the difference could be related to an electron transfer from Au to Cu, as previously reported for gold and copper alloys [27]. Although Auger measurement for Cu can help to distinguish between Cu^0 and Cu^{1+} , the short exposition time required to avoid copper reduction led to a very weak and noisy Cu_{LMM} signal that could not be used. The shoulder at *ca.* 934 eV, together with satellite peaks at higher binding energy suggest the presence of Cu^{2+} species, less noticeable in the sample without hydrogen treatment due to the greater dispersion and smaller particles that favours the reduction of Cu species by the X-ray irradiation beam [28].

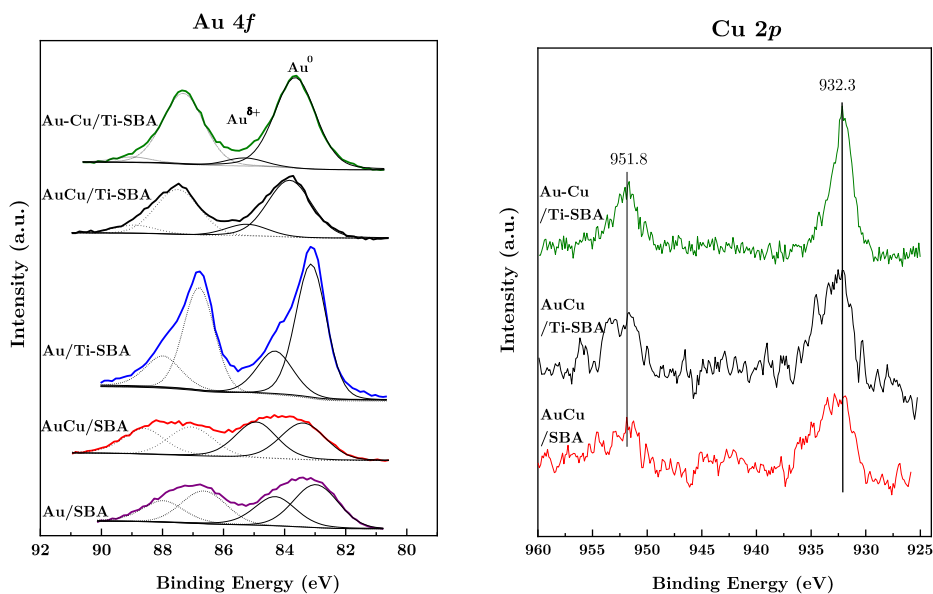


Figure 7.16: Cu 2p and Au 4f core level spectra for Au and AuCu based catalysts

Considering the atomic surface composition of the samples in **Table 7.4**, it can be observed that titania improves surface dispersion of metallic nanoparticles. In the case of bimetallic samples, it is proposed that copper is more superficially exposed as previously reported for AuCu systems [29] in samples containing titania, since the ratio Au/Cu is increased in these

samples whilst Au surface exposition is lowered, suggesting a core-shell type structure.

Table 7.4: Atomic surface composition of mono and bimetallic samples

Catalyst	Au/Cu	Au/Si	Au/(Si+Ti)	(Au+Cu)/(Si+Ti)
<i>Au/SBA</i>	-	0.019	0.019	0.019
<i>AuCu/SBA</i>	0.65	0.018	0.018	0.047
<i>Au/Ti-SBA</i>	-	0.099	0.051	0.051
<i>AuCu/Ti-SBA</i>	0.49	0.061	0.035	0.105
<i>Au-Cu/Ti-SBA</i>	1.33	0.101	0.071	0.123

7.2.6. DRUV-Vis spectroscopy

The photoresponse of the catalysts as well as their band gap were studied by means of diffusive reflectance UV-Vis spectroscopy. The signals were collected in the range from 300 to 800 nm, and spectra and band gap values are displayed in **Figure 7.17 A** and **Table 7.5**, respectively. Band gap energy (E_g) was calculated from the intercept of the tangent to the absorption curves in the graphical representation of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$), where h stands for Planck's constant and ν is the frequency (s^{-1}), as depicted in **Figure 7.17 B**. All samples present an absorption band characteristic of titania-containing materials below 400 nm. A second, broader peak is present in metallic samples, with maximum around 600 nm, thus in the visible region, is associated with Localized Surface Plasmon Resonance (LSPR) phenomenon taking place in metal nanoparticles, that allow the confinement of light within the nanometre region as well as a large electric field produced at the LSP condition [30]. This phenomenon has been reported to be dependent on both the shape and size of metallic nanoparticles together with the dielectric constant of the ambient Ti-containing support medium [31]. In the case of the sample subjected to hydrogen treatment, AuCu/Ti-SBA, the maximum of this peak is slightly shifted to higher wavelength which could be related to the formation of an alloy between gold and copper nanoparticles. Regarding band gap values

(see **Table 7.5**), bare Ti-SBA support presents a band gap close to that of bare titania, 3.13 eV. However, when adding metal nanoparticles, this band gap is diminished up to 22% in the sample AuCu/Ti-SBA, which indicates that highly dispersed alloyed metal nanoparticles enhance scattering efficiency.

Table 7.5: Band gap values for titania-containing samples

Catalyst	E_g (eV)
<i>Ti-SBA</i>	3.13
<i>Au/Ti-SBA</i>	2.99
<i>AuCu/Ti-SBA</i>	2.43
<i>Au-Cu/Ti-SBA</i>	2.49

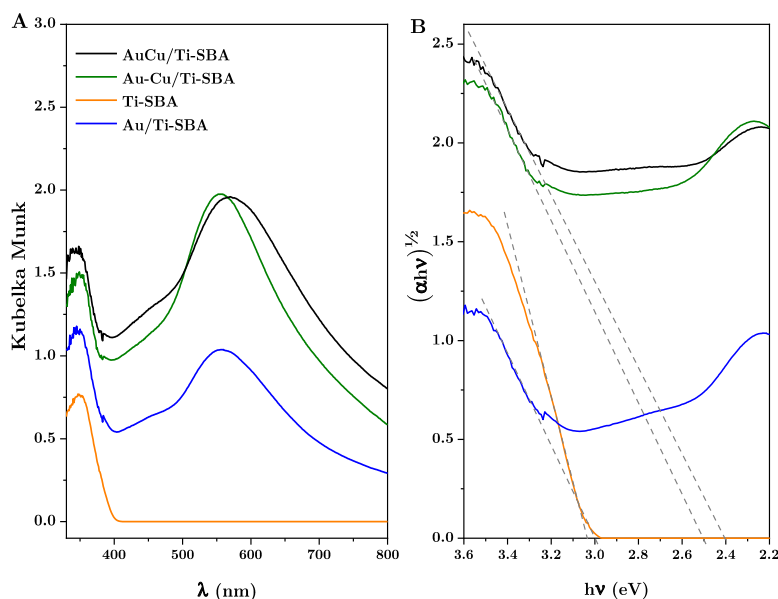


Figure 7.17: (A) DRUV-vis spectra for Ti containing samples and (B) $(\alpha h\nu)^{1/2}$ vs photoenergy (h)

7.3. Discussion

In this chapter, the photocatalytic activity of Au and Cu based catalysts supported on bare SBA and Ti-containing SBA mesoporous solids has been studied for two reaction systems: methylene blue photodegradation

and preferential oxidation of CO in a hydrogen-rich stream under simulated solar light. From the catalytic results, it can be concluded that an enhancement of the photoactivity is achieved when both titania and bimetallic nanoparticles are present in the catalyst formulation. This fact can be justified taking into consideration the characterization results obtained:

On the one hand, XRD analyses show that titania is mostly present as anatase that is the most photoactive phase, with an optimal crystal size for photocatalytic processes of ca. 24 nm [7]. Moreover, titania has been effectively incorporated into SBA matrix, both on the surface and inside the pore channels, with close interaction due to covalent bonding between Si and Ti, as demonstrated by ss-NMR results. Thus, the electrostatic adsorption capacity of SBA due to Si-OH groups interaction together with titania's ability to produce $\text{OH}\cdot$ radicals [32] enhance not only the photocatalytic activity, but also favours the complete mineralization of the dye thanks to the confinement of reaction intermediates into Ti-containing SBA pore channels.

On the other hand, BET surface area values obtained from N_2 adsorption-desorption isotherms show that, although titania is partially blocking SBA mesoporous channels, all catalysts present a relatively high specific surface area that increases the interface metal/semiconductor sites therefore improving the photocatalytic performance, which is also supported by HR-TEM images that show a great dispersion of metal nanoparticles into the support matrix. Nonetheless, it was observed that although metal nanoparticles are highly dispersed on the support surface especially in bimetallic samples, they are preferably located onto titania agglomerates. Regarding the size of metal nanoparticles, it has been confirmed that the incorporation of a second metal diminishes particle size. Likewise, it was observed that titania did not have any influence in particle size, contrary to the hydrogen treatment, but it promoted homogeneity in size.

As far as surface composition and chemical environment is concerned, XPS analyses support the formation of Ti-O-Si bonds in the support matrix as already evidenced from ss-NMR analysis. In addition, the formation of a gold-copper alloy in H₂-treated samples is also suggested from the shift in the Au 4*f* spectra of bimetallic samples compared to monometallic ones, which indicates a theoretically unexpected electron transfer from Au to Cu due to electron deficiency in copper together with the greater work function of gold. In addition, by XPS analysis, a stronger interaction of titania with gold rather than with copper was observed and two main consequences arise from this fact: on the one hand, Ti-Au interaction promotes an electron transfer from titania to gold and therefore favouring the obtention of gold in its metallic state; on the other hand, copper's weaker interaction with Ti in the support let this second metal more superficially exposed, which could lead to the formation of a core-shell type structure.

Lastly, DRUV-Vis spectroscopy results justify the enhancement of the photocatalytic activity under UV-vis irradiation in samples containing both titania and bimetallic particles thanks to both LSPR phenomenon and to the decrease in titania's band gap due to a greater scattering efficiency in dispersed AuCu nanoparticles.

Ti- SBA type materials have already been tested for dye and drugs degradation reactions [33], [34], demonstrating an effective Ti incorporation into SBA mesopore channels that promoted the complete mineralization of the dye. Likewise, several research groups have strived to develop gold-titania catalytic systems that result photoactive in degradation and both oxidation and reduction reactions. For example, Zhang et al. [35] studied methylene blue photodegradation using Au/TiO₂ as photocatalyst, achieving conversion of ca. 50% after six hours reaction. Li et al [36] also studied nanohybrid Au/TiO₂ systems containing microporous windows and mesoporous walls in p-nitrophenol photoreduction under visible light

irradiation, in which gold nanoparticles act as electron relay to overcome the intrinsic kinetic barrier on this reaction, attaining almost complete conversion after 20 minutes reaction. The role of copper in titania containing systems has also been investigated in dyes photodegradation, reporting that copper not only increased photocurrent density, but also it introduced oxygen vacancies in the structure that could act as electron traps therefore diminishing charge carrier recombination [37].

To the best of our knowledge, AuCu/(Ti)SBA catalytic systems have not been previously studied neither in methylene blue photodegradation nor in photo-PROX reaction, and they have shown remarkable results at ambient conditions. In both reactions, AuCu/Ti-SBA catalyst has resulted the most photoactive, attaining 79% of CO conversion and 81% of CO₂ selectivity and complete mineralization of the dye under UV irradiation after 2 hours of reaction. The presence of well-dispersed titania into SBA mesoporous channels together with bimetallic nanoparticles acting as electron relays are the responsible for the better photocatalytic performance of this catalyst. Moreover, the close contact between nanoparticles and the semiconductor creates a Schottky barrier that has also been reported to favour photoactivity [38].

Taking into consideration all above, it could be concluded that the use of mesoporous supports as matrix for titania semiconductor hosting as well as the addition of a second non-noble, low-cost metal for obtaining novel catalyst containing highly dispersed nanoparticles in mesoporous Ti-containing solids have demonstrated a synergistic effect in two UV-light driven reactions carried out at mild operating conditions.

7.4. Conclusions

A set of gold, and gold-copper nanoparticles with low metal loading (2.0 wt.%) supported on mesoporous SBA and Ti-SBA solids have been synthesized, fully characterized, and tested in methylene blue

photodegradation under UV light and in preferential CO oxidation in a H₂-rich stream under simulated solar light. It has been demonstrated by XRD and BET measurements that post-synthesis titania's incorporation in SBA matrix did not modify the hexagonal mesoporous structure characteristic of SBA type materials. Moreover, not only was the structure maintained after the addition and further reduction of both gold and copper nanoparticles, but also titania presence in the mesoporous matrix enhanced particle growth and dispersion of these nanoparticles, as evidenced by XPS analysis. Regarding the photocatalytic activity, in both reactions, the AuCu/Ti-SBA photocatalyst resulted the most active one, thanks to the concurrence of several beneficial phenomena: the formation of an Schottky barrier between metal nanoparticles and the semiconductor that hinders charge-carrier recombination, and the presence of localized surface plasmon resonance thanks to which metal nanoparticles act as electron harvesters, and finally the formation of a gold-copper alloy.

In conclusion, the use of bimetallic AuCu alloyed nanoparticles supported on titania containing mesoporous matrix arises as a feasible route to extend these photoreactions to the visible light scope yet using mild operating conditions.

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8. CeTNT and CeTNP nanostructures for Methylene Blue photodegradation

Summary

In this chapter, the influence of morphology in the photocatalytic activity of hydrothermally synthesized ceria-doped titania catalysts in the photodegradation reaction of the cationic dye methylene blue under UV irradiation at room temperature and atmospheric pressure was investigated. To this end, two sets of photocatalysts were prepared: one based on ceria-doped titania nanotubes doped with a ceria loading ranging from 0.25 to 5 wt.%, named CeTNTx, where x stands for the ceria loading; and a second one based on ceria-titania nanoparticles with the same dopant loading as the nanotubes' counterpart set, named CeTNPx. P25 benchmark photocatalyst was also tested and characterized for comparison purposes.

The catalysts were synthesized following the procedure in sections 3.2.2.1. and 3.2.2.2. of the chapter *Materials and Methods* for Ce-doped titania nanotubes and Ce-doped titania nanoparticles, respectively. The samples were referred with the acronyms CeTNTx and CeTNPx, where Ce stands for ceria, T for titania, NT for nanotubes and NP for nanoparticles. X represented the ceria loading in weight percentage, therefore $x = 0.25, 0.5, 1.0, 2.5$ and 5 wt.% CeO_2 .

8.1. Catalytic test

The methylene blue photodegradation test was carried out as described in the Materials and Methods section. The pH was fixed at 5.5 taking into consideration the recommended values for methylene blue in aqueous media [1] and also the point of zero charge values for titania (6-6.5) and ceria (7.2) [2], [3].

The reaction evolution was followed by UV-Vis spectra ranging from 300 to 900 nm at reaction times -30 (standing for dark adsorption period), 5, 10, 15, 20, 40, 60, 90 and 120 minutes and registered data for CeTNT5 and CeTNP5 samples are displayed in **Figure 8.1** as an example. In

addition, to check the stability of the methylene blue solution at pH 5.5, special attention was paid to leucomethylene blue absorption peak at 520 nm. The reason is that methylene blue is easily reduced to colourless leucomethylene blue which will eventually be oxidized to former methylene blue [4], whose absorption peaks associated with benzene rings and heteropoly-aromatic linkages [5] appear at 613 and 664 nm [6]. The fact that no colour change was observed together with the absence of peaks at 520 nm confirmed the stability of the methylene blue solution and that no leucomethylene blue was present during the whole reaction period monitored for both catalyst sets. Moreover, the characteristic peaks of methylene blue were gradually diminished, indicating that the bleaching observed during the reaction was exclusively due to the methylene blue degradation.

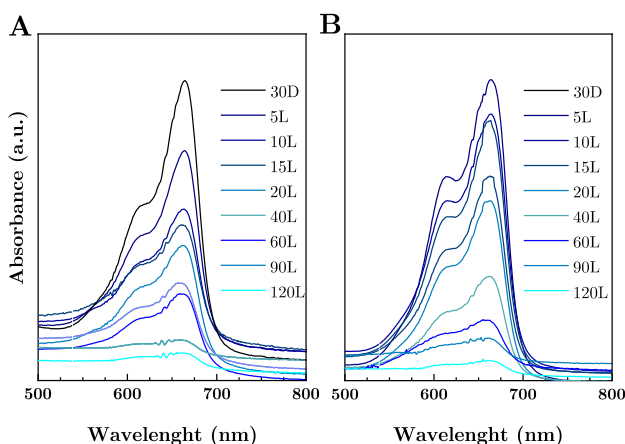


Figure 8.1: UV-Vis spectra registered for CeTNT5 and CeTNP5 samples at different reaction times

Preceding the photocatalytic test, the catalyst was suspended in the methylene blue solution and kept in the dark for 30 minutes to reach adsorption equilibrium. The adsorption was *ca.* 40% in CeTNTx catalysts containing high ceria loading, while for CeTNPx it was less than 40% in all cases and negligible in CeTNP2.5 and CeTNP5 samples, probably due to the low specific surface area in these materials.

Figure 8.2 A and **B** show the photocatalytic performance of the CeTNTx series in methylene blue photodegradation under UV irradiation and simulated solar light, respectively, for 120 minutes of reaction. As expected, under UV irradiation, an exponential decrease in methylene blue concentration in the first 30 minutes is achieved, then reaction rate becomes constant as the reaction proceeds, indicating that stationary regime is achieved. In undoped samples, P25 presented a better photocatalytic performance than pure titania nanotubes, probably due to the lower specific surface area of these samples, as evidenced by N₂ physisorption analysis. In the case of ceria-doped samples, the decrease in methylene blue concentration is more pronounced in samples with low ceria loading, being the most photoactive one the sample with the lowest Ce content, CeTNP025, with a kinetic constant of 0.123 min⁻¹ (see **Table 8.1**), followed by CeTNT1 sample, eliminating almost all the dye after 120 minutes. The worsening in photoactivity for samples containing greater loading of ceria could be due to ceria particles covering the catalyst's surface, thus hindering the access of methylene blue to titania active sites.

Contrary to the trend followed under UV light, under simulated solar light the samples containing the greatest ceria loading presented the best photocatalytic performances. In this case, CeTNT2.5 was the most photoactive catalyst with a kinetic constant of 0.019 min⁻¹ (see **Table 8.1**), closely followed by CeTNT5 with $k = 0.012$, which suggests that ceria loadings over 2.5 wt.% result detrimental for the catalytic activity because of the covering of titania active sites. The better performance of these catalysts under simulated solar light could be explained considering that ceria induces a decrease in titania's band gap [7], [8], extending its photoactivity to the visible light scope. Likewise, the worsening of photoactivity in pure titania samples is also explained considering the wide band gap of commercial P25 and TNT samples, 3.15 eV and 3.2 eV, respectively (see **Table 8.1**) that require the use of UV irradiation.

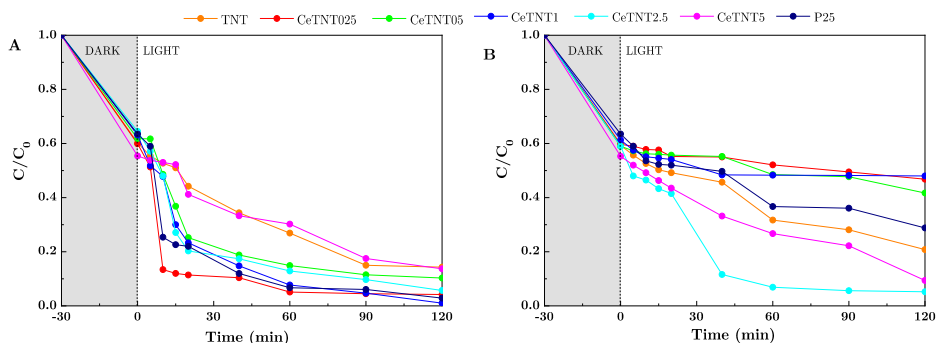


Figure 8.2: Methylene blue photodegradation using CeTNTx as photocatalysts (A) under UV irradiation and (B) under simulated solar-light

The same photocatalytic tests were carried out using CeTNPx series, and results are plotted in **Figure 8.3**. Under UV light (**Figure 8.3 A**) all samples presented an exponential decrease in methylene blue concentration irrespective of the ceria loading, attaining almost 100% elimination of the dye after 60 minutes of reaction. Analogously to CeTNTx series, the catalyst presenting the best photocatalytic performance was CeTNP025, with a kinetic constant of 0.146 min^{-1} (see **Table 8.1**), achieving 95% of methylene blue conversion in 20 minutes of reaction. Therefore, it could be suggested that ceria acts as a promoter in this reaction, since with very low loadings a remarkable increase in the photocatalytic performance is achieved.

Under simulated solar light (**Figure 8.3 B**), the photocatalysts were able to degrade up to 60-80% of methylene blue in the monitored time. The most photoactive samples were those with the highest ceria loading, CeTNP2.5 and CeTNP5, with kinetic constants of 0.054 min^{-1} and 0.052 min^{-1} , respectively, again thanks to titania's band gap diminishing due to ceria incorporation, as will be seen by DRUV-Vis spectroscopy results.

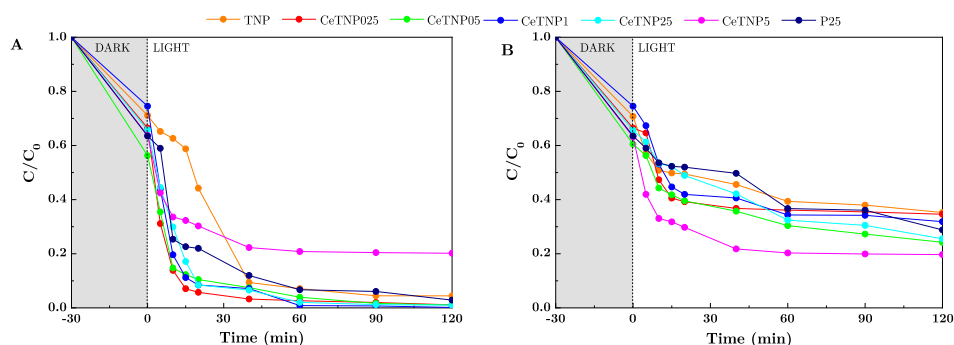


Figure 8.3: Methylene blue photodegradation using CeTNPx as photocatalysts (A) under UV irradiation and (B) under simulated solar light

To study the stability and recyclability of the catalysts, the most active catalyst of both series, CeTNP025 and CeTNP05, were subjected to 3 reaction cycles under UV light irradiation at the previously used operating conditions, and the results are plotted in **Figure 8.4 A** and **B**, respectively. After each photocatalytic test, the catalyst was recovered by centrifugation, washed with deionized water and dried overnight. It is easily noticed that both catalysts presented a great physical and chemical stability, although a small decrease in photodegradation efficiency and also in adsorption in the dark occurred, both probably related to a partial blockage of reaction and adsorption sites by reaction intermediates that are kept in the structure. To support this finding, after the third cycle, samples were recovered by centrifugation, washed and dried at 110 °C before post-reaction characterization by XRPD and N₂ physisorption at -196 °C and will be further discussed in the characterization results section.

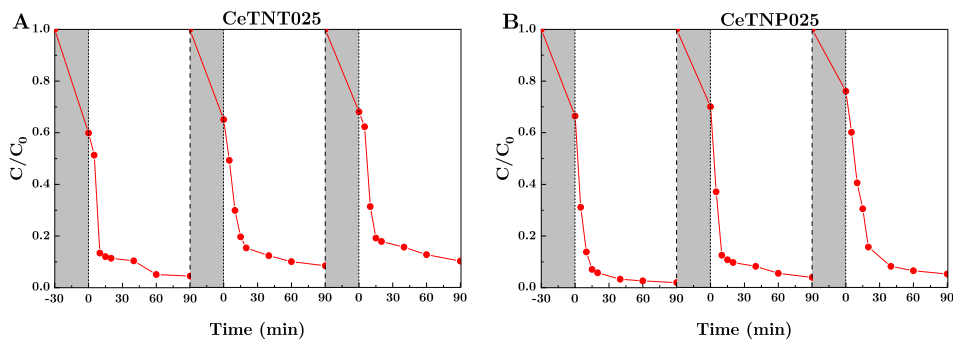


Figure 8.4: Recycling methylene blue photodegradation tests under UV light irradiation for (A) CeTNT025 and (B) CeTNP025

8.2. Characterization results

8.2.1. X-Ray Diffraction (XRD)

High angle X-Ray diffraction measurements were carried out for phase identification of both CeTNTx and CeTNPx series as well as for commercial benchmark photocatalyst P25, and measurements are displayed in **Figure 8.5 A** and **B**. Anatase, rutile and CeO₂ patterns have also been included for comparison purposes.

Although diffraction peaks associated with CeO₂ were not expected in samples containing less than 1 wt% Ce for these percentages being below the detection limit, this phase was neither identified in samples with higher loadings (2.5 and 5 wt%), suggesting that this phase is present as small particles highly and homogenously dispersed in the titania matrix in both catalyst sets. This conclusion is also supported by Raman spectroscopy results in **Figure 8.6**, where no ceria phase was detected.

Despite the larger ionic radius of Ce⁴⁺ (0.97 Å) than that of Ti⁴⁺ (0.68 Å) [9], it has been reported that at low ceria loading under 13 wt%, the formation of a solid solution Ce_xTi_{1-x}O₂ could occur, provoking a deformation in the TiO₂ lattice. At higher ceria loading, saturation of anatase lattice takes place and amorphous ceria could be formed and separated from the lattice, inducing an increase in anatase crystallite size

and limiting anatase cell volume [10]. Therefore, the formation of a ceria-titania solid solution in these materials could be suggested, given the low ceria loading incorporated.

Regarding the crystalline phases for titania, only the anatase phase was detected for the CeTNTx samples, while both anatase and rutile were detected for the CeTNPx set, with characteristic peaks of anatase (PDF No.: 73-1764) at 2θ ($^{\circ}$) = 25.5, 37.9, 48.1 and 54.7; and those of rutile (PDF No.: 21-1276) at 2θ ($^{\circ}$) = 36.0 and 54.1. HighScore Plus software (P'Analytical, Almelo, The Netherlands) was used to obtain the average contribution of both crystalline phases semi-quantitatively: approximately 80% anatase and 20% rutile, similar to that of the commercial photocatalyst P25.

The Scherrer equation was used to calculate mean crystal size. CeTNTx series presented a smaller crystal size, 18 nm, whereas CeTNPx counterparts had almost doubled mean crystal size, 32 nm.

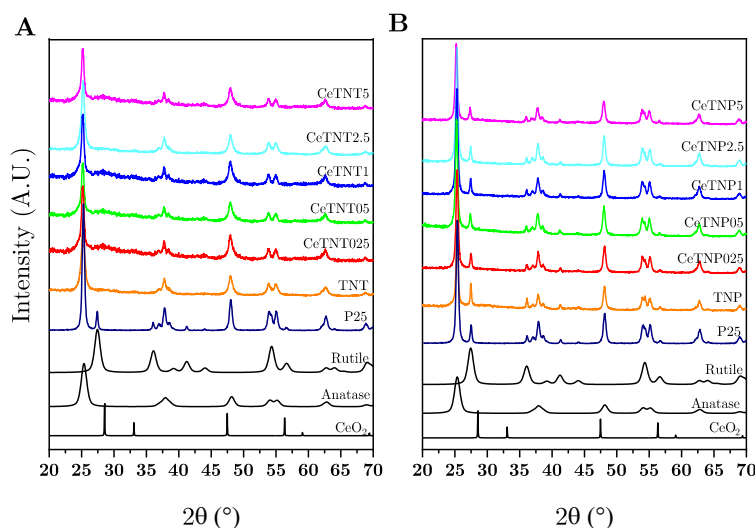


Figure 8.5: XRD of commercial P25 photocatalyst, anatase, rutile, CeO₂ and (A) CeTNTx and (B) CeTNP patterns

High angle XRD patterns for the recycled sample of each set, CeTNT025 and CeTNP025, were also registered, and no changes in the

titania crystallite size was detected. In addition, no new peaks related to titanium- or cerium-based phases were identified after the 3-cycle photoreaction.

8.2.2. Raman spectroscopy

To confirm the crystalline phases evidenced by XRPD analysis, Raman spectroscopy was carried out and the spectra for selected samples are displayed in **Figure 8.6**. Anatase phase Raman active modes were detected at 397 (B_{1g}), 514 (A_{1g}) and 630 (E_{2g}) cm^{-1} , similar to the values reported in literature [11]. The broadening of the peaks could indicate oxygen vacancies in solid solutions [12]. Some weak peaks (marked with *) can also be observed that are associated with the reagents used in the synthesis of the CeTNTx set. In the case of the CeTNPx series, active modes for rutile were also detected, that was already confirmed by XRPD analysis, as plotted in the inset of **Figure 8.6 b)** at *ca.* 447 cm^{-1} . No bands related to ceria phases were observed due to high dispersion and low ceria loading in all samples.

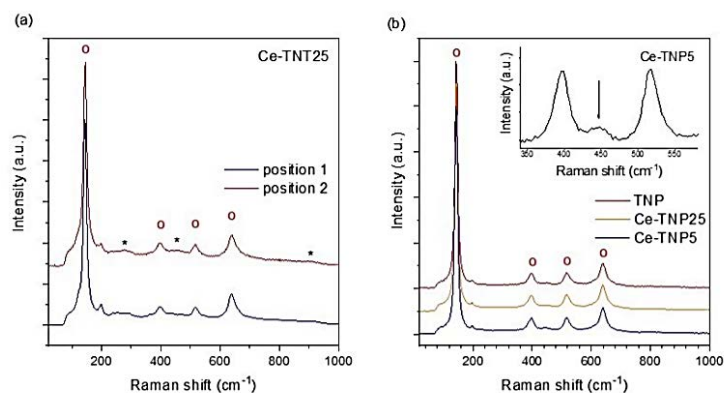


Figure 8.6: Raman spectra of (a) Ce-TNT25 recorded at two different positions and (b) TNP, Ce-TNP25 and Ce-TNP50. Red circles mark anatase peaks. Asterisks in (b) mark weak peaks coming from reagents. Inset in (a): expanded view of the Ce-TNP5 sample, highlighting the presence of Rutile phase (black arrow)

8.2.3. Nitrogen adsorption-desorption isotherms

The main textural properties of the prepared photocatalysts as well as of P25 commercial titania, were studied by means of N_2 adsorption-desorption at $-196\text{ }^{\circ}\text{C}$. Both catalytic sets presented type IV isotherms with H3 hysteresis loop (not shown), indicating the mesoporous nature of these materials. Nonetheless, substantial differences are found in textural features such as specific surface area, S_{BET} and pore volume, V_p , summarized in **Table 8.1**.

Quite small S_{BET} values were obtained for the CeTNTx series: pure titania nanotubes sample, TNT, was the one with the highest specific surface area with just $27\text{ m}^2 \cdot \text{g}^{-1}$, whereas the lowest value was obtained for the sample with the highest ceria loading, CeTNT5, with only $20\text{ m}^2 \cdot \text{g}^{-1}$, which could explain that all CeTNT samples presented a similar adsorption in the dark in the catalytic test. Likewise, the very low specific surface area of TNT in comparison with commercial P25 ($55\text{ m}^2 \cdot \text{g}^{-1}$) could also justify the worse photocatalytic performance of prepared titania nanotubes. On the contrary, pure titania nanoparticles sample, TNP, presented a relatively high (compared to commercial P25) specific surface area of $118\text{ m}^2 \cdot \text{g}^{-1}$, with a total pore volume of $0.55\text{ cm}^3 \cdot \text{g}^{-1}$ compared to that of TNT, $0.13\text{ cm}^3 \cdot \text{g}^{-1}$. In the case of the CeTNPx series, S_{BET} values were decreased as ceria loading was increased, obtaining the lowest value, $65\text{ m}^2 \cdot \text{g}^{-1}$ for CeTNP5. This fact suggests that in the case of samples containing higher amounts of ceria, partial pore blocking may occur, which could also explain the negligible adsorption during the dark period in the photocatalytic reaction for samples CeTNP2.5 and CeTNP5. Nevertheless, the variation in S_{BET} and total pore volume values is small, indicating that titania nanoparticles' textural properties are not significantly affected by changes in sample composition.

Table 8.1: Textural properties, TiO₂ crystalline phases contributions, optical parameters, and kinetic constants of MB photodegradation in aqueous solution under UV and simulated solar light irradiations for CeTNTx and CeTNPx series

Catalyst	CeO ₂ loading (wt.%)	^a S _{BE} T	^b Pore vol.	^c TiO ₂ phases X _A -X _R		^d E _g	^e K _{UV}	^f K _{Sola} r
<i>TNT</i>	-	27	0.13	100.0	-	3.20	0.011	0.010
<i>CeTNT025</i>	0.25	26	0.15	100.0	-	3.10	0.123	0.003
<i>CeTNT05</i>	0.5	26	0.16	100.0	-	3.05	0.036	0.004
<i>CeTNT1</i>	1.0	26	0.15	100.0	-	3.03	0.046	0.008
<i>CeTNT2.5</i>	2.5	21	0.14	100.0	-	2.90	0.055	0.019
<i>CeTNT5</i>	5.0	20	0.18	100.0	-	2.65	0.004	0.012
<i>TNP</i>	-	118	0.55	73	27	3.0	0.069	0.034
<i>CeTNP025</i>	0.25	99	0.45	79	21	3.00	0.146	0.029
<i>CeTNP05</i>	0.5	98	0.44	81	19	3.00	0.134	0.033
<i>CeTNP1</i>	1.0	92	0.41	81	19	2.95	0.105	0.039
<i>CeTNP2.5</i>	2.5	71	0.36	85	15	2.75	0.097	0.054
<i>CeTNP5</i>	5.0	65	0.35	79	21	2.75	0.056	0.052
<i>P25</i>	-	55	0.06	83	17	3.15	0.079	0.014

^aSpecific surface area (m² · g⁻¹) calculated by Brunauer-Elmet-Teller method.

^bPore volume (cm³ · g⁻¹) ^cContributions (wt.%) of anatase and rutile. ^dEnergy gap (eV).

^eKinetic constant under UV light (min⁻¹) and ^fKinetic constant under simulated solar light (min⁻¹)

Textural properties of the recycled CeTNT025 and CeTNP025 samples were also studied. A slight decrease in S_{BET} value was observed, from 26 to 22 m² · g⁻¹ for CeTNT025 sample and from 99 to 91 m² · g⁻¹ for CeTNP025 counterpart. This decrease could be associated with to partial pore blocking by reaction intermediates, which would also explain the ever-decreasing adsorption in the dark after 3 reaction cycles.

8.2.4. High Resolution Transmission Electron Microscopy (HR-TEM)

Morphology and ceria dispersion in titania nanostructures were elucidated by HR-TEM and images are collected in **Figure 8.7** for the CeTNTx series and in **Figure 8.8** for the CeTNPx counterparts.

The TNTx HR-TEM images confirmed the presence of titania nanotubes with uniform length between 100 and 120 nm. CeTNTx containing low ceria loading presented randomly distributed titania nanotubes with an average length (calculated using ImageJ software) of approximately 120 nm and 6 nm of diameter. By HAADF images, it was evidenced that ceria nanoparticles were hosted inside these nanotubes and presented an average diameter of 2 nm in samples under 2.5 wt.% of ceria loading, which could explain the absence of ceria diffraction peaks in XRPD measurements. In samples containing higher ceria loading, titania nanotubes were shorter and wider, with *ca.* 97 and 8 nm of length and diameter, respectively. Moreover, not only nanotubes but also titania nanospheres are found, which indicates that the conversion of the nanopowder from the first step of the synthesis, the sol-gel process, to the second one, the hydrothermal process under basic conditions, was not completed [13]. This fact could also explain the worsening in the photocatalytic performance under UV light irradiation in samples with high ceria loading: the relatively high coverage of the surface by ceria nanoparticles could hinder the access of pollutant molecules to titania active sites. Regarding ceria nanoparticles' diameter, in CeTNT5 sample the mean diameter was found to be *ca.* 1.6 nm, which confirms that, as previously reported [14], ceria nanoparticles grow inside titania nanotubes, allowing intimate contact between both phases and promoting the intermixing of cerium and titanium oxides thus favouring the formation of Ce^{3+} cations.

Ceria nanoparticles' dispersion was analysed by means of EDX mapping in STEM mode. As observed in **Figure 8.7**, ceria nanoparticles

are highly dispersed inside titania nanotubes, as suggested by XRPD analysis. Moreover, from the EDX spectrum a mass percentage of 3 wt.% and 5 wt.% (from **Figure 8.7 D**) of Ce was calculated for CeTNT2.5 and CeTNT5 samples, respectively, indicating a very good dispersion of ceria into titania nanotubes, given the similarity to theoretical mass percentages. Na presence in the EDX spectrum is related to the basic hydrothermal treated used of CeTNT synthesis.

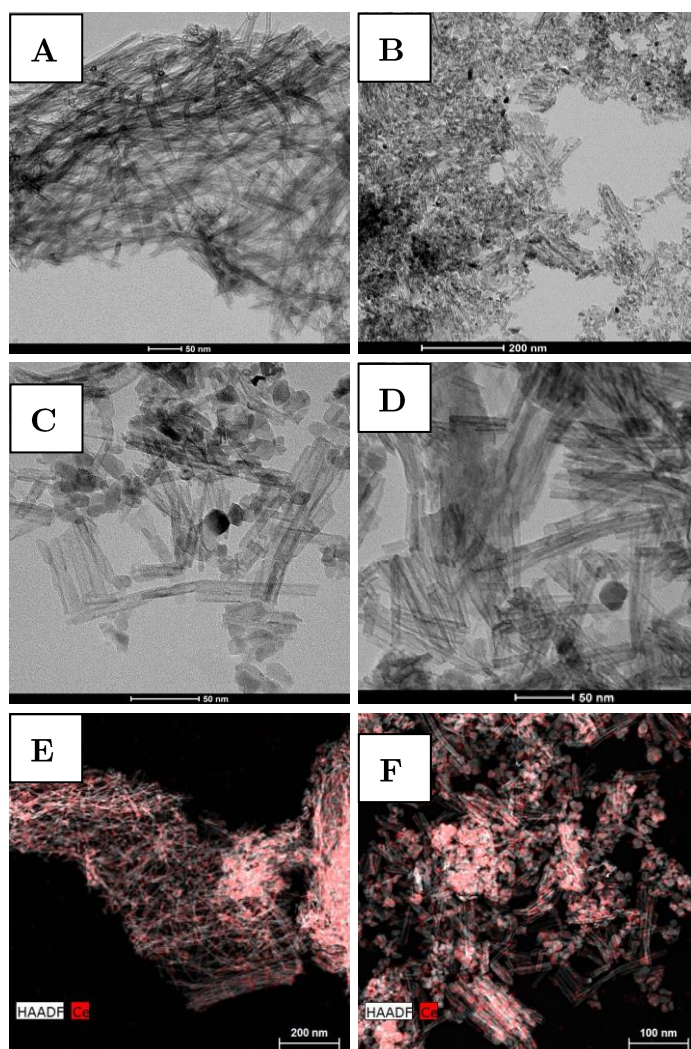


Figure 8.7: HRTEM images: (A) CeTNT025; (B),(C), (D) CeTNT5; EDX mapping of Ce overlapping the STEM image in (E) CeTNT025 and (F) CeTNT5

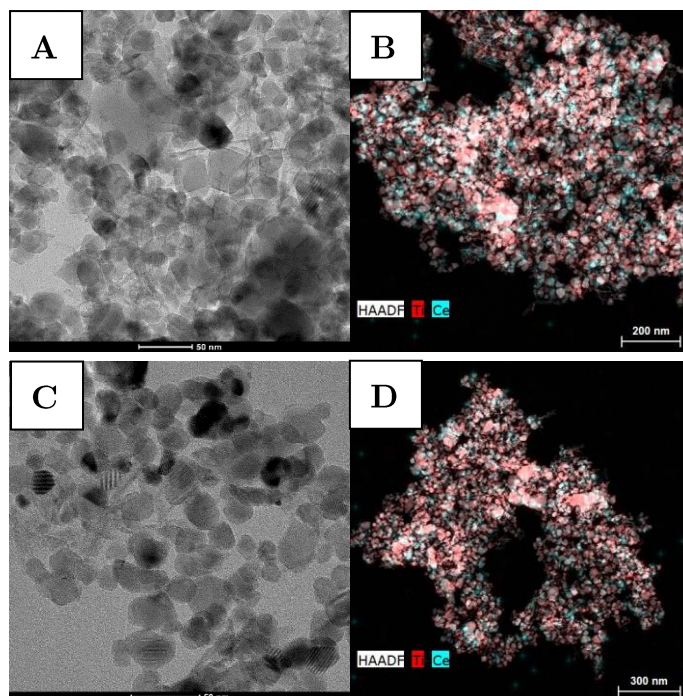


Figure 8.8: Representative HRTEM (A), (C) and EDX mapping of Ce overlapping the STEM (B)(D) images of nanoparticle systems: (A) (B) CeTNP0.25 and (C), (D)CeTNP5

Contrary to CeTNTx series, the morphology of the CeTNPx samples seemed not to be significantly affected by ceria loading and all samples presented square-shaped nanoparticles with diameters ranging 20-25 nm, with the largest ones found in the CeTNP5 sample. However, although with the same morphology, with EDX-STEM mapping it is evidenced that together with well-dispersed ceria nanoparticles, some agglomerates were found in the CeTNP2.5 sample (see **Figure 8.8**). Nevertheless, all samples presented a good ceria dispersion and are ceria-rich, which again are supported by the Raman and XRPD results obtained: Ce atoms tend to concentrate mainly on the surface of titania nanostructures, therefore neither ceria phases nor distortion of the crystal lattice were detected by Raman and XRPD, respectively. Analogously to CeTNTx counterpart, from EDX spectrum quantification, 3.8 wt.% and 5.0

wt.% Ce was calculated for CeTNP2.5 and CeTNP5 samples, respectively, which are in good agreement with theoretical values.

8.2.5. X-Ray Photoelectron Spectroscopy (XPS)

The surface composition and chemical environment of the tested samples were studied using X-Ray photoelectron spectroscopy and O 1s, Ti 2p and Ce 3d core levels spectra are displayed in **Figure 8.9** for the CeTNTx and CeTNPx catalysts set. Additionally, **Table 8.2** shows binding energies of core level electrons for both catalysts series.

Table 8.2: Binding energies for CeTNTx and CeTNPx catalysts. Values In parenthesis indicate contribution in %

Catalyst	O 1s		Catalyst	O 1s		
<i>TNT</i>	530.1	531.63	<i>TNP</i>	529.7	531.5	-
	(91)	(9)		(96)	(4)	
<i>CeTNT0.25</i>	529.7	531.0	<i>CeTNP0.25</i>	529.7	531.4	533.5
	(87)	(13)		(69)	(18)	(12)
<i>CeTNT0.5</i>	529.8	531.2	<i>CeTNP0.5</i>	529.7	531.3	534.1
	(87)	(13)		(88)	(10)	(2)
<i>CeTNT1</i>	529.8	531.2	<i>CeTNP1</i>	529.7	531.5	534.0
	(92)	(8)		(89)	(9)	(2)
<i>CeTNT2.5</i>	529.9	531.3	<i>CeTNP2.5</i>	529.8	531.7	534.0
	(89)	(11)		(84)	(13)	(3)
<i>CeTNT5</i>	530	531.5	<i>CeTNP5</i>	529.8	531.4	533.7
	(89)	(11)		(92)	(7)	(1)

The O 1s core level spectra (**Figure 8.9 C and D**) showed two contributions: the main one at *ca.* 530.21 eV, related to lattice oxygen of TiO₂ and the second one at 531.6 eV associated with superficial oxygen (O-, OH-, CO₃²⁻, -CO₂²⁻) [15]. No contribution related to CeO₂ (Binding energy 529.1 eV [16]) was detected, probably due to the low ceria loading and also to the fact that CeO₂ species are located inside titania nanotubes, as evidenced by HR-TEM images. In both CeTNTx and CeTNPx catalysts

sets, the main signal suffered a slight shift to lower binding energy as ceria loading was increased, indicating an increase in oxygen mobility [17]. Likewise, in CeTNPx the signal related to lattice oxygen is also found at lower binding energy, 529.6 eV, which suggests the formation of a CeTiO solid solution considering the decrease in electronic density due to Ce incorporation. Noteworthy is the appearance of a third oxygen contribution in pure TNP sample and CeTNP025 counterpart at *ca.* 533.5 eV, which has been reported to be chemisorbed oxygen [18].

Ti 2*p* (**Figure 8.9 A**) core level spectra presented a characteristic peak at 458.4 eV related to Ti 2*p*_{3/2} and its doublet Ti 2*p*_{1/2} at 464.1 eV (5.7 eV separation), indicating that titanium is present as octahedrally coordinated Ti⁴⁺ ions and very close to the reported value for titania nanosystems [19]. In the case of CeTNPx, the main contribution Ti 2*p*_{3/2} is located at lower binding energy, which is unexpected taking into account that both anatase (binding energy 458.4 eV [20]) and rutile (binding energy 458.7 eV [21]) are present in the CeTNPx set. This finding suggests that titania's morphology, rather than its crystalline phase, is responsible for electrons lability at the core level. As in the case of O 1*s* spectra displayed in **Figure 8.9 C** and **D**, in the CeTNTx set, the incorporation of ceria provoked a shift towards lower binding energy, more accused in samples with high ceria loading, which would suggest a lower oxidation state for titanium. Nonetheless, the 5.7 eV separation between doublets indicates that titanium is present as Ti⁴⁺ ions. Unlikely, the Ti 2*p* spectra of CeTNPx experimented a shift towards higher binding energy when ceria was incorporated, probably due to ion incorporation in the substitutional site of the titania lattice or the formation of Ti-O-Ce bonds, as previously reported for ceria-titania mixed oxides in which ceria was inserted into the TiO₂ matrix [22]. In both cases, these shifts could be explained considering a greater interaction between Ti and Ce that favours oxygen mobility and give rise to oxygen vacancies that enhance photocatalytic activity since they are more reactive in redox processes [23].

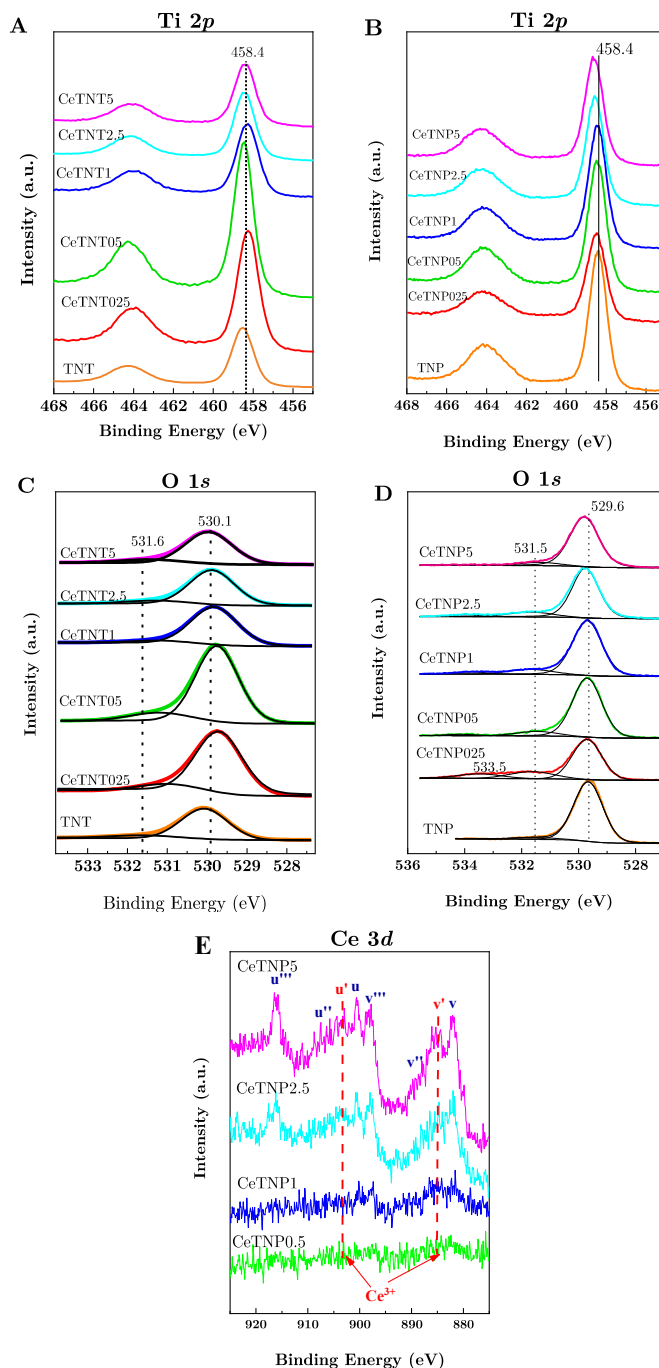


Figure 8.9: Core level spectra (A) Ti 2p for CeTNTx, (B) Ti 2p for CeTNPx (C) O 1s for CeTNTx (D) O 1s for CeTNPx and (E) Ce 3d for CeTNPx

Considering the low Ce loading used and the low specific surface area and ceria dispersion of CeTNTx series, no Ce 3d signals were detected.

Not the case of CeTNPx series, for which Ce 3d core level spectra were recorded and are displayed in **Figure 8.9**, although these signals were quite noisy and different contributions were only noticeable for ceria loadings over 0.5 wt%. In these samples, four spin-orbit doublets were identified as $v(n)$ and $u(n)$: three related to Ce^{4+} species ($v(\sim 882 \text{ eV})$ and $u(\sim 900.7 \text{ eV})$; $v''(\sim 888.8 \text{ eV})$ and $u''(\sim 907.2 \text{ eV})$; $v'''(\sim 898.2 \text{ eV})$ and $u'''(\sim 916.5 \text{ eV})$) and one ascribed to Ce^{3+} ones ($v'(\sim 884.5 \text{ eV})$ and $u'(\sim 903.3 \text{ eV})$) [24]. Ce^{4+} species were the main ones in all samples, with Ce^{3+} only being detected in samples with ceria loading over 2.5 wt%.

8.2.6. DRUV-Vis spectroscopy

The CeTNTx and CeTNPx photo-response was evaluated by DRUV-Vis spectroscopy and spectra are displayed in **Figure 8.10**, from which optical band gap (E_g) values, collected in **Table 8.1**, have been estimated from the intercept of the extrapolated linear fit for the plotted experimental data of $(\alpha h\nu)^{1/2}$ (the exponent $\frac{1}{2}$ was chosen for the indirect bandgap in titania) *versus* the incident photon energy ($h\nu$) near the absorption edge.

TNT sample presented an intrinsic interband absorption in the UV region (wavelengths under 400 nm) with an E_g value of 3.20 eV. A red shift in absorbance was observed as ceria loading increased, with E_g between 3.10 and 3.03 eV for samples with a ceria loading under 1 wt.% and 2.90 eV for CeTNT2.5 and 2.65 eV for CeTNT5 samples. The formation of Ce^{3+} cations have been reported to be responsible for this narrowing in titania's band gap thanks to the formation of some mid-gap states in the band gap [3], [25].

As for the CeTNPx counterpart, a decrease in E_g values can also be observed in **Table 8.1**, although less noticeable than in the case of CeTNTx. Pure titania nanoparticles sample presented a lower E_g value than TNT, 3.0 eV, and no significant changes were noticed for low ceria loading

samples. Nevertheless, with ceria loadings over 2.5 wt.% a considerable decrease is observed, with an E_g value of 2.75 eV for both CeTNP2.5 and CeTNP5 samples.

The diminishing in E_g values in samples containing higher ceria loading could explain the better photocatalytic performance of these samples under simulated solar light. Therefore, it could be concluded that the incorporation of ceria species induces a red shift in the absorbance of titania nanotubes that extend the available spectral region for photocatalytic processes to the visible light scope, since it allows visible light harvesting and generates a higher number of charge carriers that actively participate in oxidation and reduction reactions.

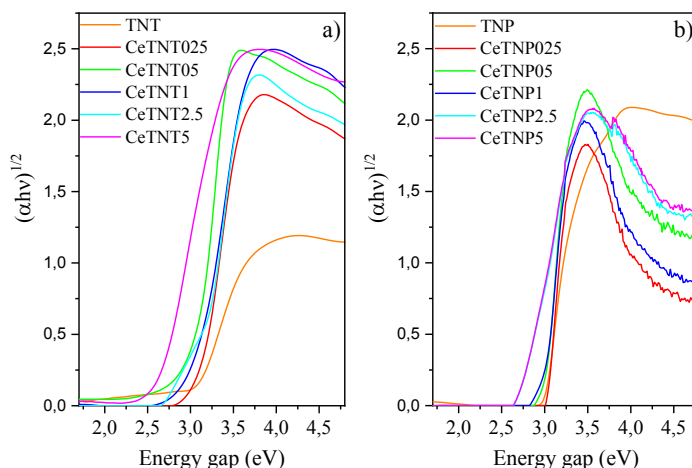


Figure 8.10: $(\alpha h\nu)^{1/2}$ plot against photo energy (eV): a) undoped and ceria-doped TNT samples; b) undoped and ceria-doped TNP samples

8.2.7. Time resolved photoluminescence (TRPL)

Charge dynamics in the two series of samples was studied by means of time-resolved photoluminescence analysis by monitoring the modification of the photoluminescence decay spectra upon methylene blue addition in suspensions containing the catalysts. Jin et al. [26] already proposed this analysis with other luminophores to study the photoluminescence quenching properties of electron scavengers during photocatalytic processes. With the

aim of studying $4f-5d$ transition of Ce^{3+} , 400 and 250 nm were selected as emission (λ_{em}) and excitation (λ_{ex}) wavelengths, respectively [27]. The emission at 400 nm was also observed for the TNP sample, which is similar to previously reported photoluminescence of ultrafine TiO_2 powder [28]. The presence of methylene blue in the solution induces a fast charge transfer from the excited electrons in the conduction band of the mixed oxide to the lowest unoccupied molecular orbital (LUMO) of methylene blue. As this recombination competes with the radiative recombination originating the studied photoluminescence, time decay behaviour is affected.

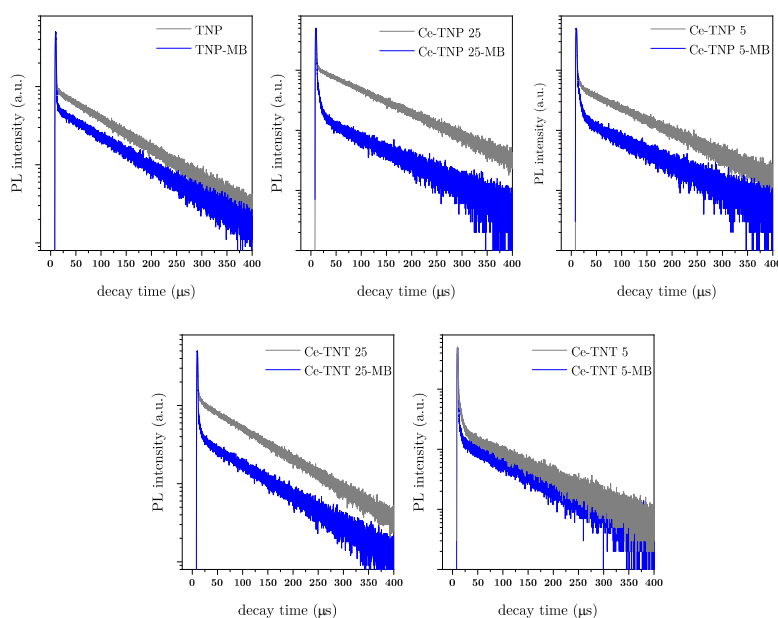


Figure 8.11: TRPL decay spectra for selected samples of the two TNP and TNT series. $\lambda_{\text{ex}} = 250$ nm; $\lambda_{\text{em}} = 400$ nm

TRPL emission wavelength intensity curves at 400 nm for samples from both catalyst sets with the highest ceria loading (2.5 and 5 wt.%), as well as pure titania nanoparticles (TNP), were measured in methylene blue absence and presence, and the results are plotted in **Figure 8.11**. Two time constant decays are present in all samples: the first one with the characteristic decay time in the range of a few μs falling at the limit of the instrument, and the second one in the order of around 110 μs . In the

presence of methylene blue, the relative intensity of the fast decay increased, and the opposite occurred for the slow decay. Nonetheless, the long decay constant of 110 μ s was the same in both CeTNTx and CeTNPx catalysts studied, which supports the hypothesis that methylene blue acts as a carrier scavenger for Ce-TiO₂. In addition, this fact justifies that the degradation of methylene blue did not introduce any new excited state around 400 nm. The largest drop in the slow decay component after methylene blue addition was obtained for the CeTNT2.5 sample, which is in good agreement with the photodegradation results in **Figure 8.2**.

8.3. Discussion

With the aim of studying the influence of morphology on ceria-titania nanostructures, two sets of catalysts based on ceria-doped titania nanotubes and nanoparticles were studied in the photodegradation of the cationic dye methylene blue under UV light irradiation and simulated solar light. From the photocatalytic and characterization results, it could be assumed that the ceria-titania composite can lead to the formation of a heterojunction structure, with synergistic effects for harvesting visible light and hindering photogenerated charge carriers' recombination.

Two different factors influencing the photocatalytic activity have been analysed in this chapter:

On the one hand, it has been observed that ceria doping has a beneficial effect on the photocatalytic performance. Interestingly, under UV light irradiation, the ceria benefits are most noticeable at low ceria loadings. When acting as a promoter, enough titania surface where the dye can be adsorbed and degraded is available, while ceria ions allow the production of electrons that are transferred to titania, leading to an efficient separation of photogenerated electrons and holes across the TiO₂-CeO₂ boundary and decreasing charge carriers recombination rate. On the contrary, ceria loadings over 2.5 wt.% have resulted detrimental due, as seen by HR-TEM

images, to the great coverage of the titania active sites by CeO_2 particles that even form agglomerates onto the titania surface. Conversely, under simulated solar light, high ceria loadings present the best photocatalytic performances thanks to the decrease of the titania's band gap. By DRUV-Vis spectroscopy, a red shift in absorbance was observed as the ceria loading increased, therefore extending the operating scope to the visible region of the spectrum. From the photocatalytic results obtained, 0.25 and 2.5 wt.% Ce loadings resulted the most photoactive under UV and simulated solar light, respectively. Moreover, CeTNPx catalysts presented better photocatalytic performances, probably due to the higher specific surface area compared to that of their CeTNTx counterparts increasing the accessibility of titania active sites and also the ceria dispersion, as evidenced by S_{BET} values and EDX-STEM mapping.

On the other hand, it has been demonstrated that morphology plays a key role in the photocatalytic performance. The CeTNPx series presented lower adsorption during the dark period and higher methylene blue photodegradation rates both under UV and simulated solar-light. It has been reported that less ordered nanostructures are more photoactive than more uniform structures like nanotubes or nanosheets. For example, Xiu et al. [29] studied ceria-doped TiO_2 nanosheets containing *ca.* 1.5 wt% Ce in methylene blue and methylene orange photodegradation under visible light irradiation, attaining *ca.* 70% degradation of the dyes in 180 minutes of reaction, with a kinetic constant of 0.0073 min^{-1} . Likewise, Tuyen et al. [30] carried out methylene blue photodegradation under visible light irradiation using 15 wt% CeO_2 - TiO_2 nanotubes, achieving almost total conversion in 150 minutes of reaction with a kinetic constant of 0.032 min^{-1} , thanks to the decrease in titania's band gap due to high ceria loading and to the coexistence of $\text{Ti}^{3+}/\text{Ti}^{4+}$ and Ce^{3+} into the TiO_2 lattice. Lastly, Bonfanti-Vieira et al. [31] tested Ce-doped titania with different morphologies such as nanosheets, nanotubes and nanoparticles and suggested that ceria addition induces the disorder in these nanostructures. Moreover, under

similar conditions to the one studied in the present chapter (even though with lower photocatalytic performances) over 90% degradation of methylene blue and polyvinylpyrrolidone (PVP) was achieved. Not only is the order of the nanostructure that improves the photocatalytic performance, but also its surface area to volume ratio. In fact, three-dimensional nanostructures with high light absorbance and large surface area to volume ratio have recently arisen as promising candidates for photocatalytic processes. Photodegradation of ciprofloxacin under UV-Vis irradiation using one-dimensional and three-dimensional TiO_2 nanostructures was studied by Li et al. [32], and they reported that 90% degradation was obtained with the tripyramid-like architecture, whereas just 50% for its rod-like counterpart, which could be related to the improved surface area due to the special three-dimensional nanostructures. Additionally, Bergamonti et al. [33] reported the total degradation of amoxicillin under UV-Vis irradiation using titania-supported chitosan scaffolds, which opens up a wide range of possibilities of tuning shape and size of these nanostructures, as well as increasing stability and manipulation of titania-based photocatalysts.

In summary, the CeTNTx and CeTNPx catalyst sets have demonstrated remarkable photocatalytic activity under UV light and simulated solar-light irradiation thanks to both ceria incorporation and morphology. From the catalytic results it can be concluded that ceria resulted more beneficial as a promoter when the reaction is performed under UV light irradiation, being the most active catalysts CeTNT025 and CeTNP025, since there are enough titania active sites available for dye adsorption and ceria ions are highly dispersed onto titania nanostructures, which decreases charge carriers' recombination rate. Conversely, under simulated solar light, samples with ceria loadings over 2.5 wt.% have resulted more active, due to the diminishing in the titania's band gap after ceria incorporation.

8.4. Conclusions

Two sets of ceria-doped titania catalysts with different ceria loadings ranging from 0.25 to 5 wt.%, and two different morphologies, nanotubes and nanoparticles, have been tested in methylene blue photodegradation under UV light and simulated solar light at ambient conditions. By XRPD results, it was demonstrated that in the CeTNTx catalysts, titania was present as anatase, the most photoactive phase, while the CeTNPx set presented both anatase and rutile in a similar proportion to that of the commercial benchmark titania photocatalyst P25. No ceria phases were detected due to both the low metal loading and to the high dispersion of ceria, as evidenced by HR-TEM images and EDX-STEM mapping analysis. Regarding textural properties, the CeTNTx samples presented a very low specific surface area, which could explain the worse photocatalytic performance of these samples in comparison to their CeTNPx counterparts, with S_{BET} values between 118 and $65 \text{ m}^2 \cdot \text{g}^{-1}$. By XPS analysis it was concluded that Ti was in its (IV) oxidation state, and that ceria, as well as highly dispersed on titania's surface, was present mainly as Ce^{4+} , although the samples with high ceria loading also shows a Ce^{3+} contribution.

To sum up, with this work it is evidenced that less ordered titania nanostructures doped with low ceria loadings (less than 5 wt.%) resulted highly photoactive in methylene blue photodegradation under mild conditions, extending the operating spectral scope to the visible light region thanks to ceria-titania interactions, that enhances oxygen mobility and hinder charge carriers' recombination, as well as decreasing titania's wide band gap.

8.5. References

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9. CONCLUSIONS

9. Conclusions

From the hydrodeoxygenation studies in chapters 4, 5 and 5, the following conclusions can be extracted:

- The incorporation of Ni, Fe and Co to Nb-based supported on SBA-15 mesoporous materials promoted anisole HDO conversion and selectivity to cyclohexane and benzene, following the trend $\text{NiNb} > \text{CoNb} > \text{FeNb}$. The higher activity of Ni-containing sample was related to a greater interaction between nickel and niobium, better dispersion and high hydrogenating activity of nickel, together with a higher exposure of niobium oxides in this sample.
- In mixed oxides derived from layered double hydroxides, it was observed that there is a limitation in Ce loading that can be incorporated before losing hydrotalcite-like structure. Ni hydrogenating activity was also evidenced by the product selectivity, being the main one cyclohexane. Also, it was observed that the catalytic activity is governed by the cerium loading and oxidation state used in the synthesis: the sample with the best photocatalytic performance was NAC-4,10 due to the higher specific surface area, better dispersion of NiO phase and weak acidity.
- The bifunctionality of $\text{Pt-Fe}_2\text{O}_3$ supported on SBA-15 catalysts was confirmed given the catalytic behaviour observed in this set of catalysts, in which products distribution and characterization results revealed that Pt acts as the hydrogenating part and Fe as the oxophilic counterpart with acid nature. In addition, it was demonstrated that higher hydrogen pressure promoted higher HDO conversion, but higher temperatures derived in enhance selectivity to oxygenated by-products.

Future work on these sets of catalysts could cover the study of stability and deactivation of the catalysts working over days on stream. Likewise, the

study of their catalytic behaviour in hydrodeoxygenation reaction of other model compounds or even lignocellulosic biomass-derived bio-oil could be of great interest.

Likewise, From the results obtained with the photocatalytic tests and the characterization techniques carried out for photodegradation and photo-PROX reactions in chapters 7 and 8, the following conclusions are gathered:

- Samples containing both gold and copper supported on Ti-containing SBA-15 support presented a better photocatalytic performance in the two reaction systems tested than those with just Au or Cu supported on bare SBA. Titania can be effectively incorporated into SBA-15 mesoporous structure. Moreover, gold and copper incorporation resulted in highly dispersed nanoparticles in close contact between each other and with the Ti-containing support. The formation of a AuCu alloy can be suggested after hydrogen treatment of the samples.
- The morphology of ceria-titania nanostructures strongly influenced the photocatalytic activity, obtaining better performances over less ordered structures nanoparticles than over nanotubes. Interestingly, under UV light irradiation, Ce addition favoured the photodegradation of methylene blue when added at very low loadings (0.25 wt.%), indicating that more than as a co-catalyst, it could act as a promoter. Conversely, under simulated solar light, samples with Ce loadings around 2.5-5 wt.% resulted the most photoactive ones, since at higher Ce contents, titania's band gap is diminished and therefore applicable light scope is extended to the visible light region.

Given the potential of these catalysts in photo-assisted reactions carried out at ambient conditions, the study of the photodegradation of other pollutants such as drugs could be covered. Likewise, the research of the

optimal morphology of ceria-titania structures as well as ceria loading in order to maximize the photocatalytic yield could be an engrossing continuation of this research line.

APPENDIX

List of signs and acronyms

A	Anisole
AIE	Agencia Internacional de la Energía
B	Bencene
BE	Binding energy
CH	Cyclohexane
CHME	Cyclohexyl methyl ether
DDO	Direct deoxygenation
DME	Demethylation
D_p	Pore diameter (nm)
DRUV-Vis	Diffusive reflectance UV-Visible spectroscopy
EDS	Escenario de desarrollo sostenible
E_g	Energy gap (eV)
FTIR	Fourier Transform Infrared
GEI	Gases de efecto invernadero
GHG	Greenhouse gases
GHSV	Gas hourly space velocity (h ⁻¹)
H₂-TPR	Hydrogen thermoprogrammed reduction
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurization
HR-TEM	High resolution transmission electron microscopy
HYD	Hydrogenation
IEA	International Energy Agency
LDH	Layered double hydroxide
LHSV	Liquid hourly space velocity (h ⁻¹)
NH₃-TPD	Ammonia thermoprogrammed desorption
NP(s)	Nanoparticle
P	Pressure (bar, Mpa)
PDF	Powder diffraction file
PEMFC	Proton exchange membrane fuel cell
PH	Phenol
Photo-PROX	photo-assisted preferential CO oxidation
RWGS	Reverse water gas shift reaction
S	Selectivity (%)

S_{BET}	Specific surface area calculated by Brunauer-Emmet-Teller method ($\text{m}^2 \cdot \text{g}^{-1}$)
SDS	Sustainable development scenario
SEM	Scanning electron microscopy
T	Toluene
T	Temperature ($^{\circ}\text{C}$)
TGA	Thermogravimetric analysis
TK	Transalkylation
TMC	Transition metal carbide
TMN	Transition metal nitride
TMP	Transition metal phosphide
TMS	Transition metal sulphide
V_p	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)
WGS	Water gas shift reaction
WHSV	Weight hourly space velocity (h^{-1})
wt. %	Weight percentage
X	Conversion (%)
XHDO	HDO conversion (%)
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

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ARTICLES

Bimetallic Niobium-Based Catalysts Supported on SBA-15 for Hydrodeoxygenation of Anisole

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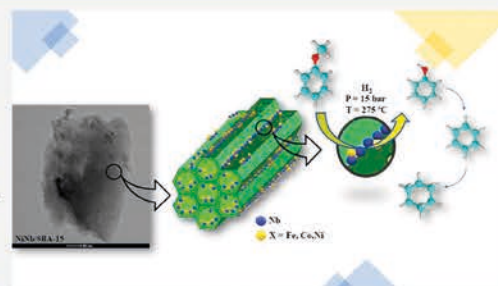
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ABSTRACT: The effect of adding iron, cobalt or nickel to a prepared niobium-supported catalyst using mesoporous silica SBA-15 as a support was evaluated in the hydrodeoxygenation (HDO) reaction of anisole, chosen as a model compound in lignocellulosic biomass derived bio-oil. HDO activity as well as selectivity toward O-free products were highly dependent on the catalyst formulation: Ni incorporation showed the highest anisole conversion and selectivity to deoxygenated products, followed by Co and Fe counterparts. The activity was explained in terms of acidity, metal surface exposure and reducibility as a function of the interaction between the phases present. Regarding the characterization results, the better performance of NiNb/SBA-15 was associated with its lower acidity, higher Nb/Si surface exposure, NbO₂/Nb₂O₅ ratio and better interaction between Ni and Nb species.



1. INTRODUCTION

The obtention of liquids fuels from biomass has gained great attention recently, since the scientific community is looking for cleaner energy solutions that not only supply the increasing energetic demand, but also that will be friendly with the environment.^{1–4} The production of transportation bifuels from biomass can be conducted by different synthetic routes: gasification to produce syngas, hydrothermal liquefaction or fast pyrolysis to produce bio-oil.^{5,6} The bio-oil includes many oxygenated hydrocarbons (alcohols, aldehydes, carboxylic acids, ketones, and phenolics), that confer undesired properties, such as thermal instability, polymerization, low calorific value and storage difficulties, as well as immiscibility with fossil-fuel-derived compounds. Therefore, a significant upgrading is required before it can be used as transportation fuel.^{6,7} In this regard, the oxygen content of the bio-oil can reach up to 50%, for bio-oil from fast pyrolysis.^{8–10}

Recently, one of the approaches performed to lower the oxygen content in bio-oil is hydroprocessing, being that hydrotreatment one of the most important processes in the petroleum industry, where several heteroatoms can be removed in the presence of hydrogen and a proper catalyst (hydrosulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) to remove S, N, and O, respectively). In many occasions, these hydrotreatments are accompanied by processes of hydrogenation (saturation) of olefins and aromatic compounds.¹¹ The upgrading of bio-oil

through HDO partially or totally removes the oxygenated compound, being the most common upgrading route, despite its high consumption of hydrogen and the requirement of high pressures at moderate temperatures (300–600 °C).^{9,12} A possible solution that can allow a reduction in hydrogen pressure is the preparation of effective bifunctional HDO catalysts, which combine supports with acidic nature^{13–15} and metal centers with HDO activity as niobium-containing catalysts. Niobium-based catalysts are becoming promising materials capable of catalyzing reactions such as oxidation, hydration, dehydration, hydrolysis, esterification, hydrodeoxygenation, alkylation, condensation, and photocatalysis, since they are acid, stable and present high tolerance to water.^{16,17} Dumesic et al.¹⁸ were the first to report a niobium-containing catalyst, Pt/NbOPO₄, for total HDO reaction. Later, Wang et al.¹⁹ observed that Pt/NbOPO₄ was more active than Pt/SiO₂–Al₂O₃ in the reaction of ring-opening/hydrogenation of 4-(2furyl)-3buten-2-one to octane. That catalyst, under very mild conditions (165–175 °C, 25 bar), was able to not only convert octanediols to octane via dehydration/hydrogenation

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NiAlCe mixed oxides obtained from layered double hydroxides applied to anisole hydrodeoxygenation

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ABSTRACT

Bio-oil derived from the pyrolysis of lignocellulosic biomass residues cannot be used directly as biofuel due to the high content of oxygenated compounds. As an alternative, bio-oil must undergo a deoxygenation process, such as catalytic hydrodeoxygenation (HDO). In this sense, this work studied the effect of different concentrations of Ce^{3+} and Ce^{4+} in layered double hydroxides (LDHs) in order to obtain mixed oxide catalysts containing NiAlCe ($\text{NiO-NiAl}_2\text{O}_4\text{-CeO}_2$) with low cost and high performance for the hydrodeoxygenation of anisole as a model bio-oil compound. Mixed oxides were obtained from the thermal decomposition of layered double hydroxides (LDHs) by using terephthalic acid as compensation anion, with molar ratio: $\text{Ni}^{2+}/(\text{Al}^{3+} + \text{M}) = 1.0$, where $\text{M} = \text{Ce}^{3+}$, Ce^{4+} or $\text{Ce}^{3+}\text{-Ce}^{4+}$; and Al/Ce ratios of 9 and 1. Characterization analyses confirmed the formation of LDHs for all materials, although at lower Al/Ce ratio it is observed a loss of crystallinity, due to a greater repulsion and distortion of the layer structure caused by the incorporation, in greater amount, of cations with a high ionic radius. The increase in the content of cerium in mixed oxides also led to an increase in the acidity of the catalysts, in addition to a reduction in the surface area, justified by the pore blockage by CeO_2 on the catalyst surface. The greater structural and thermal stability was evidenced in the LDHs derived from Ce^{4+} , as well as a greater dispersion of the NiO phase in the corresponding mixed oxides, and therefore presenting greater anisole conversion. The obtained data indicated that the presence of Ce^{4+} ions on the catalyst surface was decisive in the conversion of anisole to cyclohexane, the main deoxygenated product, obtained via the direct deoxygenation and hydrogenation mechanism.

1. Introduction

The burning of fossil fuels and deforestation are the main causes that has contributed to the increase in the concentration of CO_2 in the atmosphere to levels above 415 ppm in 2019. The high concentration of CO_2 has caused great environmental and economic issues with the hottest last years, extreme climatic events and ocean acidification [1]. Even with the recent drop in fossil fuel consumption due to slowing global growth [2], the concentration of CO_2 in the atmosphere needs to

decrease. The main solution is to increase the use of renewable energies and biofuels. Due to the current low oil prices, biofuels must be produced from biomass residues.

Lignocellulosic biomass is a renewable resource that is widely available in the environment and comprises vegetable organic matter, agro-industrial waste or processing waste from vegetable organic matter [3–5]. The use of lignocellulosic biomass is a viable way to produce renewable fuels from unconventional sources that would not normally have commercial value. One of the best ways to convert biomass into

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Article

Au and AuCu Nanoparticles Supported on SBA-15 Ordered Mesoporous Titania-Silica as Catalysts for Methylene Blue Photodegradation

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Abstract: The photocatalytic degradation of methylene blue (MB) dye has been performed under UV irradiation in aqueous suspension, employing photocatalysts based on Au (1.5 wt %) and AuCu (Au/Cu = 1, 2.0 wt %), and supported on SBA-15-ordered mesoporous silica, with and without titania (Si/Ti = 3), in order to evaluate the versatility of this mesoporous support in this type of reaction of great impact from the environmental point of view. Samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption-desorption at −196 °C, and X-ray photoelectron spectroscopy (XPS), so as to study their structural, optical, and chemical properties. All the prepared catalysts were found to be active in the test reaction. The bimetallic AuCu-based catalysts attained very high MB degradation values, in particular AuCu/SBA-15 titania-silica sample reached 100% of dye oxidation after the monitored reaction period (120 min).

Keywords: pollutant degradation; methylene blue; photocatalysis; SBA-15 mesoporous silica; nanoparticles (NPs); Au NPs; AuCu NPs

1. Introduction

Photocatalysis plays a significant role in air, water, and pollutant degradation. Due to the heavy industrialization the modern world is experiencing nowadays, water remediation, involving water cleaning and sanitation, is a serious environmental issue for both human and aquatic life, as a notorious number of industries releases industrial effluents during their regular activity, that constitute a threat to water quality. These effluents contain refractory, toxic, and potentially carcinogenic organic and inorganic compounds, employed either as raw materials or as reaction intermediates, that are chemically stable and non-biodegradable. Pollutants, such as heavy metals, pesticides, solvents, or dyes, the latter responsible for a major visual impact due to their bright and long-lasting colors, not only obstruct light penetration (and hence reduce photosynthetic activity of aquatic life), but also disturb the food chain of the water ecosystem [1], and cause clean water scarceness [2]. About 15% of the total world production of dyes is lost during the dyeing process and is discharged as textile effluents. The release of those colored dyes in wastewaters is disrupting the ecosystem. Originally, dye photodegradation was extensively studied by a real need to treat contaminated water effluents from textile, leather tanning, and paper industries, among others [3–5]. Nonetheless,

Article

CO Preferential Photo-Oxidation in Excess of Hydrogen in Dark and Simulated Solar Light Irradiation over AuCu-Based Catalysts on SBA-15 Mesoporous Silica-Titania

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Abstract: In this work, SBA-15 silica and silica-titania have been used as supports for photocatalysts based on AuCu alloy (Au:Cu = 1) to be used in the preferential oxidation of CO (CO-PROX) in excess of hydrogen at room temperature and atmospheric pressure both in the dark and under simulated solar light irradiation. To study their textural, structural, chemical and optical properties, the samples were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), adsorption-desorption of N₂ at −196 °C, ¹³C and ²⁹Si solid state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance ultraviolet-visible (DRUV-vis) spectroscopy. Titanium was present mainly in the form of titania aggregates, but also as small particles interacting with the SBA support. In both catalysts, the metal alloy nanoparticles displayed an average size of 4 nm as demonstrated by TEM measurements. AuCu/Ti-SBA turned out to be photoactive and selective in the photo-CO-PROX reaction showing the highest activity, with conversion and selectivity towards CO₂ of 80%, due both to the presence of titania incorporated in SBA-15 and to the synergistic effect of Cu when alloyed with Au.

Keywords: CO preferential oxidation; CO-PROX; photocatalysis; solar light response; SBA-15 mesoporous silica; Ti-SBA-15; gold nanoparticles

1. Introduction

Since Fujishima and Honda discovered the potential of TiO₂ in water splitting under ultraviolet (UV) irradiation back in 1972 [1], photocatalysis has gained the interest of the scientific community worldwide. Nowadays, photocatalysis research can be broadly classified into two categories: energy and environment; the latter being extensively studied for pollutant degradation and environmental remediation of water and air, inasmuch as these reactions can be accomplished at mild operating conditions and can be solar driven [2–5]. A recent book [6] has highlighted the current developments and future potential of the green-chemistry-oriented applications of various inorganic, organic, and hybrid photocatalysts and their importance in a broad spectrum of catalytic processes such as photocatalytic CO₂ reduction [7], photocatalytic water oxidation [8], heteropolyacid-based

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Ceria doping boosts methylene blue photodegradation in titania nanostructures†

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Ceria-doped titania photocatalysts (ceria loading 0.25–5.0 wt%) were synthesized by hydrothermal methods for water remediation. Nanotubes (CeTNTx) and nanoparticles (CeTNPs) were obtained. Ceria doping was applied to tune the electronic properties of nanostructured titania, boosting its photocatalytic activity. CeTNT nanostructures contained anatase as the only titania phase, whereas the CeTNP series consisted of both anatase and rutile polymorphs. The Ce addition induced a decrease in the energy gap, allowing enhancement of visible light harvesting. The photodegradation of methylene blue, MB, in aqueous solution was chosen to study the influence of the morphology and the ceria loading on the photocatalytic response, under UV and solar light. Both CeO₂-TiO₂ nanoparticles and nanotubes were found to be very active under UV light. The highest MB degradation rates were obtained for the 0.25 wt% CeO₂ doping, for both nanotubes and nanoparticles (0.123 and 0.146 min⁻¹, respectively), able to photodegrade completely the dye after 120 min. The two samples are stable after a 3-cycle reusability test. The photo-response under simulated solar light confirmed that doping titania with ceria allows harvesting visible light absorption, enhancing its photoactivity. A maximum efficiency of 85% under simulated sunlight at a degradation rate of 0.054 min⁻¹ was obtained. Transient photoluminescence confirmed that MB acts as a charge scavenger for the composite system. These results pointed out ceria-doped titania nanostructures as a promising class of photocatalysts for the degradation of dyes and other hazardous organic compounds in wastewater.

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Introduction

Water pollution constitutes an issue of major concern worldwide that not only affects the environment, but also jeopardizes human health. Moreover, it is a long-term problem since water pollution not only occurs in superficial water bodies but also reaches groundwater. This fact, together with the properties of water as a universal solvent, eases the degradation of water quality due to hazardous substances contained in wastewater effluents, such as heavy metals or organic

compounds that can be non-biodegradable, highly toxic or even carcinogenic.

Among all the anthropogenic sources of water pollution, it is estimated that more than 20% comes from the textile industry, which releases between 1000 and 3000 m³ of wastewater effluents for the processing of less than 20 tons of textiles per day.¹ These effluents usually contain high concentrations of organic and inorganic compounds due to the incomplete fixation of dyes onto the fabrics, which leads to synthetic dye contents in effluents up to 10–15% that negatively affect both the ecosystem and human health.¹ On the other hand, as well as colouring water even at concentrations below 1 mg L⁻¹, they totally or partially block sunlight penetration, thus hindering the appropriate functioning of microbiological processes in aquatic ecosystems. They can also interfere with photosynthesis, competing with living species for oxygen.^{2,3}

Conventional technologies for water purification of organic contaminants such as trickling filter technology, flocculation and electrodialysis are highly energy-demanding processes with considerable operation and maintenance costs that are not effective for dye removal.¹ Adsorption is usually used in the removal of dyes from wastewater effluents and it has shown

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