Catalytic upgrading of ethanol to n-butanol over a novel Ca-Fe modified mixed oxide Mg-Al catalyst from hydrotalcite-base precursor

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Abstract

n-Butanol is used in a wide range of applications and recently, the use of n-butanol as a fuel, which can be employed pure or blended with gasoline or diesel, has been proposed. So, in an attempt to deepen in the one-step catalytic process to produce n-butanol from ethanol, bifunctional catalysts in different chemical/spatial environment as MgAl- and CaFeMg-multioxide catalysts were developed, prepared and characterized. Both mixed oxides were obtained by thermal decomposition of the synthesized hydrotalcites considering the partial substitution of Mg^{2+} and Al^{3+} by Ca^{2+} and Fe^{3+}, namely MgAl-Ox and $Ca_{20}Fe_{20}$MgAl-Ox. The nature of acid and basic properties of the samples were analyzed employing NH_3 and CO_2 as probe molecules, and TPD analysis were performed to quantify the relative contribution of acidic/basic sites. $Ca_{20}Fe_{20}$MgAl-Ox sample presented an improved basicity with minimal acidity reduction.

The performances of the activated catalysts were measured in a fixed-bed reactor under transient and continuous operation modes by DRIFT-MS studies and under transient pulse experiments. It was verified that both catalysts, but specially $Ca_{20}Fe_{20}$MgAl-Ox, promotes the synthesis of C_4-compounds from ethanol due to the modulated acid and basic sites capable of modify the ethanol adsorption in the form of ethoxy-species and a combined higher basicity with centers to catalyze the hydrogenation using the ethanol as the hydrogen donor. $Ca_{20}Fe_{20}$MgAl-Ox reached an ethanol conversion values of 36% at 280 ºC and 71% at 400ºC with a higher selectivity to n-butanol and other C_4-compounds. Two parallel routes at differentiated temperatures: direct acetaldehyde self-condensation and the intermediary crotyl alcohol transfer hydrogenation, were evidenced and prevailing in n-butanol formation.

Keywords: n-butanol; Calcium-Iron modified hydrotalcite; biofuels; ethanol upgrading; mixed oxide catalyst.

1. Introduction

Nowadays, the advance of new routes for bio-ethanol synthesis from renewable and carbon-neutral biomass-based feedstock and the important issue of the increase in ethanol production during the last decades have promoted a special interest into the development of new catalytic technologies for bio-ethanol upgrading into sustainable and valuable fuels or chemicals [1–5]. The use of higher bio-alcohols as a substitution, alternative or additive for fossil-sourced fuels have gathered such more interest to the scientific community in a context where global emission regulations for automobile sector are becoming more stringent and there is a growing concern about fossil fuel depletion, oil-price fluctuations and escalating energy demands [6]. Hence, the use of long chain alcohols as diesel blends in light vehicles has currently attracted interest because of the many drawbacks of the use of ethanol and methanol as a gasoline/diesel fuel additive [7–11].

Therefore, due to its physicochemical properties compared to other alcohols, n-butanol (C_4H_9OH) has become a desirable transportation blend fuel compared, e.g., to ethanol, by reason of its higher density, viscosity, lubricity, cetane number, its miscibility with diesel fuel without additional co-solvents. Especially butanol has an energy density higher than ethanol (~30 $kJ \cdot g^{-1}$) and closer to diesel [12,13]. Then, butanol becomes more suitable for internal combustion engines as a substitution for ethanol in diesel-biodiesel blends as a large number of investigations declare [14–22].

n-butanol has been produced by fermentation of sugars (acetone-butanol-ethanol process, ABE) or through the petrochemical oxo process, but the direct condensation of ethanol into butanol is considered a more desirable method since fewer steps are necessary (through Guerbet reaction) [23,24]. Although Guerbet condensation mechanism has been in dispute, it is generally accepted Guerbet reaction consists of the following four steps: (i) ethanol dehydrogenation to acetaldehyde (ii) aldol coupling reaction of two molecules of acetaldehyde (iii) dehydration of the products formed by the aldol reaction (crotonaldehyde) and finally (iv) two successive hydrogenation yielding n-butanol.

Guerbet patented process employs homogeneous catalysts (typically based on precious metal catalysts for the sequential hydrogenation/dehydration steps and an inorganic base to aid in the aldol coupling step) but several investigations were focused on its heterogenization as an economic and green route [25–28]. Many heterogeneous systems

have been reported for this purpose, being the majority associated with acid-base properties like metal Mg-Al oxides [29–31], hydroxyapatites [32–34], zeolites [35], group II metal oxides as MgO or BaO [36–38] and multicomponent oxide catalysts [28,39,40], usually employing reaction temperatures over 300 ºC.

Ethanol upgrading condensation *via* Guerbet process strongly depends on the chemical composition and preparation method of the catalytic materials. Some authors emphasize that the development of a selective catalyst for this process implies a proper balance of acid-basic sites pairs [41]; acid ones catalyze alcohol dehydration reactions (but a strong acidity causes the molecular dehydration of ethanol to ethylene and ethers) and basic ones catalyze hydrogenation and condensation to higher chain alcohols. Hence, hydrotalcite-derived Mg-Al mixed oxides have received attention for this process due to their high surface area, structural stability and, especially, its acidic-base properties. Larina et al. [42] concluded that the conversion of EtOH and the selectivity towards resulting Guerbet alcohols essentially depend on the acid-base characteristics of the Mg-Al oxide system studying different Mg/Al ratios. These authors reported that the optimal ratio of acidic/basic sites on the catalyst surface to gain the largest butanol-yield of 17.5 % and 65.2 %-selectivity were achieved with a composition of Mg/Al = 2 at 300 ºC in a fixed-bed flow reactor under atmospheric pressure. León et al. [30] observed that hydrotalcite-derived mixed oxide Mg-Al catalyst prepared at high supersaturation conditions presented the best performance in terms of selectivity and yield to different C4 chemicals over 400 ºC, related with the presence of stronger basic sites in comparation to these prepared at low supersaturation and under sonication. Carvalho et al. [43] studied the reaction pathway of the direct synthesis of n-butanol from ethanol using Mg-Al mixed-oxide catalyst derived from hydrotalcite precursors and pure oxides MgO and Al_2O_3. The results obtained from *in situ* DRIFT tests indicated that Mg-Al oxides with Mg/Al = 3 ratio resulted in a rapid evolution of acetaldehyde and crotonaldehyde intermediates to n-butanol than Mg/Al = 1 at 350 ºC.

The addition of other elements such as Ni, Co, Mn, Ru or Pd over mixed oxides derived from hydrotalcite precursors were also studied and reported [31,44]. Furthermore, the total or partial modification of these materials can promote the decrease or increase of acidic-basic properties, being the key to the development of a catalyst for Guerbet reaction. It is known that substituting the trivalent ion (Al^{3+}) in a Mg-Al hydrotalcite-derived mixed oxides with Fe^{3+} decreases acidity in the catalyst, increasing the selectivity to acetaldehyde and long chain alcohols [45]. The partial incorporation of copper (Cu^{2+})

as a substitution of divalent cation (Mg^{2+}) in mixed metal oxide obtained from Mg-Al hydrotalcite precursor presented an increase in weak and strong basic sites (consequently the overall oxide basicity) and a slight increment of overall acidity with a little depletion of medium and strong acid sites [46]. Thus, it is remarkable that the study and knowledge of these catalytic properties are a fundamental factor for the development of materials with proper and balanced qualities, which were capable to present higher yield and more selective synthesis routes to produce butanol from of ethanol avoiding the formation of undesired co-products.

This work is focused on the improved synthesis of a Mg-Al based hydrotalcite, as a precursor of mixed oxides, with partial substitution of Mg^{2+} and Al^{3+} by Ca^{2+} and Fe^{3+}, respectively, with the aim to optimize n-butanol production from ethanol condensation and study their influence in the mechanism and activity analyzed by *in situ* DRIFT-MS analysis and under isothermal ethanol transitory response method .

2. Experimental section

2.1. Catalyst preparation

Calcium-iron-modified Mg-Al based-hydrotalcite precursor was prepared by a co-precipitation method [47] improved via sonication, using a 3:1 ratio between divalent cations and trivalent cation. Besides, partial substitution of Mg by Ca (80 %Mg^{2+} + 20 %Ca^{2+} in molar basis) and partial substitution of Al by Fe (80 %Al^{3+} + 20 %Fe^{3+} in molar basis) were considered. An adequate aqueous solution of $Ca(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (all precursors were over 98 % purity supported by *Panreac AppliChem*) was added drop-wise into a 0.2 $mol \cdot L^{-1}$ K_2CO_3 (*Panreac AppliChem*, 99 %) solution under controlled temperature (60 ºC), in constant vigorous stirring and the pH was adjusted to 10±0.2 by adding appropriate quantities of a 0.1 $mol \cdot L^{-1}$ NaOH solution. During the precipitation step, a constant nitrogen stream (20 $mL \cdot min^{-1}$) was flowing into the synthesis container to maintain an inert atmosphere in order to ensure a continuous stream of N_2 that displaces the air in the system. Once all the solution had been added, the mixture was kept overnight at 60 ºC after sonication at room temperature (Ultrasonic Processor UIP1000hd-Hielscher with a frequency of 20 KHz using a titanium sonotrode). The precipitate was washed several times with distilled water by high-speed centrifugation until pH = 7 to remove alkali metals and nitrate ions

and then, the aqueous solid suspension was sonicated before keeping it autoclaved at 100 ºC during 48 h. The gel was dried overnight under vacuum at 40 ºC and then, the powder was milled and sieved (100-80 MESH) and labelled as $Ca_{20}Fe_{20}$MgAl-LDH. Another non-modified mixed oxide hydrotalcite-base precursor, MgAl-LDH, was synthesized using the same divalent-trivalent cation ratio (Mg:Al = 3:1) and methodology. The resulting hydrotalcites were calcined at 400 ºC (5 ºC·min^{-1}) in air for 4h deriving in mixed oxides catalysts designated as $Ca_{20}Fe_{20}$MgAl-Ox and MgAl-Ox, respectively.

2.2. LDHs and oxide-derived catalysts characterization

The LDHs' morphologies were characterized by Scanning Electron Microscope (SEM) analysis where micrographs were conducted on a JEOL JSM-840 microscope equipped with an Energy Dispersive X-Ray (EDX) detector and a Philips CM200 (200kV) microscope was used for High Resolution Transmission Electron Microscope (HRTEM) images and the EDX mapping. The specific surface area ($m^2 \cdot g^{-1}$) was determined using Brunauer-Emmet-Teller (BET) method and the pore volume ($cm^3 \cdot g^{-1}$) by Barret-Joyner-Halenda (BJH) method in a Micromeritics ASAP 2020 Analyzer by adsorption-desorption of N_2 at -196 ºC in which solid was previously outgassed in vacuum ($1 \cdot 10^{-3}$ Pa) at 40 ºC. X-Ray Powder Diffraction data was recorded using an X'Pert Pro MPD diffractometer (PANanalytical) using a CuKα1 radiation (λ=1.5406 Å) and a Ge(111) primary monochromator. Measurements were done from 10 to 70 º (2Θ) and average crystallite size was calculated by Debye-Scherrer equation.

Surface basicity and acidity were studied by Temperature-Programmed Desorption (TPD) of preadsorbed CO_2 and NH_3 respectively. For TPD profiles, 60 mg of MgAl-Ox or $Ca_{20}Fe_{20}$MgAl-Ox catalysts were used (pretreated in He for 2 h at 400 ºC) and placed in a quartz U-shaped reactor (d_i = 6 mm) prior of feeding 100 mL·min^{-1} of gas with 2,000 ppm of each compound balanced in He to saturation at 60 ºC. Physisorbed compounds were removed by flowing He at 60 ºC for 2 h and finally, the samples were heated up to 400 ºC with a ramp of 10 ºC·min^{-1} in helium. The gas-off was analyzed with the QMS 200 mass spectrometer (Pfeiffer Vacuum Prisma^{TM}).

The nature and strength of basic and acidic sites was also analyzed by Fourier Transform Infrared (FTIR) spectroscopy of chemisorbed CO_2 and NH_3 respectively using a Nicolet iS10 spectrometer with a resolution of 2 cm^{-1} and 40 scans. Experiments were done using

$Ca_{20}Fe_{20}$MgAl-Ox or MgAl-Ox catalysts pressed into thin disks (≈ 20 mg) and activated in the IR cell connected with a conventional outgassing/gas-manipulation apparatus at 400 ºC in vacuum (10^{-3} Torr). The activated samples were saturated with CO_2 or NH_3 respectively (≈ 5 Torr) at 60 ºC for 20 min. IR spectra of the surface species were collected under evacuation at increasing temperatures from 60 ºC until 400 ºC. All reported spectra were obtained after subtraction of the spectrum corresponding to the activated sample.

2.3. Catalytic activity

2.3.1 Ethanol adsorption

Ethanol adsorption capacity of catalysts at 60 ºC was calculated by subtraction of the numerical integrated MS responses for C_2H_5OH fed and the C_2H_5OH line registered during a rectangular pulse of 25,000 ppm of ethanol according to Eq.1 for pretreated samples in He-atmosphere at 400ºC for 2 h:

$$\frac{C_2H_5OH^{stored}\left(mmol_{C_2H_5OH}\right)}{g_{cat}} = \frac{\int_0^{t_{sat}}\left(F^{in}_{C_2H_5OH}-F^{out}_{C_2H_5OH}\right)}{g_{cat}} \qquad \text{Eq.1}$$

where F represents the total EtOH molar gas flow ($mmol \cdot min^{-1}$).

2.3.2. DRIFT-MS analysis

Ethanol conversion experiments were performed in the range of 100-350 ºC at atmospheric pressure in a continuous flow DRIFT Harrick Praying Mantis™ fitted to FTIR Nicolet iS10 spectrometer and connected to the QMS 200 mass spectrometer *on line*. MgAl-Ox and $Ca_{20}Fe_{20}$MgAl-Ox catalysts (30 mg) were pretreated at 100 ºC for 1h in He flow (20 $mL \cdot min^{-1}$) and a constant 2.5 % Ethanol-He flow (anhydrous ethanol, *Panreac*, 99.999 %) of 20 $mL \cdot min^{-1}$, (Gas Hourly Space Velocity, GHSV = 14,000 h^{-1}) was fed at 100 ºC through a saturator. The saturator was kept at a constant temperature of 4 ºC with a cooling system. Spectra were recorded in diffuse reflectance mode (DRIFT) with 50 scans at 2 cm^{-1} resolution in the 4000-650 cm^{-1} wavenumber range when $m \cdot z^{-1}$ signals were stabilized at each operation temperature. The $m \cdot z^{-1}$ signals followed were: 2 (H_2), 4 (He), 18 (H_2O), 26 (Ethylene), 44 (Acetaldehyde), 46 (Ethanol), 56 (Butanol), 57 (Crotyl alcohol), 59 (Diethyl ether), 70 (Crotonaldehyde) and 72 (Butanal).

2.3.3. Catalytic test under ethanol transitory response method

To study the product distribution and ethanol conversion profiles, a rectangular pulse of 1% EtOH-He (280 and 400 ºC) was fed. In each experiment, 60 mg of each catalyst sample were placed in quartz fixed-bed reactor working at atmospheric pressure. The total flow of inlet gas was maintained constant at 40 $mL \cdot min^{-1}$ (GHSV = 28,000 h^{-1}) and ethanol was introduced in a He carrier gas stream through a cooled ethanol saturator as was previously described. The reactor was connected to a QMS 200 mass spectrometer (Pfeiffer Vacuum Prism™) to register on-line the product distribution. The samples were *in situ* conditioned in He up to 400 ºC for 2 h. Non-catalytic tests were performed using quartz as a blank with which the conversion was calculated by the difference between the ethanol signals for experiment and sample once steady state was reached. Carbon balance, considering the amount of ethanol used as reactant, and the concentration of ethanol and all the identified reaction products, present closures higher than 95% in all the reported experiments.

3. Results and discussion

3.1. LDHs and catalyst characterization

HR-TEM-EDX and SEM images of synthetized LDHs catalyst precursors are shown in Figure 1. TEM micrographs confirmed the characteristics of a hydrotalcite well-developed with layered structure and overlapped platelets, some regions with fibrous morphology and a similar lamellar interlayer average length close to 7 nm for both samples. The uniform composition of the prepared hydrotalcites were confirmed by EDX elemental mapping analysis, except for the modified hydrotalcite (Fig. 1.b), where some calcium carbonate aggregates were registered. In SEM images (Fig. 1.c and Fig. 1.d), the same particle aggregates with irregular shape and size (10-60 µm) were observed for LDH-samples. SEM-EDX composition analysis showed the good homogeneous dispersion of elements for MgAl-LDH and $Ca_{20}Fe_{20}$MgAl-LDH, and the ratio M^{2+}/M^{3+} was kept constant without modifying the LDH structure.

X-Ray Diffraction patterns for hydrotalcites and oxide catalysts are presented in Figure 2. LDHs (Fig. 2.a) showed the typical diffractograms of a well-formed hydrotalcite hydroxide structures for MgAl-LDH (ICDD 04-015-1683, brucite) and for

$Ca_{20}Fe_{20}$MgAl-LDH (ICDD 01-082-8043, meixnerite). Both XRD patterns exhibited signals at the 2Θ angles of 11.5º, 22.9º, 34.6º, 45.1º, 60.4º and 61.6º that correspond to the characteristic (0 0 3), (0 0 6), (0 0 9), (0 1 5), (0 1 8), (1 1 0) and (1 1 3) layered double hydrotalcite structure basal planes, respectively [48,49]. In the case of $Ca_{20}Fe_{20}$MgAl-LDH, there was no reflection associated with Fe and superimposed signals at 29.4º, 43.1º and 48.5º associated with $CaCO_3$ (ICDD 01-078-4614) were registered. The meixnerite layer structure, brucite-like [50–52], is associated with the incorporation of Fe^{3+} and Ca^{2+} cations in the LDH structure, partially modified by the hydration and carbonation, as Sangkhum et al. [49] described. Table 1 shows the values of crystallographic parameters such as the distance between cations in the lamellar layer (*a*) calculated from the *d*-spacing of (1 1 0) peak reflection ($a = 2 \cdot d_{(1\ 1\ 0)}$), the *c* parameter that corresponds to the height or interlayer space of the hydrotalcite layer form ($c = 3/2 \cdot [d_{(0\ 0\ 3)} + 2 \cdot d_{(0\ 0\ 6)}]$) and the crystallite size determined using Scherrer's equation. There is no significant difference in *a* parameter (a decrease of 0.16 %) suggesting the successful incorporation of the Ca/Fe elements in the layers. It is known that the interlayer space depends on M^{2+}/M^{3+} molar ratio, metal ionic radius, the size of anion within the interlayer and the degree of hydration [53]. Therefore, as can be observed in Table 1, the incorporation and the partial substitution of lower ionic radius Mg^{2+} (0.72 Å) and Al^{3+} (0.53 Å) by Ca^{+2} (1 Å) and Fe^{3+} (0.67 Å), respectively, resulted in a 0.9 % decrease of the value (*c*) of the modified hydrotalcite interlayer space. As it was reported [45,50,54], the substitution of aluminum by iron leads to a crystal size decrease as consequence of the higher ionic radius of Fe^{3+} species leading to lower crystal stability. In $Ca_{20}Fe_{20}$MgAl-LDH sample, the decrease is higher than in literature, due to the additional incorporation of Ca^{2+}. After LDHs calcination at 400 ºC for 4h (Fig. 2.b), it was noticeable that the layered structure was completely collapsed with the disordering in the stacking of the layers after the heat treatment deriving to mixed oxides of the elements and amorphous materials. MgAl-Ox clearly showed the amorphous phase of mixed oxide Mg(Al)O. Neither aluminum nor iron phases were observed in the diffractograms of modified-hydrotalcite, suggesting that trivalent ions are either well dispersed or forming an amorphous phase in $Ca_{20}Fe_{20}$MgAl-Ox, but the presence of MgO periclase (weak broad peaks reflections at 43º and 62º, ICDD 01-071-4938) and $CaCO_3$ phases can be observed because of the segregation of Ca [47,55] in the structure of hydrotalcite and its distribution over the structure as $CaCO_3$ in relation with HR-TEM-EDX and SEM-EDX data previously showed.

Hydrotalcites LDHs and calcined materials textural properties obtained from N_2-sorptometry are summarized in Table 1. For $Ca_{20}Fe_{20}$MgAl-LDH, BET surface area decreased (>27%), besides, pore volume and pore size decreased. The calcination at 400 ºC of MgAl-LDH and $Ca_{20}Fe_{20}$MgAl-LDH resulted in an increment of A_{BET} of 18 and 22%, respectively. Nevertheless, V_P and D_P increased for the oxide derived from non-modified LDH whereas for modified $Ca_{20}Fe_{20}$MgAl-Ox were practically maintained. The presence of two trivalent [45,50] and divalent cations [49] in the brucite-like structure would lead to mixed oxides that affect to the surface area more than pore volume and average pore diameter compared to non-modified hydrotalcite.

Basic and acid surface properties for oxide catalysts after in situ-pretreatment were studied combining CO_2 and NH_3 TPD tests and FTIR, and the results are presented in Table 2 and Figure 3 and 4. Temperature-Desorption curve of CO_2 and NH_3 are shown from 60 to 400 ºC and CO_2/NH_3-TPD FTIR profiles are presented in the range of 1900-1100 cm^{-1} where spectra of catalyst samples were collected after probe molecules desorption in vacuum at each temperature. In Table 2, the CO_2 and NH_3 net adsorption capacity (calculated from TDP adsorption curve) are shown. CO_2-TPD curves trends are similar and, it can be observed that the T_{max} desorption presented a 25 ºC of shift at higher temperatures for $Ca_{20}Fe_{20}$MgAl-LDH. The values corresponding to net CO_2 adsorption capacity revealed an increase in basic sites density, higher than ≈ 600%, for $Ca_{20}Fe_{20}$MgAl-Ox compared to MgAl-Ox. Furthermore, the value of $\mu molCO_2^{ret} \cdot m^{-2}$ for modified catalyst also revealed a high surface basic sites density. It is remarkable that the partial substitution of Mg and Al by Ca and Fe leads to an increase (Fig. 3.a) in the amount of the weakest basic sites (60-200 ºC) associated to weakly CO_2-adsorbed such as metal hydroxide and the medium basic sites assigned to metal-oxygen ion pairs (M^{2+}-O^{2-} and M^{3+}-O^{2-}) at 250-450 ºC temperature range [49,56]. This fact suggests that the incorporation Ca^{2+} significantly affects the CO_2 adsorption capacity of the material while the partial exchange of Al^{3+} to Fe^{3+} does not alter the Mg-Al hydrotalcite basic properties as León et al. [45] described. CO_2-FTIR-TPD spectra (Fig. 3.b) confirmed the higher concentration of weak-medium basic as Brønsted sites (1650 and 1550 cm^{-1} [30,57]) in modified sample due to the stability of bidentate carbonates at low temperature. It was also established the higher stability of strong basic sites (monodentate species) linked to 1385 cm^{-1} signal in $Ca_{20}Fe_{20}$MgAl-Ox which were maintained until 300 ºC compared to MgAl-Ox (1410 cm^{-1}) catalyst where monodentate carbonates disappeared at 250 ºC [45].

Spectra evolution during the temperature increase after evacuation showed that bidentate carbonates as Brønsted sites were stronger in modified catalyst since they were maintained until 150 ºC (1650 cm^{-1}) and disappeared at 250 ºC (1550 cm^{-1}). Monodentate carbonates species related to strong basic sites (1385 cm^{-1}) were maintained at higher temperatures (350 ºC) in $Ca_{20}Fe_{20}$MgAl-Ox compared to MgAl-Ox (1410 cm^{-1}) although they totally disappeared at 300 ºC.

The curves obtained from NH_3-TPD (Fig. 4.a) seemed to be similar. A symmetrical desorption curve is presented in the range between 60 ºC and 400 ºC for MgAl-Ox, with a maximum at 220 ºC and as indicated in Table 2, it corresponds to 0.42 $mmolNH_3 \cdot g_{cat}^{-1}$ which in terms of surface density would be 4.1 $\mu molNH_3^{ret} \cdot m^{-2}$. The modified material showed a curve, although also quasi-symmetric, much wider with a maximum centered at 260 ºC. The calculated values, 0.20 $mmolNH_3 \cdot g_{cat}^{-1}$ and 3.2 $\mu molNH_3^{ret} \cdot m^{-2}$, were similar to those recorded for the unmodified material. From NH_3 desorption profiles, it was confirmed that the population of acid sites (both Lewis and Brønsted) was higher for $Ca_{20}Fe_{20}$MgAl-Ox than for MgAl-Ox. As for the thermal stability, although being higher for the modified one, no significant differences can be highlighted for both materials through the thermal evolution of the infrared spectra. Irrespective of net acidity, medium Lewis acid sites as metal ions, being registered for both mixed-oxide materials, according with the classification reported by Kustrowski et al. [58], linked to M^{3+}-O-M^{3+} and M^{3+}-O-M^{2+}, were larger at 200-400 ºC . The partial exchange of Mg^{2+} and Al^{3+} by Ca^{2+} and Fe^{3+} respectively leads to a decrease around 50 % in the surface acidity (per gram of catalyst) and a 20% less on acid sites distribution (per m^2 of catalyst). NH_3-FTIR spectra (Fig. 4.b) showed a higher NH_3 retention capacity for the MgAl system in the form of coordinated species associated with Lewis centers. Lewis acid sites are attributed to the accessible Al^{3+} cations which come from Al^{3+}-O-M^{2+} species [59], linked to 1603 cm^{-1}; in addition, a signal associated with protonic centers (NH_4^+) as Brønsted sites at 1440 cm^{-1} were similar for both at the same temperature [60]. The main source of acid sites in hydrotalcite type material is the presence of tetrahedrally coordinated trivalent ions in the crystalline structures [45,61]. In fact, the partial exchange for Ca^{2+} in the structure of Ca–Mg–Al ternary mixed oxides derived from layered double hydroxide also leads to a decrease of the amount of weak acid species and the total acidity while the level of total Lewis strong acid sites is high [49]. The substitution of up to 20% of Mg by Ca and Al by Fe produces a material that maintains the hydrotalcite-like structure and gives rise to

a complex mixed oxide with a high surface development morphology. The catalytic properties due to the double substitution improve the overall basicity partly derived from calcium and the minimal reduction in acidity is associated with the modification by incorporation of iron.

3.2. Catalytic Activity

3.2.1. Ethanol adsorption

From the numerical integration of the ethanol adsorption curve obtained at 60 ºC, the net ethanol capacity values were 9 $mmolEtOH^{ret} \cdot m^{-2}$ and 18.5 $mmolEtOH^{ret} \cdot m^{-2}$ for MgAl-Ox and $Ca_{20}Fe_{20}MgAl$-Ox derived oxides, respectively. The increase in ethanol species retained on the catalyst surface is due to a substantial increase in basic sites and a partial decrease in acidic sites per unit of catalyst area due to the incorporation of the new components.

3.2.2. DRIFT-MS ethanol experiments

DRIFT-MS experiments feeding a constant flow of ethanol-He (2.5 % of ethanol) were performed, and the data are displayed in Figure 5. DRIFT spectra recorded from 100 to 320 ºC were shown together with the selectivity values from maximum normalized $m \cdot z^{-1}$ intensities of the major products detected. It should be notice that DRIFT and MS are complementary techniques and that the species detected bound to the catalyst's surface may be intermediated components or spectators [62]. At low temperature and below 250 ºC, in the spectra of both materials (Fig. 5.a and 5.b) very weak or negative OH_{υ} stretching modes [36] above 3000 cm^{-1} were detected and in the 3000-2800 cm^{-1} region signals related to dissociative adsorbed ethanol as surface ethoxide species at 2972 and 2872 cm^{-1} for MgAl-oxide catalyst and 2972, 2924 and 2872 cm^{-1} for CaFeMgAl-oxide; caused by $CH_{3\upsilon(a)}$, $CH_{2\upsilon(a)}$ and $CH_{3\upsilon(s)}$ stretching modes, respectively [63,64]. These vibrations are attributed to monodentate ethoxy species (CH_3CH_2O-M) for CH_3 group and bidentate ethoxy species coordinated to two metal atoms (CH_3CH_2O-M-M) for CH_2 group, where M represents the metal [32]. The intensities were similar and close to the modes of free ethanol adsorbed on surface and the ethoxy-groups formed for ethanol-surface interaction with the ethanol desorbed as reaction detected product between 100-200ºC.

On the spectra registered for the reference MgAl-Ox catalyst (Fig. 5.a), it can be observed that signals related to monodentate ethoxy species (2972 and 2872 cm^{-1}) tended to disappear when the temperature is close to 250 ºC, appearing other signals associated with short-chain aldehyde, $\upsilon(CH)_{ald}$, at 2725 cm^{-1} and carboxylate species at 1417 cm^{-1}. Above 300 ºC, a signal at 1600 cm^{-1} was evidenced that was registered as mode related to crotonaldehyde surface formation at 320 ºC. MS-signals for the products, except ethanol, were very low and non-detected until 250 ºC where the fraction of butanol and crotyl alcohol increased until 320 ºC, likewise diethyl ether formation from direct ethanol dehydration and secondary butadiene formation also increased.

Concerning to the spectra registered for $Ca_{20}Fe_{20}$MgAl-Ox catalyst (Fig. 5.b), as can be observed, others additional and superimposed signals were also evidenced at the same temperature range. A change related to ethoxy species ratio on surface was detected when the reaction temperature increased. It was noticeable that dissociative adsorbed ethanol species as monodentate and bidentate were more evident than the observed in MgAl-Ox, they are also stable up to 300ºC. The band associated with molecular gas-phase ethanol (1055 cm^{-1}) decreased while temperature was increasing, whereas a weak band at 1115 cm^{-1} assigned to C-C-O stretch-mode from ethoxy-species, coming from deprotonated ethanol species, could act as surface stable intermediate species up to 320ºC, by interacting with cationic-Mg center as coordinated species as was also reported using MgO under Guerbet reaction conditions [65,66]. A weak signal close to 2725 cm^{-1} appeared at 200 ºC and increased until 320 ºC, characteristic of the $\upsilon(CH)$ of aldehydic species [43,67]. Associated with this band, signals at 1780 and 1345 cm^{-1} also appeared linked to C=O aldehyde stretching modes [68] and C4-aldehyde $\delta(CH)$ modes of aldehydes species on the surface during the reaction pathway [69]. Carboxylate surface spectator-species can also be observed, which related to the well-defined bands registered at 1580 and 1417 cm^{-1} between the 220 and 250 ºC, respectively [43,70,71]. Above 250 ºC, the signal centered at 1624 cm^{-1} that is characteristic of the C=O of acetyl or acyl species vibrational mode [72] suddenly disappeared. However, at 300 ºC a signal shifted at 1600 cm^{-1} appeared [73] that it must be associated with crotonaldehyde, as adsorbed surface reaction intermediate, whose maximum intensity was detected at 320 ºC. In the lower wavenumber region, the evolution of the band centered at 940 cm^{-1} linked to CH_3 rocking and C-H bending vibration modes, as reported by Quesada et al. [68], is related to the formation of surface alkoxides or derived methoxy-species of different

intermediates involved in the reaction pathway. The evolution of the species detected indicated that this $Ca_{20}Fe_{20}$MgAl-Ox catalyst promoted the aldehyde formation and their surface population because of the higher distribution and stability of ethoxy species formed, together with the high reactivity due to higher basicity that improves the proper interaction aldehyde surface species. Probably, monodentate and bidentate ethoxy adsorption species ratio balances the performance due to consecutive reactions of the aldehyde/acetate species to form undesirable products. Parallelly, the interaction aldehyde-derived species with the ethanol together with ethanol retention capacity justify both routes for the relative distribution of formed products. On the right side of the figure, from 250 ºC to the highest tested temperature of 320 ºC, it was possible to observe the increase in the fraction of butanol and crotonaldehyde, even butadiene, as the main products formed from ethanol conversion reaction. These facts indicated that the balance of monodentate and bidentate ethoxide groups anchored on basic-acid sites together with the species that act as spectators were responsible for the formed intermediary or side products, favoring the butanol selectivity between 250 ºC to 320 ºC and decreasing the presence of crotyl alcohol, butadiene and crotonaldehyde. In fact, there was practically an inhibition of all secondary products such as diethyl ether (DEE) mainly hindered by lower-residual Lewis acidity exhibited by this modified oxide catalyst respect to the Mg-Al oxide reference catalyst used. So, the preferential formation of monodentate/bidentate ethoxy species and adsorbed EtOH are identified as the key factors for n-butanol production from ethanol.

3.2.3. Catalytic test under ethanol transitory response method

Transitory response experiments were performed under ethanol pulse admission and isothermally, at 280 and 400 ºC, and the results are presented in Figure 6. Rectangular pulse of ethanol (dark blue) of 10,000 ppm were fed into fix-bed reactor once the catalyst was pretreated and stabilized at the reaction temperature. The signal evolution corresponding to the ethanol pulse (left-axis) without catalyst (using quartz as inert) is included with a dotted grey line as a blank. In Figure 6, the mass intensity of each product (right-axis) was shown for the tests performed for $Ca_{20}Fe_{20}$MgAl-Ox catalyst and MgAl-Ox reference catalyst and the legend color code are maintained as in Figure 5.

At 280 ºC, which is considered in the low temperature range (Fig. 6.a), MgAl-Ox catalyst showed that the predominant and simultaneously produced species were diethyl ether and crotyl alcohol. After 100 min of reaction, DEE signal decreased up to a constant value, while crotyl alcohol formation, as the major product, was stabilized with the reaction time up to end of pulse. Both butanol and butadiene (at a magnitude order lower) were also detected maintaining the trend practically without modification. It can be noted that at low temperature (280ºC) the Mg-Al oxide reference catalyst presented a faster saturation, and the ethanol conversion has been calculated by integration of saturation curve registering a value of 20 %.

The product distribution obtained at 400 ºC over MgAl-Ox catalyst is shown in the Figure 6.c. Initially, the main detected products were crotyl alcohol and DEE. Once more, the crotyl alcohol fraction was higher than diethyl ether and it presented a maximum signal during the first third of the pulse decreasing until its stabilization at almost the end of the pulse. Crotyl alcohol formation compared with the signal at 280ºC was much higher than diethyl ether production. Butadiene formation presented an opposite trend to the crotyl alcohol disappearance probably for being in balance both species. At this temperature there was also the initial formation of n-butanol being higher than that registered at the temperature of 280ºC. From the numerical integration considering the difference between the ethanol rectangular pulse and the less-fast saturation curve, it was observed how an increase in temperature caused a considerable increase of ethanol conversion being for MgAl-Ox a 58%; i.e., an increase of 62 % conversion respect to 280 °C.

The product profile distribution for $Ca_{20}Fe_{20}$MgAl-Ox at 280 ºC (Fig. 6.b) points butanol and crotyl alcohol as the first products observed occurring simultaneously. As ethanol conversion increased during the pulse extension, with a fast saturation curve, it was detected that the amount of butanol initially formed as mayor component, decreased progressively, although the crotyl alcohol contribution was similar in the first part of cycle. However, an increase of crotyl alcohol was noticed, with a simultaneous decrease in butanol; probably because they are associated and linked by internal hydrogenation processes. Butadiene fraction was maintained constant although its intensity was very low and the trend was similar to that registered for crotyl alcohol. Both butanal and DEE signals were not perturbed showing an extremely low contribution practically negligible. Taking the rectangular ethanol pulse in the non-catalytic test as a reference, since it was observed that none of the analyzed compounds were perturbed with time, the steady-state

ethanol conversion calculated by integration of saturation curve. At low temperature (280ºC) a faster saturation reaching an ethanol conversion value of 36 %. This conversion value was slightly higher from those reported by O.V. Larina et al. for an optimized hydrotalcite Mg-Al-Ce [74] and a n-butanol selectivity of 68 % in a fixed bed flow reactor at atmospheric pressure and 300 ºC with GHSV of 79.4 h^{-1}. For a Cu-modified Mg-Al derived hydrotalcite, in a batch reactor system, P. Benito et al. [75] found a 29.8% of ethanol conversion at 215ºC.

At 400ºC, for $Ca_{20}Fe_{20}$MgAl-Ox catalyst, the performance on the ethanol conversion (Fig. 6.d) leads to butanol as well crotyl alcohol, this last as the major product detected. At this temperature, butanol formation was remarkable with respect to crotyl alcohol during the first part of the pulse, whereas during the last part of the cycle (after 60 minutes of reaction) a evident formation of crotyl alcohol was detected; suggesting an additional and sequential *via* for the n-butanol formation. DEE formation was hindered and butadiene formation, with a low but constant evolution, was also observed by ulterior dehydration. Both crotonaldehyde and butanal showed the same practically negligible trend as that observed at lower temperature tested (280 ºC). It is interesting to note the slow ethanol saturation curve registered at the higher temperature tested, being much more noticeable for $Ca_{20}Fe_{20}$MgAl-Ox catalyst. From the numerical curve integration respect the non-catalytic contribution pulse it was observed how the increase in temperature caused a considerable increase in the overall ethanol conversion reaching 71 %. As can be seen, an increase in temperature favors the conversion of ethylene, as observed by M. León et al. [30], in turn, these authors indicate a conversion higher than 80% for Mg–Al mixed oxides derived from hydrotalcites above 400 ºC with WHSV of 0.215 h^{-1}. Besides, at higher temperature range, Carvalho et al. [43] reported nearly 40 % conversion of ethanol at 350 ºC using a MgAl (1:1) mixed oxide while using a mixture of $MgO+Al_2O_3$ in a fixed bed reactor at atmospheric pressure under 12 % ethanol/N_2 at 40 $mL \cdot min^{-1}$, they achieved approximately 90 % ethanol conversion with a partially total selectivity to ethylene. Cimino et al. [41] reported a negligible activity of hydroxyapatite (HAP) up to 300 ºC whereas between 300 and 400 ºC a complete ethanol conversion was observed, likewise, γ-Al_2O_3 provided around 80 % conversion of ethanol up to 500 ºC producing DEE/Ethylene associated to traces of aldehydes under fixed bed reactor feeding 3 %v/v ethanol in N_2.

From the numerical integration of the curve for each of the components detected in the experiments, some selectivity data were obtained. At low temperature (280 ºC), it was remarkable the increase of DEE-production of 78.25 % as undesired product for the case of MgAl-Ox compared to $Ca_{20}Fe_{20}$MgAl-Ox being this increase associated with the presence of the high acidity of the system. Both materials were selective to crotyl alcohol presenting a difference of 7.6 % in total production levels during the whole reaction time. Regarding butanol production, a notable increase of 45.30 % was observed due to the partial substitution of the metals in the catalytic system. These values remained similar comparing both materials in high temperature range except for crotyl alcohol, which presented a decrease in the overall production of 35.10 % for $Ca_{20}Fe_{20}$MgAl-Ox. An increase in temperature showed that for the non-modified system, all the generated compounds had a higher production, especially crotyl alcohol (32 %) and DEE (25 %). However, for the modified system, there was only a 44 % increase in the production of DEE with increasing temperatures and a slight increase in both butanol and crotyl alcohol, whereas their production profiles were different.

From the acidity-basicity study, it was observed that the modified catalyst by Fe^{3+} and Ca^{2+}, presented a slight reduction of acidity, although the strength and stability of the Lewis acid centers were maintained and led an increased population of Brønsted-type basic sites as well as the basicity. This net increase in basicity and slight decrease in acidity seems to be a proper relation among acid-basic sites that substantially improved the catalytic activity for this process by decreasing the temperature for n-butanol production through two different routes.

It was found that reference catalyst, MgAl-Ox respect to $Ca_{20}Fe_{20}$MgAl-Ox, is more selective to DEE production via direct ethanol dehydration over acid sites (Lewis Acid Sites, LAS) for the whole temperature range. The less-desired DEE formation mainly occurs at lower reaction temperatures due to its exothermic character [32], so its production decreases almost a 20% at 400 ºC. For $Ca_{20}Fe_{20}$MgAl-Ox catalyst the residual acidity as Lewis acidic sites of high temperature and different strength, yield a negligible formation of DEE by dehydration as pathway of ethanol consumption would be considered further inhibited.

According to the DRIFT spectra and ethanol flow experiments, it was confirmed the bifunctional nature is strongly affected by the nature multioxide matrix the catalyst favoring acetaldehyde kinetic production by the interaction between ethanol and the catalyst basic-centers [33] progressing by its self-condensation to generate crotyl alcohol

and butanol and cross-condensation, with a lesser extension, to form crotonaldehyde as is represented in the mechanistic scheme of Figure 7. In the Figure, blue line indicates the major reaction pathway, meanwhile red line indicates inhibited or minor reaction. The results of EtOH-adsorption runs have shown that there was a larger population of ethoxide species retained on the surface in the form of monodentate and bidentate ethoxides, which would favor an alternative route of dissociative adsorption of ethanol to form monoethoxide groups promoted mainly by the basic sites for subsequent dissociation into acetaldehyde. At this point, acetaldehyde is considered a reaction intermediate for the production of n-butanol as widely reported in literature [27,29,32,76]. The high population and strength of basic sites preferentially Ca-O-Ca, Ca-O-Mg, and Ca-O-Mg-Al(Fe^{3+}) were the responsible for an effective non-oxidative dehydrogenation and decomposition of the ethoxide species.

For modified catalyst ($Ca_{20}Fe_{20}$MgAl-Ox), DEE (diethyl-ether) production, by direct ethanol dehydration, was partially inhibited, and the preferential route would be the formation of crotyl alcohol via acetaldehyde self-condensation and n-butanol by the sequential occurrence of transfer hydrogenation reaction, on Lewis acid-base pair sites being ethanol the hydrogen source (donor) for hydrogenation reaction. The dominant species depend on the surface density of ethanol (donor) and acceptor molecules and temperature (and probably of the kinetic) that determine the stability of the species involved in the equilibrium. The presence of crotonaldehyde, although much less significant for this catalyst, indicated a parallel pathway that involved ethanol and acetaldehyde cross-condensation and a subsequent hydrogenation to butanol with the formation of a water molecule, as Scalbert et al. [27] reported. This justified the non-presence of butanal as a side product as stated in the literature [27,37,77] since butanal would be more likely to be formed from the hydrogenation of butanol over basic oxides sites. Hydrogen transfer equilibrium between these products was evidenced, since crotylalcohol could be also derived from the produced crotonaldehyde. So, there is a hydrogenation-dehydrogenation balance through catalytic transfer on these C_4-species and where ethanol acts as the hydrogen donor and the hydrogenation occurs (hydride transfer and hydrogenolysis of alcohol) involving Lewis pair-sites by Meerwein-Ponndorf-Verley-Oppenhauer (MPVO) reduction reaction mechanism with ethanol as the reductant agent as previously reported [32].

The partial modification of hydrotalcite-Mg-Al derived mixed oxides by Fe^{3+} and Ca^{2+}, respectively, provided a tunned acid-basic balanced property for an enhanced catalyst for

ethanol condensation process. Reactions that primordially involve acetaldehyde self-condensation linked to the sequential fast transfer hydrogenation produce a most selective to butanol reaction to make the ethanol condensation process feasible and sustainable in the near term, working toward its use as an additive in Biodiesel-Petrodiesel-Oxygenated ternary blends due to its physical and chemical properties at energy level and its feasibility in utilization in light diesel engine vehicles to reduce fuel consumption and pollutant emissions.

4. Conclusions

An attempt catalytic upgrading for butanol production intensification process form ethanol was approached developing a novel Ca-Fe partially modified mixed oxide Mg-Al hydrotalcite-base precursor catalyst. This novel bifunctional catalyst it based on multi-oxide catalyst-design and addressed for an improved catalytic performance and has been verified that it depends largely on the ethanol adsorption capacity to form ethoxides species population and a combined basicity with a tunned hydrogen transfer centers capacity. This $Ca_{20}Fe_{20}MgAl$ catalyst exhibited a competitive activity and selectivity, upgrading the ethanol conversion to n-butanol compared to other Mg-Al oxides because the combination of the preferential routes as the direct acetaldehyde self-condensation and a higher-temperature via that involves crotyl alcohol formation combined with transfer-hydrogenation on Lewis sites, acting ethanol as donor.

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References

[1] E. Voegele, OECD-FAO outlook report predicts growth in ethanol productionNo Title, Ethanol Prod. Mag. (n.d.). http://ethanolproducer.com/articles/11264/oecd-fao-outlook-report-predicts-growth-in-ethanol-production.

[2] A. Galadima, O. Muraza, Zeolite catalysts in upgrading of bioethanol to fuels range hydrocarbons: A review, J. Ind. Eng. Chem. 31 (2015) 1–14. https://doi.org/10.1016/j.jiec.2015.07.015.

[3] W. Michaels, H. Zhang, W.L. Luyben, J. Baltrusaitis, Design of a separation section in an ethanol-to-butanol process, Biomass and Bioenergy. 109 (2018) 231–238. https://doi.org/10.1016/j.biombioe.2017.12.031.

[4] S.M.A.H. Siddiki, A.S. Touchy, Challenges and future prospects in heterogeneous catalysis for biorefinery technologies, in: Adv. Funct. Solid Catal. Biomass Valorization, Elsevier, 2020: pp. 225–250. https://doi.org/10.1016/b978-0-12-820236-4.00010-6.

[5] Q. Zhang, W. Liu, B. Chen, S. Qiu, T. Wang, Upgrading of aqueous ethanol to fuel grade higher alcohols over dandelion-like Ni-Sn catalyst, Energy Convers. Manag. 216 (2020) 112914. https://doi.org/10.1016/j.enconman.2020.112914.

[6] B. Rajesh Kumar, S. Saravanan, Use of higher alcohol biofuels in diesel engines: A review, Renew. Sustain. Energy Rev. 60 (2016) 84–115. https://doi.org/10.1016/j.rser.2016.01.085.

[7] M. Lapuerta, J. Rodríguez-Fernández, D. Fernández-Rodríguez, R. Patiño-Camino, Cold flow and filterability properties of n-butanol and ethanol blends with diesel and biodiesel fuels, Fuel. 224 (2018) 552–559. https://doi.org/10.1016/j.fuel.2018.03.083.

[8] M.K. Yesilyurt, M. Aydin, Experimental investigation on the performance, combustion and exhaust emission characteristics of a compression-ignition engine fueled with cottonseed oil biodiesel/diethyl ether/diesel fuel blends, Energy Convers. Manag. 205 (2020) 112355. https://doi.org/10.1016/j.enconman.2019.112355.

[9] M.K. Yesilyurt, A detailed investigation on the performance, combustion, and exhaust emission characteristics of a diesel engine running on the blend of diesel fuel, biodiesel and 1-heptanol (C7 alcohol) as a next-generation higher alcohol, Fuel. 275 (2020) 117893. https://doi.org/10.1016/j.fuel.2020.117893.

[10] S. Wang, Y. Liang, J. Zhu, M. Raza, J. Li, L. Yu, Y. Qian, X. Lu, Experimental and modeling study of the autoignition for diesel and n-alcohol blends from ethanol to n-pentanol in shock tube and rapid compression machine, Combust. Flame. 227 (2021) 296–308. https://doi.org/10.1016/j.combustflame.2021.01.019.

[11] Q. Ma, Q. Zhang, Z. Zheng, An experimental assessment on low temperature combustion using diesel/biodiesel/C2, C5 alcohol blends in a diesel engine, Fuel. 288 (2021) 119832. https://doi.org/10.1016/j.fuel.2020.119832.

[12] P. Dürre, Biobutanol: An attractive biofuel, Biotechnol. J. 2 (2007) 1525–1534.

https://doi.org/10.1002/biot.200700168.

[13] X. Zhen, Y. Wang, D. Liu, Bio-butanol as a new generation of clean alternative fuel for SI (spark ignition) and CI (compression ignition) engines, Renew. Energy. 147 (2020) 2494–2521. https://doi.org/10.1016/j.renene.2019.10.119.

[14] W.R. da S. Trindade, R.G. dos Santos, Review on the characteristics of butanol, its production and use as fuel in internal combustion engines, Renew. Sustain. Energy Rev. 69 (2017) 642–651. https://doi.org/10.1016/j.rser.2016.11.213.

[15] M. Kadir, T. Eryilmaz, M. Arslan, A comparative analysis of the engine performance , exhaust emissions and combustion behaviors of a compression ignition engine fuelled with biodiesel / diesel / 1-butanol (C4 alcohol) and biodiesel / diesel / n- pentanol (C5 alcohol) fuel blends, Energy. 165 (2018) 1332–1351. https://doi.org/10.1016/j.energy.2018.10.100.

[16] J.L.S. Fagundez, D. Golke, M.E.S. Martins, N.P.G. Salau, An investigation on performance and combustion characteristics of pure n-butanol and a blend of n-butanol/ethanol as fuels in a spark ignition engine, Energy. 176 (2019) 521–530. https://doi.org/10.1016/j.energy.2019.04.010.

[17] K. Hwan, B. Choi, S. Park, E. Kim, D. Chiaramonti, Emission characteristics of compression ignition (CI) engine using diesel blended with hydrated butanol, Fuel. 257 (2019) 116037. https://doi.org/10.1016/j.fuel.2019.116037.

[18] S. Li, J. Liu, F. Wang, J. Wang, M. Wei, S. Yang, Experimental study on combustion and emission characteristics of a diesel engine fueled with diesel-gasoline-iso-butanol blends, Fuel. 255 (2019) 115761. https://doi.org/10.1016/j.fuel.2019.115761.

[19] X. Zhou, W. Qian, M. Pan, R. Huang, L. Xu, J. Yin, Potential of n-butanol / diesel blends for CI engines under post injection strategy and di ff erent EGR rates conditions, Energy Convers. Manag. 204 (2020) 112329. https://doi.org/10.1016/j.enconman.2019.112329.

[20] H.E. Saleh, Performance and emissions characteristics of direct injection diesel engine fueled by diesel-jojoba oil-butanol blends with hydrogen peroxide, Fuel. 285 (2021) 119048. https://doi.org/10.1016/j.fuel.2020.119048.

[21] A. Atmanli, B. Yüksel, E. Ileri, Experimental investigation of the effect of diesel-cotton oil-n-butanol ternary blends on phase stability, engine performance and exhaust emission parameters in a diesel engine, Fuel. 109 (2013) 503–511. https://doi.org/10.1016/j.fuel.2013.03.012.

[22] K. Thakkar, S. Singh, P. Kodgire, Combustion investigation of ternary blend mixture of biodiesel / n-butanol / diesel : CI engine performance and emission control, Renew. Sustain. Energy Rev. 137 (2021) 110468. https://doi.org/10.1016/j.rser.2020.110468.

[23] M. Uyttebroek, W. Van Hecke, K. Vanbroekhoven, Sustainability metrics of 1-butanol, Catal. Today. 239 (2015) 7–10. https://doi.org/10.1016/j.cattod.2013.10.094.

[24] B. Ndaba, I. Chiyanzu, S. Marx, n-Butanol derived from biochemical and chemical routes: A review, Biotechnol. Reports. 8 (2015) 1–9.

https://doi.org/10.1016/j.btre.2015.08.001.

[25] A. Galadima, O. Muraza, Catalytic Upgrading of Bioethanol to Fuel Grade Biobutanol: A Review, Ind. Eng. Chem. Res. 54 (2015) 7181–7194. https://doi.org/10.1021/acs.iecr.5b01443.

[26] J.T. Kozlowski, R.J. Davis, Heterogeneous Catalysts for the Guerbet Coupling of Alcohols, ACS Catal. 3 (2013) 1588–1600. https://doi.org/10.1021/cs400292f.

[27] J. Scalbert, F. Thibault-Starzyk, R. Jacquot, D. Morvan, F. Meunier, Ethanol condensation to butanol at high temperatures over a basic heterogeneous catalyst: How relevant is acetaldehyde self-aldolization?, J. Catal. 311 (2014) 28–32. https://doi.org/10.1016/j.jcat.2013.11.004.

[28] V.N. Panchenko, E.A. Paukshtis, D.Y. Murzin, I.L. Simakova, Solid Base Assisted n - Pentanol Coupling over VIII Group Metals : Elucidation of the Guerbet Reaction Mechanism by DRIFTS, (2017) 13310–13321. https://doi.org/10.1021/acs.iecr.7b01853.

[29] J.I. Di Cosimo, C.R. Apesteguı&́a, M.J.L. Ginés, E. Iglesia, Structural Requirements and Reaction Pathways in Condensation Reactions of Alcohols on MgyAlOx Catalysts, J. Catal. 190 (2000) 261–275. https://doi.org/10.1006/jcat.1999.2734.

[30] M. León, E. Díaz, S. Ordóñez, Ethanol catalytic condensation over Mg–Al mixed oxides derived from hydrotalcites, Catal. Today. 164 (2011) 436–442. https://doi.org/10.1016/j.cattod.2010.10.003.

[31] J. Quesada, L. Faba, E. Díaz, S. Ordóñez, Tuning the selectivities of Mg-Al mixed oxides for ethanol upgrading reactions through the presence of transition metals, Appl. Catal. A Gen. 559 (2018) 167–174. https://doi.org/10.1016/j.apcata.2018.04.022.

[32] M. Pinzón, M. Cortés-Reyes, C. Herrera, M.Á. Larrubia, L.J. Alemany, Ca-based bifunctional acid-basic model-catalysts for n -butanol production from ethanol condensation, Biofuels, Bioprod. Biorefining. (2020) bbb.2155. https://doi.org/10.1002/bbb.2155.

[33] S. Hanspal, Z.D. Young, J.T. Prillaman, R.J. Davis, Influence of surface acid and base sites on the Guerbet coupling of ethanol to butanol over metal phosphate catalysts, J. Catal. 352 (2017) 182–190. https://doi.org/10.1016/j.jcat.2017.04.036.

[34] T. Tsuchida, S. Sakuma, T. Takeguchi, W. Ueda, Direct Synthesis of n -Butanol from Ethanol over Nonstoichiometric Hydroxyapatite, (2006) 8634–8642. https://doi.org/10.1021/ie0606082.

[35] A. Galadima, O. Muraza, Zeolite catalysts in upgrading of bioethanol to fuels range hydrocarbons: A review, J. Ind. Eng. Chem. 31 (2015) 1–14. https://doi.org/10.1016/j.jiec.2015.07.015.

[36] A. Chieregato, J. Velasquez Ochoa, C. Bandinelli, G. Fornasari, F. Cavani, M. Mella, On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions, ChemSusChem. 8 (2015) 377–388. https://doi.org/10.1002/cssc.201402632.

[37] A. Ndou, Dimerisation of ethanol to butanol over solid-base catalysts, Appl. Catal.

A Gen. 251 (2003) 337–345. https://doi.org/10.1016/S0926-860X(03)00363-6.

[38] P. Dziugan, K.G. Jastrzabek, M. Binczarski, S. Karski, I.A. Witonska, B. Kolesinska, Z.J. Kaminski, Continuous catalytic coupling of raw bioethanol into butanol and higher homologues, Fuel. 158 (2015) 81–90. https://doi.org/10.1016/j.fuel.2015.05.015.

[39] C. Lopez-Olmos, A. Guerrero-Ruiz, I. Rodríguez-Ramos, Optimization of Cu-Ni-Mn-catalysts for the conversion of ethanol to butanol, Catal. Today. (2019). https://doi.org/10.1016/j.cattod.2019.05.058.

[40] O.M. Perrone, F. Lobefaro, M. Aresta, F. Nocito, M. Boscolo, A. Dibenedetto, Butanol synthesis from ethanol over CuMgAl mixed oxides modified with palladium (II) and indium (III), Fuel Process. Technol. 177 (2018) 353–357. https://doi.org/10.1016/j.fuproc.2018.05.006.

[41] S. Cimino, L. Lisi, S. Romanucci, Catalysts for conversion of ethanol to butanol: Effect of acid-base and redox properties, Catal. Today. 304 (2018) 58–63. https://doi.org/10.1016/j.cattod.2017.08.035.

[42] O. V. Larina, K. V. Valihura, P.I. Kyriienko, N. V. Vlasenko, D.Y. Balakin, I. Khalakhan, T. Čendak, S.O. Soloviev, S.M. Orlyk, Successive vapour phase Guerbet condensation of ethanol and 1-butanol over Mg-Al oxide catalysts in a flow reactor, Appl. Catal. A Gen. 588 (2019) 117265. https://doi.org/10.1016/j.apcata.2019.117265.

[43] D.L. Carvalho, L.E.P. Borges, L.G. Appel, P. Ramírez de la Piscina, N. Homs, In situ infrared spectroscopic study of the reaction pathway of the direct synthesis of n-butanol from ethanol over MgAl mixed-oxide catalysts, Catal. Today. 213 (2013) 115–121. https://doi.org/10.1016/j.cattod.2013.03.034.

[44] J. Quesada, L. Faba, E. Díaz, S. Ordóñez, Enhancement of the 1-butanol productivity in the ethanol condensation catalyzed by noble metal nanoparticles supported on Mg-Al mixed oxide, Appl. Catal. A Gen. 563 (2018) 64–72. https://doi.org/10.1016/j.apcata.2018.06.037.

[45] M. León, E. Díaz, A. Vega, S. Ordóñez, A. Auroux, Consequences of the iron–aluminium exchange on the performance of hydrotalcite-derived mixed oxides for ethanol condensation, Appl. Catal. B Environ. 102 (2011) 590–599. https://doi.org/10.1016/j.apcatb.2010.12.044.

[46] M. Rechi Siqueira, O. Micali Perrone, G. Metzker, D.C. de Oliveira Lisboa, J.C. Thoméo, M. Boscolo, Highly selective 1-butanol obtained from ethanol catalyzed by mixed metal oxides: Reaction optimization and catalyst structure behavior, Mol. Catal. 476 (2019) 110516. https://doi.org/10.1016/j.mcat.2019.110516.

[47] R.I. Walton, Layered Double Hydroxides: Present and Future., Clay Miner. 38 (2003). https://doi.org/10.1180/0380139.

[48] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-Type Anionic Clays: Preparation, Properties and Applications, Catal. Today. 11 (1991) 173–301. https://doi.org/10.1016/0920-5861(91)80068-K.

[49] P. Sangkhum, J. Yanamphorn, A. Wangriya, C. Ngamcharussrivichai, Ca–Mg–Al ternary mixed oxides derived from layered double hydroxide for selective

etherification of glycerol to short-chain polyglycerols, Appl. Clay Sci. 173 (2019) 79–87. https://doi.org/10.1016/j.clay.2019.03.006.

[50] K.S. Triantafyllidis, E.N. Peleka, V.G. Komvokis, P.P. Mavros, Iron-modified hydrotalcite-like materials as highly efficient phosphate sorbents, J. Colloid Interface Sci. 342 (2010) 427–436. https://doi.org/10.1016/j.jcis.2009.10.063.

[51] M. Mokhtar, A. Inayat, J. Ofili, W. Schwieger, Thermal decomposition, gas phase hydration and liquid phase reconstruction in the system Mg/Al hydrotalcite/mixed oxide: A comparative study, Appl. Clay Sci. 50 (2010) 176–181. https://doi.org/10.1016/j.clay.2010.07.019.

[52] A. Navajas, I. Campo, A. Moral, J. Echave, O. Sanz, M. Montes, J.A. Odriozola, G. Arzamendi, L.M. Gandía, Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel, Fuel. 211 (2018) 173–181. https://doi.org/10.1016/j.fuel.2017.09.061.

[53] O.P. Ferreira, S.G. de Moraes, N. Durán, L. Cornejo, O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, Chemosphere. 62 (2006) 80–88. https://doi.org/10.1016/j.chemosphere.2005.04.009.

[54] L. Xiao, W. Ma, M. Han, Z. Cheng, The influence of ferric iron in calcined nano-Mg/Al hydrotalcite on adsorption of Cr (VI) from aqueous solution, J. Hazard. Mater. 186 (2011) 690–698. https://doi.org/10.1016/j.jhazmat.2010.11.052.

[55] X. Kou, C. Li, Y. Zhao, S. Wang, X. Ma, CO2 sorbents derived from capsule-connected Ca-Al hydrotalcite-like via low-saturated coprecipitation, Fuel Process. Technol. 177 (2018) 210–218. https://doi.org/10.1016/j.fuproc.2018.04.036.

[56] I.-C. Marcu, N. Tanchoux, F. Fajula, D. Tichit, Catalytic Conversion of Ethanol into Butanol over M–Mg–Al Mixed Oxide Catalysts (M = Pd, Ag, Mn, Fe, Cu, Sm, Yb) Obtained from LDH Precursors, Catal. Letters. 143 (2013) 23–30. https://doi.org/10.1007/s10562-012-0935-9.

[57] J.C. Lavalley, Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules, Catal. Today. 27 (1996) 377–401. https://doi.org/10.1016/0920-5861(95)00161-1.

[58] P. Kuśtrowski, L. Chmielarz, E. Bozek, M. Sawalha, F. Roessner, Acidity and basicity of hydrotalcite derived mixed Mg-Al oxides studied by test reaction of MBOH conversion and temperature programmed desorption of NH3 and CO2, Mater. Res. Bull. 39 (2004) 263–281. https://doi.org/10.1016/j.materresbull.2003.09.032.

[59] J. Shen, M. Tu, C. Hu, Structural and Surface Acid / Base Properties of Hydrotalcite-Derived MgAlO Oxides Calcined at Varying Temperatures, 301 (2000) 295–301.

[60] F. Giraud, C. Geantet, N. Guilhaume, S. Loridant, S. Gros, L. Porcheron, M. Kanniche, D. Bianchi, Individual amounts of Lewis and Brønsted acid sites on metal oxides from NH3 adsorption equilibrium: Case of TiO2 based solids, Catal. Today. (2020). https://doi.org/10.1016/j.cattod.2020.08.015.

[61] V. Crocellà, G. Cerrato, G. Magnacca, C. Morterra, F. Cavani, S. Cocchi, S. Passeri, D. Scagliarini, C. Flego, C. Perego, The balance of acid , basic and redox

sites in Mg / Me-mixed oxides : The effect on catalytic performance in the gas-phase alkylation of m -cresol with methanol, J. Catal. 270 (2010) 125–135. https://doi.org/10.1016/j.jcat.2009.12.011.

[62] G. Busca, Infrared studies of the reactive adsorption of organic molecules over metal oxides and of the mechanisms of their heterogeneously-catalyzed oxidation, Catal. Today. 27 (1996) 457–496. https://doi.org/10.1016/0920-5861(95)00162-X.

[63] M. Dömök, M. Tóth, J. Raskó, A. Erdohelyi, Adsorption and reactions of ethanol and ethanol-water mixture on alumina-supported Pt catalysts, Appl. Catal. B Environ. 69 (2007) 262–272. https://doi.org/10.1016/j.apcatb.2006.06.001.

[64] H. Nair, J.E. Gatt, J.T. Miller, C.D. Baertsch, Mechanistic insights into the formation of acetaldehyde and diethyl ether from ethanol over supported VOx, MoOx, and WOx catalysts, J. Catal. 279 (2011) 144–154. https://doi.org/10.1016/j.jcat.2011.01.011.

[65] T.W. Birky, J.T. Kozlowski, R.J. Davis, Isotopic transient analysis of the ethanol coupling reaction over magnesia, J. Catal. 298 (2013) 130–137. https://doi.org/10.1016/j.jcat.2012.11.014.

[66] M.M. Branda, A.H. Rodríguez, P.G. Belelli, N.J. Castellani, Ethanol adsorption on MgO surface with and without defects from a theoretical point of view, Surf. Sci. 603 (2009) 1093–1098. https://doi.org/10.1016/j.susc.2009.02.021.

[67] M. Singh, N. Zhou, D.K. Paul, K.J. Klabunde, IR spectral evidence of aldol condensation : Acetaldehyde adsorption over TiO 2 surface, J. Catal. 260 (2008) 371–379. https://doi.org/10.1016/j.apcatb.2011.06.026.

[68] J. Quesada, L. Faba, E. Díaz, S. Ordóñez, Role of the surface intermediates in the stability of basic mixed oxides as catalyst for ethanol condensation, Appl. Catal. A Gen. 542 (2017) 271–281. https://doi.org/10.1016/j.apcata.2017.06.001.

[69] B. Hauchecorne, D. Terrens, S. Verbruggen, J.A. Martens, H. Van Langenhove, K. Demeestere, S. Lenaerts, Elucidating the photocatalytic degradation pathway of acetaldehyde: An FTIR in situ study under atmospheric conditions, Appl. Catal. B Environ. 106 (2011) 630–638. https://doi.org/10.1016/j.apcatb.2011.06.026.

[70] A. Yee, S.J. Morrison, H. Idriss, A Study of the Reactions of Ethanol on CeO2 and Pd/CeO2 by Steady State Reactions, Temperature Programmed Desorption, and In Situ FT-IR, J. Catal. 186 (1999) 279–295. https://doi.org/10.1006/jcat.1999.2563.

[71] J. Araña, J.M. Doña-Rodríguez, C.G.I. Cabo, O. González-Díaz, J.A. Herrera-Melián, J. Pérez-Peña, FTIR study of gas-phase alcohols photocatalytic degradation with TiO 2 and AC-TiO2, Appl. Catal. B Environ. 53 (2004) 221–232. https://doi.org/10.1016/j.apcatb.2004.04.024.

[72] J. Raskó, A. Hancz, A. Erdőhelyi, Surface species and gas phase products in steam reforming of ethanol on TiO2 and Rh/TiO2, Appl. Catal. A Gen. 269 (2004) 13–25. https://doi.org/10.1016/j.apcata.2004.03.053.

[73] Z.D. Young, S. Hanspal, R.J. Davis, Aldol Condensation of Acetaldehyde over Titania, Hydroxyapatite, and Magnesia, ACS Catal. 6 (2016) 3193–3202. https://doi.org/10.1021/acscatal.6b00264.

[74] O. V. Larina, K. V. Valihura, P.I. Kyriienko, N. V. Vlasenko, D.Y. Balakin, I. Khalakhan, K. Veltruská, T. Čendak, S.O. Soloviev, S.M. Orlyk, Catalytic performance of ternary Mg-Al-Ce oxides for ethanol conversion into 1-butanol in a flow reactor, J. Fuel Chem. Technol. 49 (2021) 347–358. https://doi.org/10.1016/S1872-5813(21)60028-2.

[75] P. Benito, A. Vaccari, C. Antonetti, D. Licursi, N. Schiarioli, E. Rodriguez-Castellón, A.M. Raspolli Galletti, Tunable copper-hydrotalcite derived mixed oxides for sustainable ethanol condensation to n-butanol in liquid phase, J. Clean. Prod. 209 (2019) 1614–1623. https://doi.org/10.1016/j.jclepro.2018.11.150.

[76] F. Papers, Importance of the Nature of the Active Acid / Base Pairs of Hydroxyapatite Involved in the Catalytic Transformation of Ethanol to n -Butanol Revealed by Operando DRIFTS, (2019) 1–15. https://doi.org/10.1002/cctc.201801880.

[77] C. Yang, Z.Y. Meng, Bimolecular Condensation of Ethanol to 1-Butanol Catalyzed by Alkali Cation Zeolites, J. Catal. 142 (1993) 37–44. https://doi.org/10.1006/jcat.1993.1187.

List of Tables

Table 1. Lattice parameters and morphological data of LDHs and oxide derived catalysts.

Sample	a (Å)	c (Å)	Crystal (Å)	A_{BET} ($m^2 \cdot g^{-1}$)	V_P ($cm^3 \cdot g^{-1}$)	D_P (Å)
MgAl-LDH	3.067	23.313	307.7	66	0.19	110
$Ca_{20}Fe_{20}$MgAl-LDH	3.062	23.106	221.8	49	0.11	91
MgAl-Ox	-	-	-	81	0.31	156
$Ca_{20}Fe_{20}$MgAl-Ox	-	-	-	62	0.13	86

Table 2. Values of CO_2 and NH_3 storage capacity calculated from TPD-experiments.

Sample	CO_2-TPD		NH_3-TPD	
	CO_2-stored ($mmolCO_2 \cdot g_{cat}^{-1}$)	$\mu molCO_2^{sto} \cdot m^{-2}$	NH_3-stored ($mmolNH_3 \cdot g_{cat}^{-1}$)	$\mu molNH_3^{sto} \cdot m^{-2}$
MgAl-Ox	0.48	5.9	0.42	4.1
$Ca_{20}Fe_{20}$MgAl-Ox	3.38	54	0.20	3.2

Figure Captions

Figure 1. (a,b) HR-TEM images and EDX-mapping of (a) MgAl-LDH and (b) $Ca_{20}Fe_{20}$MgAl-LDH; (c, d) SEM images of (c) MgAl-LDH and (d) $Ca_{20}Fe_{20}$MgAl-LDH.

Figure 2. XRD patterns of (a) synthetized LDHs catalyst precursors and (b) mixed oxide catalysts.

Figure 3. (a) CO_2-Temperature Desorption profiles and (b) FTIR spectra collected of CO_2-adsorbed after evacuation at different temperatures for both oxide samples.

Figure 4. (a) NH_3-Temperature Desorption profiles and (b) FTIR spectra collected of NH_3-adsorbed after evacuation at different temperatures for both oxide samples.

Figure 5. DRIFT spectra collected and product distribution expressed as $m \cdot z^{-1}$ intensity registered for (a) MgAl-Ox and (b) $Ca_{20}Fe_{20}$MgAl-Ox catalysts, feeding 25,000 ppm of ethanol in He, increasing the temperature from 100 to 320 ºC.

Figure 6. Product distribution for 1% EtOH-He rectangular pulse in steady-state regime experiments for mixed oxides catalyst at low and high temperature: (a) MgAl-Ox and (b) $Ca_{20}Fe_{20}$MgAl-Ox at 280 ºC; (c) MgAl-Ox and (d) $Ca_{20}Fe_{20}$MgAl-Ox at 400 ºC.

Figure 7. Scheme of the reactions involved in the n-butanol formation from ethanol using $Ca_{20}Fe_{20}$MgAl-Ox.