



## Ru supported on Mg/Al hydrotalcites for phenol hydrogenation

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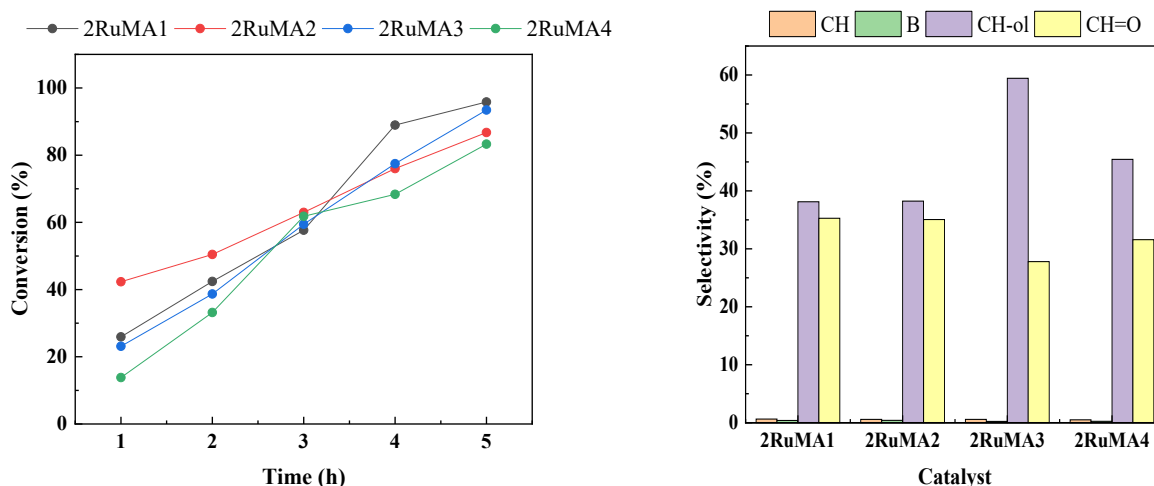
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Cyclohexanone and cyclohexanol are high value-added products widely used in polymer and chemical industry as organic solvents in oil paints or varnishes [1] or as intermediates in nylon, oxalic acid, caprolactam and adipic acid syntheses [2]. These compounds have been traditionally obtained from cyclohexane oxidation, a tedious and energy consuming process with low selectivity for the desired cyclohexanone and cyclohexanol. Thus, hydrogenation of phenol has emerged as a promising alternative to the former process with greater selectivity and, considering that phenol could be obtained from the degradation of lignin, which is a widespread, sustainable, carbon neutral precursor, this synthetic route has gained the attention of the scientific community. It has been reported that in phenol hydrogenation, hydrogen is added to the aromatic ring by a spill-over mechanism in which both phenol and hydrogen are adsorbed on metal sites, and that the adsorption configuration is strongly related to the number of acid and basic sites around metal sites [3]. In addition, it is known that supports with acid-base properties and moderate specific surface area improve both thermal stability and metallic phase dispersion. With respect to metallic sites, noble metals like Pd or Ru are benchmark hydrogenating agents [4].

In this work, catalysts containing 2 wt.% Ru supported on non-commercial hydrotalcites with different Mg/Al molar ratios were tested in the hydrogenation of phenol in a batch reactor with semiautomatic sample collection working at 200 °C and 30 bar. The catalysts were fully characterized by means of XRD, N<sub>2</sub> adsorption-desorption at -196 °C, XPS and HR-TEM.

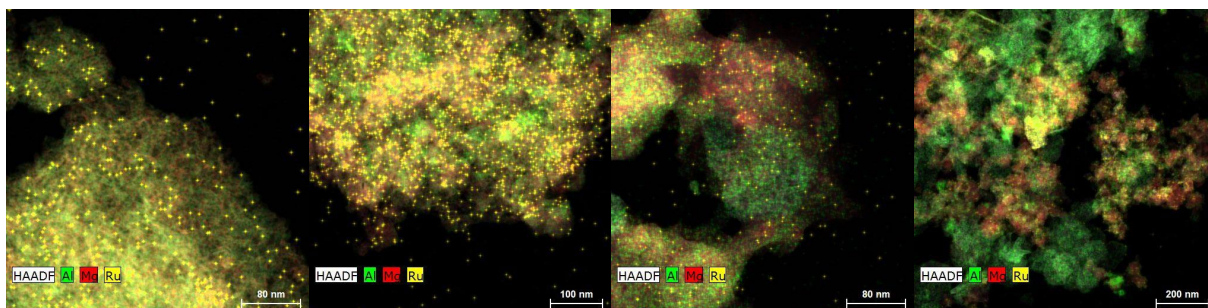


**Figure 1.** (a) Conversion on stream for all 2RuMA catalysts; (b) Selectivity at five hours of reaction for all 2RuMA catalysts



### 9<sup>th</sup> Czech - Italian - Spanish Conference on Molecular Sieves and Catalysis

The characterization results confirmed the obtention of mesoporous supports with a good dispersion of ruthenium (with a particle size of 1-2 nm), as evidenced by EDX-STEM mapping in Figure 2, in which aggregates of Mg and Al can also be observed as Mg/Al molar ratio increased. XRD measurements confirmed the presence of characteristic hydrotaalcite phases. XPS results of the reduced and used catalysts revealed the presence of ruthenium in metallic state, as well as RuO<sub>2</sub>. It is also noticeable that as the Mg/Al ratio increases, the proportion of RuO<sub>2</sub> increased and the metallic ruthenium decreased. After reaction, no significant changes were observed except that Ru<sup>0</sup> was the main contribution due to hydrogen presence during the reaction.



**Figure 2.** EDX-STEM mapping for (a) 2RuMA1, (b) 2RuMA2, (c) 2RuMA3 and (d) 2RuMA4.

In all cases the expected reaction products were obtained: cyclohexanone and cyclohexanol, the catalyst with the best catalytic performance being the ruthenium catalyst supported on the hydrotaalcite with a molar ratio Mg/Al = 1 (2RuMA1), showing a total conversion of 96% (see Figure 1(a)) and a selectivity towards cyclohexanone and cyclohexanol of 35.3% and 38.1%, respectively, as shown in Figure 1(b). This better performance could be associated with the higher specific surface area of the catalyst, the high dispersion of ruthenium on the surface and the significant contribution of metallic ruthenium as an active phase in the catalysis.

**Acknowledgements:** The authors thank Ministerio de Ciencia e Innovación, project PID2021-126235OB-C32 and FEDER funds for economical support. IBM thanks University of Málaga for a postdoctoral grant.

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