

Sorption enhanced steam reforming of ethanol for hydrogen production, over Mg/Al hydrotalcites modified with K (P-4H)

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1. Introduction

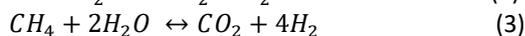
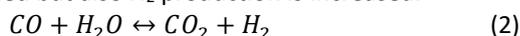
The approach of H₂ as an energy vector is not new, however recently research have been intensified on its production from different sources, purification, and application particularly in fuel cells [1]. Development of new and cleaner H₂ technologies is related to the climate restrictions which, according to the IPCC 2018, establish that to limit global warming below 2°C in 2030, the CO₂ emissions need to decline 25% respect to 2010 and reach net zero around 2070 [1]. To achieve this goal, it is necessary to reduce the cost of low-carbon H₂ production and expand its implementation [1].

In this context H₂ production as an energy vector by steam reforming of alcohols obtained from biomass, such as bioethanol (Equation 1), is a sustainable alternative. H₂ can be transform into energy in fuel cells, such as PEM ones, which demands high purity H₂ to be effective.



Taking into account that the H₂ produced from this process contains significant amounts of CO, which poisons the anode at the PEM fuel cell, therefore it must be removed. The gaseous product stream from the reforming unit contains mainly H₂, CO₂, CO and CH₄, so to minimize CO content operational units arranged in series are used. These units are based in Water Gas Shift Reaction (WGSR) and Preferential Oxidation of CO (COPROX).

Lately, several studies [2, 3] have been published on sorbent materials that, working in the same reforming unit, reduce significantly the CO produced in ethanol reforming through selective capture of CO₂, by shifting the equilibrium of WGSR reaction (Equation 2) and methane steam reforming (MSR, Equation 3). This process is known as sorption enhanced ethanol steam reforming (SE-ESR). Therefore, in presence of CO₂ sorbent material, not only CO content is reduced but also H₂ production is increased.



In last years, SE-ESR has become an interesting approach for industry, since it offers high purity H₂ in a simpler and smaller system. To improve feasibility on this process, it must be operated in multicyclic sorption-regeneration scheme, becoming important the use of materials that work under ethanol steam reforming conditions (atmospheric pressure, 500-600°C). Several CO₂ sorbent materials have

been studied, such as CaO materials; lithium zirconates, lithium orthosilicates or sodium zirconate and hydrotalcites [3].

Hydrotalcites (HT), a layered double hydroxide material, have shown selective CO₂ capture capacity and stability in multicyclic operation under mild temperatures [2, 3, 4, 5]. Even when HT sorbents have lower CO₂ sorption capacity compared to CaO ones, these are promising materials since its sorption capacity might be improved increasing its basicity by addition of alkaline metals such as Na, K, Cs [4].

In this study CO₂ sorbents based on Mg/Al HT, modified with different loadings of potassium (K) are analyzed, and their performance in the cyclic CO₂ sorption-desorption process is compared. Finally, these sorbents are tested under SE-ESR conditions with a Ni based catalysts, comparing H₂ purity obtained.

2. Experimental

2.1 Sorbent and catalysts synthesis

The sorbents are developed using a synthetic hydrotalcite (HT), supplied by Merck (CAS. 11097-59-9). This solid has been modified with different loadings of K through incipient wetness impregnation, following the procedure described by Halabi et al. [6]. First, commercial HT is sieved to particle size between 177-297 μm and calcined at 400°C for 4h. Then, it is mixed with a suitable volume of an aqueous solution of K₂CO₃ of known concentration, which is determined based on HT poral volume. After that, the solid is dried to 120°C for 12h and calcined at 500°C for 4h. Sorbents are labeled as NKHT(x), where N is the nominal loading of K, N = 0, 10, 15, 20wt.%, and x refers to the calcination temperature in °C.

Catalyst used in sorption-enhanced steam reforming of ethanol tests, is obtained after the activation of a Ni-Mg-Al hydrotalcite precursor previously developed for our group [7]. This catalyst was named HT-4 and its nominal composition is denoted by molar ratios Ni/Mg = 4 and [Ni(II) + Mg(II)]/Al(III) = 3.

2.2 Sorbent characterization

The unpromoted and K promoted hydrotalcites are characterized by: BET surface area and pore size distribution by N₂ sorption on a Quantachrome Autosorb; elemental analysis by inductively coupled plasma- optical emission spectrometry (ICP-OES) in a Perkin Elmer ICP OPTIMA 2100

spectrometer; powder X-ray diffraction (PXRD) obtained in a Shimadzu XD-D1 diffractometer with Cu K α ; CO₂ temperature programmed desorption (CO₂-TPD) and CO₂ sorption-desorption test are performed in a Micromeritics Autochem II. The CO₂ sorption capacity of the samples is determined based the obtained results for CO₂ sorption test and the following expression:

$$C_i = \frac{P V_{CO_2}}{R T m_{sorb}} \quad (4)$$

Where: C_i : sorption capacity in i cycle (mol CO₂/kg of sorb); V_{CO_2} : adsorbed CO₂ volume (mL CO₂); P : atmospheric pressure (1 atm); R : constant (82.06 atm.mL/mol CO₂. K); m_{sorb} : sorbent mass (kg).

Additional information regarding characterization test was referred in previous work [8].

Complete conversion of ethanol is ensured in all SE-ESR tests. During the analysis, molar fractions of N₂, H₂, CO₂, CO and CH₄ are followed. Results are reported as H₂ and CO purities in dry basis, as expressed in Equation 6.

$$P_j = \frac{y_j}{1 - y_{Ar} - y_{N_2}} 100 \quad (6)$$

Where: y_j : molar fraction of j product at reactor outlet, H₂ or CO₂; y_{N_2} , y_{Ar} : molar fraction of N₂ and Ar, respectively.

2.3 Sorption enhanced ethanol steam reforming

Sorption enhanced ethanol steam reforming tests are performed in a fixed-bed reactor. The reactor packing consists in a homogeneous mixture of 0.62g of Ni based catalyst and 2.38g of sorbent. The reaction is performed at 500°C. Additional information in presented in a previous work [8].

3. Results and discussion

Textural properties of unpromoted hydrotalcites with different K loadings are shown in Table 1. For the unpromoted hydrotalcite, a small reduction of BET area is detected with calcination temperature. When comparing the promoted hydrotalcites, BET area and poral volume significantly diminish with increasing K loading, while average pore radius increases. These results are consistent with the blockage of the pores due to the impregnation of the hydrotalcites with K.

Table 1. Textural properties of hydrotalcites fresh and spent in 19 sorption-desorption cycles, determined by N₂ physisorption.

Sample	BET Area (m ² /g)	Poral Volume (cm ³ /g)	Average pore radius (Å)
Fresh			
OKHT(400)	225.8	0.22	22.0
OKHT(500)	220.6	0.24	24.1
10KHT(500)	31.9	0.16	84.2
15KHT(500)	16.8	0.14	123.5
20KHT(500)	8.6	0.10	135.0
Spent (19 cycles)			
10KHT(500)	32.2	0.15	85.5
15KHT(500)	15.4	0.12	137.6
20KHT(500)	12.1	0.09	158.8

Figure 1 shows PXRD patterns for unpromoted and promoted hydrotalcites. For all the samples diffraction signals occur at $2\theta = 37^\circ$, 43° and 62° , corresponding to MgO

periclase phase (JCPDS 45-946). For 20KHT(500) diffraction signals associated to K phases are detected at $2\theta = 30^\circ$, 32.2° , and 32.7° , which according to Lee et al. [9], can be attributed to crystalline phases of K₂CO₃.

Meis et al [10] proposed a mechanism on impregnation of K₂CO₃ in hydrotalcites, where some Mg²⁺ ions in the surface of mixed oxide MgAlO_x are replaced by K⁺ ions creating O²⁻ vacancies. This could explain why no segregation of K₂CO₃ is distinguished at low potassium content.

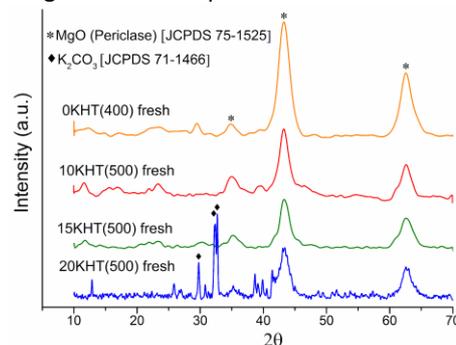


Figure 1. PXRD patterns for HT(400) and NKHT(500) samples.

In Figure 2, CO₂-TPD profiles for fresh sorbent samples are shown. According to literature [11], [12], three types of basic sites are detected. Between 50 and 300°C takes place CO₂ desorption from weak sites, which are associated to the more labile bicarbonate species [11]. Basic sites of intermediate strength are located between 300 and 700°C, and in accordance with Walspurger et al. [12] this peak is broadened with its maximum shifting to higher temperatures as K loading increases.

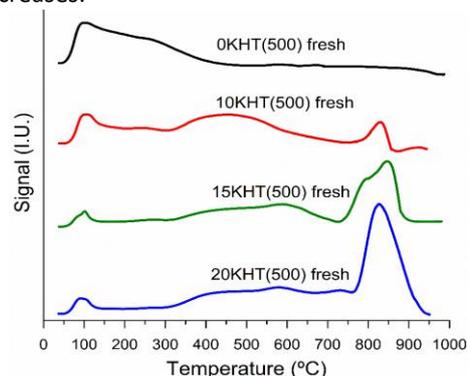


Figure 2. CO₂-TPD profiles of fresh unpromoted and K-promoted hydrotalcites.

In hydrotalcites with K, occurs a CO₂ desorption event with a maximum around 830°C [12, 13] that can be attributed to decomposition of bulk potassium carbonate or bidentate carbonate K⁺; accordingly, its intensity increases with K loading.

The distribution of basic sites for each sample has been determined by deconvolution and integration of the CO₂-TPD profiles (Table 3). A clear behavior is noted: the basic character of the samples increases with K loading.

Table 3. Proportion of basic sites calculated from CO₂-TPD profiles of fresh hydrotalcites.

Sample	Proportion of basic sites (%)		
	Weak (%)	Interm. (%)	Strong (%)
OKHT(500)	64.9	25.1	9.9

10KHT(500)	27.7	60.3	12.0
15KHT(500)	12.5	42.1	45.4
20KHT(500)	8.9	35.5	55.6

Furthermore, unpromoted hydrotalcite presents the higher proportion of weak basic sites, while the proportion of strong basic sites increases with K loading. Regarding the sites of intermediate strength, proportion of these reaches an optimum with K loading for 10KHT(500).

The results for CO₂ sorption tests are presented in Figure 3. Based on sorption results, the pre-breakthrough period, is longer for K promoted hydrotalcites compared to unpromoted one, which confirms that addition of K enhances CO₂ sorption capacity. Concerning breakthrough period, although the differences between sorption capacities are relatively small, it is observed that CO₂ volumes captured follow a trend as K content: 15KHT(500) > 20KHT(500) > 10KHT(500) > 0KHT(500). Moreover, 15KHT(500) presented the higher stability after 19 samples; while 10KHT(500) the lowest (not shown).

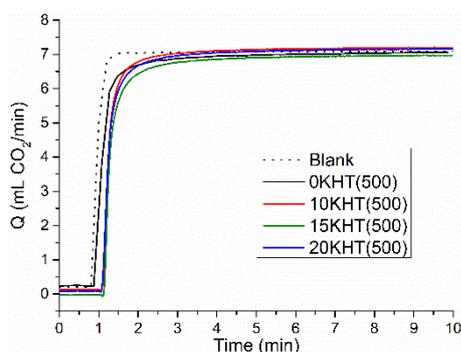


Figure 3. CO₂ Sorption profiles for unpromoted and K-promoted hydrotalcites. Conditions: total flow of 50 mL/min of CO₂:N₂ (15:85) at 500°C during 10 min.

SE-ESR has been performed with K promoted and unpromoted hydrotalcites mixed with Ni based catalyst, Figure 4.

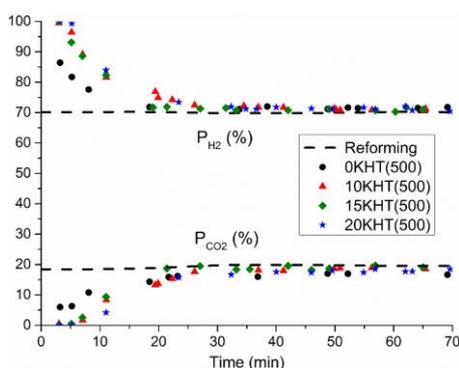


Figure 4. Purities to H₂ and CO₂ under sorption enhanced steam reforming of ethanol at 500°C for NKHT(500), being N=0,10,15,20wt.%. --- corresponds to purities obtained for ethanol steam reforming

The K promoted hydrotalcites presented higher H₂ purities and lower CO₂ purities during the pre-breakthrough period. Additionally, in accordance with CO₂ sorption test, pre-breakthrough period is longer for promoted sorbents compared to unpromoted ones. Finally, no significant difference is observed in the performance of promoted hydrotalcites in SE-ESR, related to K loading.

4. Conclusions

Potassium promoted materials have higher CO₂ sorption and desorption capacities compared to unpromoted solids. Moreover, CO₂ sorption multicycle tests denote the existence of an optimum K loading. This is due to the opposite effects produced by K impregnation: in one side, as K loading increases BET area reduces, hindering CO₂ sorption; meanwhile, basic character of samples increases with K, favoring CO₂ capture. Furthermore, it is confirmed that K-promoted hydrotalcites can be regenerated under inert atmosphere at the same temperature of CO₂ sorption. Finally, it is evident the beneficial behavior of K-promoted hydrotalcites as sorbents in sorption enhanced ethanol steam reforming, reaching nearly 100% in H₂ purity with the latest type of materials, with minimal discern between K loadings.

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