Synthesis, characterization and catalytic properties for the ethanol transformation of La-Mg hydrotalcites

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Ethylene is considered a key feedstock for the chemical industry because it is possible to obtain a wide range of products such as ethylene oxide, ethylbenzene, 1,2-dichloroethane, polyethylene resin, ethylene glycol, among others [1]. Traditionally, ethylene has been synthesized by steam cracking, however, this process requires a high-energy cost. Therefore, it is necessary to develop an alternative process that is less expensive and friendly to the environment. In this sense, it is possible to obtain ethylene from the dehydration reaction of ethanol produced in sugar platforms for the transformation of lignocellulosic biomass from agricultural waste [2].

In this work, MgO/La_2O_3 catalysts with different Mg/La molar ratios have been prepared. All the catalysts had been calcined at 600ºC/3h with a heating ramp of 2ºC/min. The catalysts were tested in the reaction system to study their activity in the ethanol gas-phase conversion. The catalysts were characterized by XPS, XRD, TEM-EDX, CNH analysis, adsorption-desorption of N_2 at -196 ºC, NH_3-TPD and CO_2-TPD.

With the increase in the amount of La, the catalytic activity increased from an ethanol conversion of 20.4% over MgO to 84.2% on the Mg/La=1 mixed oxide (Table 1). The ethylene selectivity increased with the La amount, going from 16% over the MgO catalyst to 87% over the mixed oxide with a Mg/La=1 molar ratio. It was verified for the Mg/La=3 sample that by decreasing the temperature from 400 to 350 ºC there was a drastic decrease in the EtOH conversion, from 75.4% to 20.2%, respectively. In this case, ethylene was again the main product and its selectivity increased from 51.9% to 77.6%.

Table 1. Ethanol conversion and selectivity. Reaction conditions: 5 v/v% EtOH in N_2, P: 1 atm, T_R: 400ºC, WHSV: 0.30 $g_{EtOH}/(g_{cat} \cdot h)$.

	Conversion, Selectivity (%)								
Sample	EtOH	Acetalde-hyde	1-Butanol	Butenes	Ethylene	CO_2	Higher Alcohols	Ketones	Others
MgO	20.4	30.7	23.5	11.8	16.0	1.0	5.2	3.9	11.3
Mg/La=4	74.4	4.2	3.0	6.8	57.8	10.0	0.0	13.6	4.6
Mg/La=3	75.4	4.6	4.0	6.7	51.9	10.0	0.0	16.1	4.7
Mg/La=2	72.4	1.6	0.9	5.1	77.5	6.0	0.0	4.4	4.7
Mg/La=1	84.2	1.0	0.1	4.9	87.0	4.0	0.0	1.6	2.0
La_2O_3	28.9	5.9	0.8	-	72.8	4.0	0.0	10.6	6.2

It is important to note that, in catalysts with excess of Mg it is also observed the formation of acetaldehyde/1-butanol, by a Guerbet mechanism, which decreases when increasing the La content.

Surface analysis showed that the specific surface area is small (16-31 m^2/g) in all Mg/La samples and that the pore volume increases with Mg content. The same trend was observed when studying the basicity by CO_2-TPD: as the amount of magnesium increases, the density of basic sites increases due to MgO (weak strength), while stronger basic sites are attributed to the presence of La_2O_3.The quantification and the strength of the acid sites were analyzed by NH_3-TPD. The obtained data revealed that the amount of acid sites was negligible in comparison to the basic ones.

In the fresh samples, XPS and XRD revealed that the La_2O_3 catalyst is more prone to suffer carbonation than the rest of the catalysts. In the same way, the progressive incorporation of Mg-species diminishes the trend to carbonation. The analysis of C 1s core level spectra of the used catalysts showed the increase of the contribution ascribed to carbonate species in all cases (also seen by XRD), and a new contribution located about 286.0-286.5 eV, which was assigned to C-OH or C-O-C bonds, was also observed. This signal could be ascribed to the adsorption between the basic sites with the alcohols.

XRD analysis showed that the La_2O_3 sample displays narrower peaks, which implies higher crystallinity and lower porosity. As the amount of magnesium species increases, diffraction peaks of greater width and lower intensity are observed, which translates into smaller particles that therefore generate more voids in the structure, giving rise to a greater surface area. These results correspond to those obtained in the textural analysis.

Mapping by EDX showed how La- and Mg-species were agglomerated in zones, discarding the formation of the $MgLa_2O_4$ spinel.

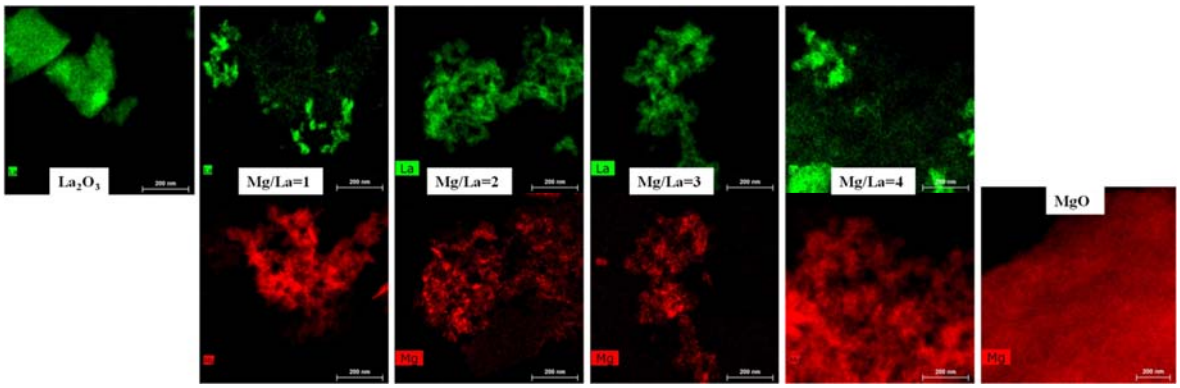

Figure 1. Mapping for the fresh samples.

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References.

1. Ghanta M, Fahey D, Subramaniam B (2014) Environmental impacts of ethylene production from diverse feedstocks and energy sources. Applied Petrochemical Research 4:167–179. https://doi.org/10.1007/s13203-013-0029-7
2. Gonçalves MCP, Romanelli JP, Cansian ABM, et al (2022) A review on the production and recovery of sugars from lignocellulosics for use in the synthesis of bioproducts. Industrial Crops and Products 186:. https://doi.org/10.1016/j.indcrop.2022.115213