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Catalytic Activity of Polymetallic and Hydrotalcite-like Catalysts in the Synthesis of Methanol by Carbon Dioxide Hydrogenation

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Abstract. Two Cu-Zn-Al catalysts prepared by the coprecipitation method, both differing in their type of structure, one as a mixed oxide (polymetallic catalyst) and the other as a hydrotalcite-like catalyst, were used for the synthesis of methanol by hydrogenation of CO_2 in a fixed bed reactor system, operating under conditions of low pressure (6 bar) and temperature of 265°C. The effect of the composition of the catalyst on its catalytic activity under low pressure conditions was investigated. The main results show that the highest CO_2 conversion is found with Cu-Zn-Al polymetallic catalyst, however, the best selectivity to methanol is shown for Cu-Zn-Al hydrotalcite-like catalyst.

Key words. Methanol, hydrogenation, carbon dioxide, catalytic activity.

1. Introduction

Over the last few years, technological advances to improve the quality of life led to a gradual degradation of natural resources and increased levels of pollutants in the atmosphere, thus contributing to global warming ("greenhouse effect") and inducing significant climate changes [1]. The main anthropogenic greenhouse gas is CO_2 and many countries are very committed to reducing their atmospheric concentration using various solutions, such as the use of other energy sources such as solar and nuclear energy [1, 2].

Despite the adoption of alternative energy sources and efficient energy systems to reduce carbon dioxide (CO_2) emissions, the cumulative amount of CO_2 in the atmosphere still needs to be reduced to limit the detrimental impact of climate change [3]. Several strategies to mitigate CO_2 emissions have been proposed over the last decades, among which carbon utilization by conversion to fuels and chemicals appears promising [4]. Nowadays, CO_2 capture and storage are widely used, but scientists are increasingly interested in transforming CO_2 into a recoverable product [5, 6]. In fact, the use of CO_2 as a "reagent" to produce bulk chemicals such as methanol, dimethyl ether (DME) and hydrocarbons [7, 8] is particularly interesting because these products are considered possible substitutes for traditional automotive fuels [1, 9].

Of the various products that can be directly synthesized from CO_2, much effort is being put on the development of technologies for methanol production. Methanol is commonly used as solvent and feedstock to produce a variety of chemicals as well as a fuel additive [10,11]. Currently, methanol is commercially produced from syngas ($CO/CO_2/H_2$) under high temperature (220-300ºC) and high pressure (50-100 bar) over $CuO/ZnO/Al_2O_3$-based catalysts, and the development of a few large-scale plants based on CO_2/H_2 is in progress [12-16]. This catalytic system is also, of interest for the potential use of methanol as a sustainable synthetic fuel obtained by hydrogenation of captured CO_2 [17]. Methanol synthesis is severely limited by thermodynamics because this reaction is extremely exothermic. The effect of temperature on methanol synthesis has already been reported in several studies [1, 16, 18]. Developing a low temperature process for methanol synthesis will greatly reduce the production cost, and high CO_2 conversion becomes available at low temperature [13]. This process requires the preparation of an efficient catalyst that must be highly active and selective for methanol [2]. Copper based catalysts ($Cu–ZnO/Al_2O_3$) were found to be effective towards methanol synthesis through CO or CO_2 hydrogenation [14, 15, 19–22].

In this work, catalysts based on Cu–Zn–Al prepared under different precipitation conditions were studied in the synthesis of methanol, using a fixed-bed reactor system. The ultimate objective of this process will be to use as feedstock the gas obtained from anaerobic digestion of organic waste such as agricultural, livestock and from gardens and golf courses, provided it is poor in methane. In order to initially test the prepared catalytic materials, the reactions have been carried out with commercial CO_2.

2. Experimental

2.1. Catalyst preparation

In this work, two types of catalysts with $CuO/ZnO/Al_2O_3$ composition are studied, in the first case a mixed oxide (MO) and the second case a hydrotalcite-like compound (HTLC). Both catalytic solids were prepared by the coprecipitation method. Mixed oxide catalyst, Cu-Zn-Al (Cu/Zn/Al = 2/4/1 mol ratio), was prepared using an aqueous solution containing Cu^{2+}, Zn^{2+} and Al^{3+} with the total metal ion concentration of 1.0 mol/L added dropwise to an aqueous solution of Na_2CO_3 (0.5 mol/L) under stirring at 70°C. During coprecipitation pH was controlled at 7 by the simultaneous dripping of an aqueous NaOH solution (3.0 mol/L). This suspension was maintained at 50°C for 1 h with stirring, then filtered off and washed with distilled water, dried overnight at 80°C in air and calcined at 550°C for 5 h.

HTLC was prepared using appropriate amounts of $Al(NO_3)_3$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$ keeping dissolved in water to obtain 1.0M aqueous solution, and the molar ratio of Cu/Zn/Al was kept constant at 2:1:1. The Cu–Zn–Al HTLC precursor was precipitated from the $Cu^{2+}/Zn^{2+}/Al^{3+}$ nitrate solution with an aqueous solution of NaOH (0.3 M) and Na_2CO_3 (0.05 M) as the precipitating agent. The reaction was carried out at a constant pH value ($pH=10 \pm 0.4$) at 70°C and 24 hours of aging. The precipitates were recovered by filtration, washing with water, and drying at 80 °C for 12 h. Afterwards, the dried powder was ground and then calcined in air at 320°C for 3 h.

The schematic diagram of the catalyst preparation apparatus is shown in Fig. 1

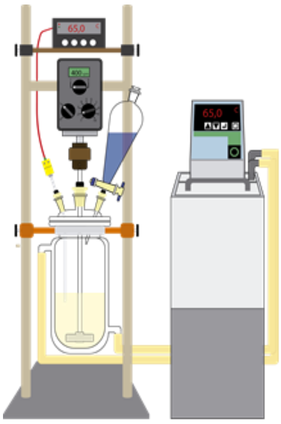

Fig. 1. Schematic diagram of the catalyst preparation apparatus.

2.2. Characterization of the catalyst

X-ray powder diffraction (XRD) measurements were used to determine the properties of the Cu–Zn–Al precursors and the crystalline phase of the calcined catalysts, which were performed on a Panalytical XPert PRO diffractometer (SEGAI, Universidad de La Laguna, Tenerife, Spain) with Cu Kα radiation (λ=1.54 Å), scanning 2θ angles in the range of 5–85°.

The surface area, total pore volume and average pore diameter were measured by N_2 adsorption/desorption, using an ASAP 2020 Micromeritics (SEGAI, Universidad de La Laguna, Tenerife, Spain) at 77 K. Samples were degassed at 200°C for 4 h prior to analysis.

Scanning electron microscopy (SEM) characterization was performed on a ZEISS EVO 15 scanning electron microscope (SEM) with 2 nm resolution with 50 mm^2 XMAS Oxford X-ray scattering energy microanalyzer (EDX) (SEGAI, Universidad de La Laguna, Tenerife, Spain) to observe the morphology and microstructure of the samples.

2.3. Catalytic test

Carbon dioxide hydrogenation was performed in a continuous flow fixed bed reactor (12.5-mm id) made of stainless-steel. 2 g of catalyst was placed in the tubular reactor with a coaxially centered thermocouple in contact with the catalytic bed. Prior to reaction, the sample was reduced in situ at 350°C at a heating rate of 5 °C/min with a flow of H_2 (61 mL/min, 99.99 % H_2) for 4 h at pressure of 6 bar. After that, a gas mixture ($H_2/CO_2 = 5$) was introduced into the reactor at the reaction temperature of 265°C and pressure of 6.0 bar. The schematic diagram of the catalyst test apparatus is shown in Fig. 2.

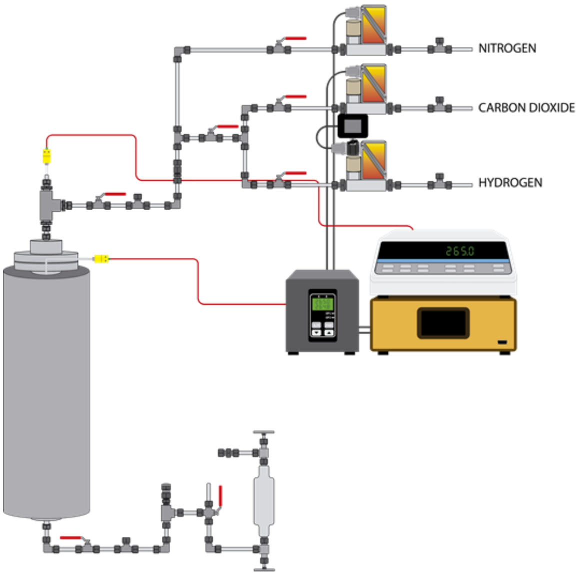

Fig. 2. Schematic diagram of the catalyst test apparatus.

The liquid products were separated from the gas products in the gas liquid separator and condenser. The gas products were recollected and analysed by Agilent Technologies 7820A gas chromatograph system, with two columns, and a thermal conductivity detector (TCD).

The CO_2 conversion ($\% X_{CO_2}$) and methanol selectivity ($\% Se_{MeOH}$) were calculated using the following equations.

$$\% X_{CO_2} = \frac{(Inicial\ moles\ of\ CO_2 - Final\ moles\ of\ CO_2)}{Initial\ moles\ of\ CO_2} \times 100$$

$$\% Se_{MeOH} = \frac{(Methanol\ moles)}{(Inicial\ moles\ of\ CO_2 - Final\ moles\ of\ CO_2)} \times 100$$

The error show in Fig. 6 and 7 correspond to the standard deviation of the measurements.

3. Results and discussion

The characteristics of the catalysts will be analyzed in the first place followed by the study of the catalytic activity.

3.1. Characterizations

3.1.1. X-ray powder diffraction (XDR)

The XRD patterns of the uncalcined and calcined mixed oxide and hydrotalcite catalysts are shown in Fig. 3. As seen in XRD patterns of uncalcined hydrotalcite-like Cu-Zn-Al catalyst (Fig. 3.a), a series of sharp and symmetric reflection peaks around 2θ = 11.5, 22.2, 34.7 and 61.1°, assigning to the diffraction plane (0 0 3), (0 0 6), (0 0 9) and (1 1 0) [23] respectively, showed typical characteristics of hydrotalcite-like copper-zinc-aluminium hydroxycarbonate [24]. This indicates that the prepared Cu-Zn-Al-HTLC has a regular layered structure with 3R symmetry of HTLC [25].

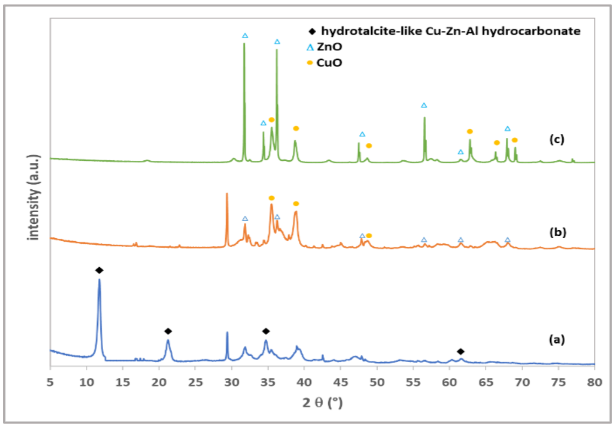

Fig. 3. XRD patterns of the Cu-Zn-Al HTLC catalyst. (a) uncalcined HTLC, (b) calcined HTLC and (c) calcinate mixed oxide.

Fig. 3.b illustrated the XRD pattern of the hydrotalcite-like Cu-Zn-Al catalyst after calcination at 320 °C and crystalline CuO and ZnO were observed. The mean peaks of CuO are observed at 2θ = 35.6° and 38.8° and those assigned to ZnO could be seen at 2θ = 31° and 36° [26, 27]. Similarly, the sample of calcined mixed oxide (Fig. 3.c) are characterized by the presence of two well-crystallized phases of CuO and ZnO. However, a peak indicative of alumina phase is detected at 2θ = 44°.This peak is characterized by a weak intensity, which implies that the alumina phase is present in a micro-crystallite state. Similar results were previously reported in the literature [28].

3.1.2. *Surface area*

Fig. 4 showed the nitrogen adsorption-desorption isotherm for the representative calcined HTLC samples. The sample had a typical IV-type isotherm, which are usually observed for materials of plate-like particles with slit-shaped mesopores [29], indicating that the plate-like morphology and layered structure of the HTLC precursor are retained in the calcined catalyst.

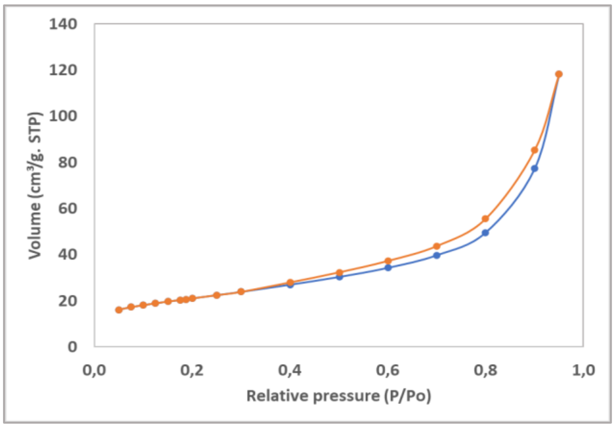

Fig. 4. N_2 adsorption–desorption isotherms of calcined hydrotalcite-like Cu-Zn-Al catalyst.

The textural properties of calcined hydrotalcite sample were obtained from the N_2 adsorption-desorption analysis showed a BET surface area (S_{BET}) of 74.1338 m²/g, a total pore volume of 0.182761 cm³/g, a micropore volume of 0.003882 cm³/g and average pore diameter of 9.86 nm. These values obtained are comparable with those reported by other authors [30].

3.1.3. *Scanning electron microscopy (SEM)*

As shown in Fig. 5, Cu-Zn-Al hydrotalcite-like catalyst consisted of quasi-cubical crystallites with a clear boundary, suggesting that the hydrotalcite-like Cu-Zn-Al catalyst nanoparticles are of high crystallinity.

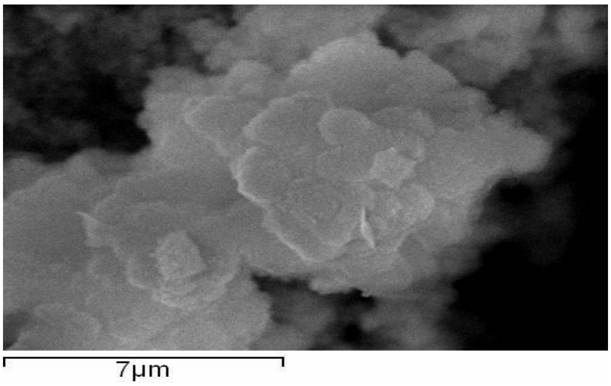

Fig. 5. SEM images of hydrotalcite-like Cu-Zn-Al catalyst

3.2. Catalytic reaction

The catalytic activity of the hydrogenation of CO_2 to methanol is presented in table 1.

Table 1. Catalytic performance for the hydrogenation of CO_2 to methanol

Catalysts	X_{CO_2} **(%)**	$Se_{MeOH\cdot}$ **(%)**	Se_{CO} **(%)**
Cu-Zn-Al (HTLC)	3.91	10.03	89.89
Cu-Zn-Al (MO)	19.02	6.88	93.12

This table clearly shows that CO and methanol are the only carbon-containing products present under the reaction conditions. The conversion of CO_2 increases with the structural change of the catalyst, the conversion obtained with structured catalyst such as hydrotalcite-like Cu-Zn-Al catalyst is less than that obtained by mixed oxide of the mass type. Meanwhile it is observed that the selectivity to methanol behaves inversely, being higher for the case of hydrotalcite-like Cu-Zn-Al catalyst.

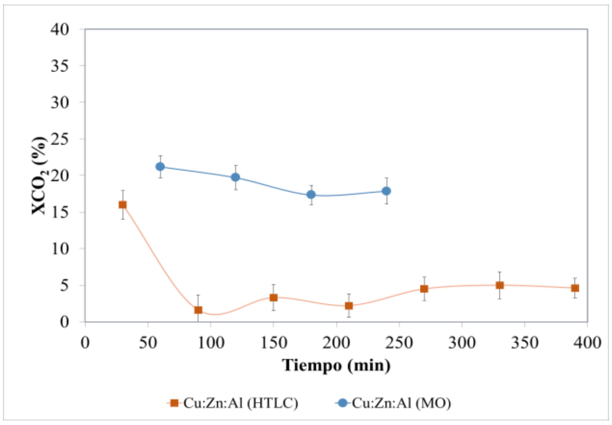

Fig. 6. Conversion of CO_2 along reaction time, where the bar shows the standard deviation.

Fig. 6 showed the conversion of CO_2 along reaction time. The best conversion is obtained with Cu-Zn-Al oxide mixed catalyst, but the highest selectivity of methanol is obtained with hydrotalcite-like Cu-Zn-Al catalyst (Fig. 7).

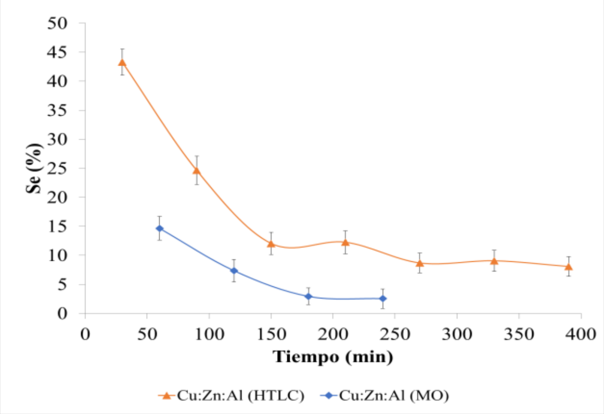

Fig. 7. Selectivity to Methanol, where the bar shows the standard deviation.

Cu-Zn-Al polymetallic catalyst in addition to having a large conversion shows greater stability throughout the reaction time, while in the case of Cu-Zn-Al hydrotalcite-like catalyst at the beginning of the reaction shows a high conversion, decreasing rapidly over time.

In the case of the selectivity to methanol, Cu-Zn-Al hydrotalcite-like catalyst presents a high selectivity at 50 minutes of reaction, which decreases drastically after 150 minutes, then remaining almost constant until the end of the reaction.

Table 2 shows the CO_2 conversion and methanol selectivity results reported on Cu-Zn-Al hydrotalcite and Cu-Zn-Al polymetallic synthesized by different preparation methods and reaction conditions.

When comparing the conversion results obtained in this work with those by other authors a lot of similarity can be seen, even though the pressure conditions established in this work are 5 times lower than those used by other authors which is an encouraging result. On the other hand, the selectivity to methanol is much lower. In view of these results, it is necessary to continue conducting studies with this type of catalytic solids in order to achieve similar results to those reported, but at less severe reaction conditions in relation to pressure or to be able to explain why the selectivity to methanol is so low.

Table 2. Comparison of CO_2 hydrogenation activity results for Cu-Zn-Al system.

Catalyst	**Temp., °C/Pres., bar**	**GHSV h^{-1}**	X_{CO_2} **(%)**	$Se_{\mathrm{MeOH}\cdot}$ **(%)**	**Reference**
Cu-Zn-Al (HTLC)	265/6.0	1860	3.91	10.03	Present work
Cu-Zn-Al (MO)	265/6.0	1860	19.02	6.88	Present work
CuZnAl-111 HT	260/30	8800	18.7	37.6	[30]
CuZnAl*	260/30	8800	20.8	34.3	[30]
CZA	250/30	2400	12.0	91.0	[31]

*Commercial benchmark catalyst

4. Conclusion

Cu-Zn-Al polymetallic catalyst show higher conversion (19%) than hydrotalcite-like Cu-Zn-Al catalyst (4%), but it shows lower selectivity to methanol.

The results obtained from the conversion of polymetallic and hydrotalcite catalysts are comparable to those obtained by other authors.

It is necessary to understand why although the conversion is comparable to that of other authors, the selectivity to methanol turns out to be much lower.

Although the pressure in this work is 10 times lower than the pressure used commercially, good conversion results are obtained, even when the selectivity results are very low.

The next step will be studding the influence of the different reaction variables in the process, as well as to varying the proportion of metals in the composition of the catalyst.

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