

# Effect of La and Ce addition on the catalytic hydrogenation of carbon dioxide over CuO-ZnO/SiO<sub>2</sub>-type catalysts

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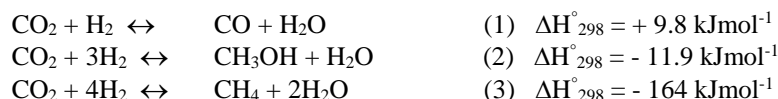
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**Introduction** - Catalytic hydrogenation of CO<sub>2</sub> into value-added chemicals, such as methanol and methane is an attractive approach for utilizing CO<sub>2</sub> as an economic and ecological C<sub>1</sub> source (Arena, 2009). Methanol is an important intermediate in the petrochemical industry (Lei, 2015), and, in the future, a substantial increase in its demand is expected. Indeed, methanol is used as fuel additive and as clean burning fuel. Moreover, methanol is the starting point for the production of high added value products as formaldehyde, methyl-tetra-butyl-ether (MTBE) and various solvents. For such a reason, and in particular in the case of oxygen-containing compounds, lots of efforts have been done in order to develop new processes based on heterogeneous catalysis and gas-phase reactions to improve the selectivity to the desired products. The production of catalytic hydrogenation of carbon dioxide has been then widely investigated in the last decades. Among the others, some of the reactions commercially interesting are:



The Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst, that is commonly used in CO hydrogenation, is not very efficient in the CO<sub>2</sub> hydrogenation to methanol, but it can be use as the base to develop new catalysts with a higher activity and improved selectivity to methanol.

Several studies indicate that the catalyst composition affects the activity of Cu-based catalysts in the CO<sub>2</sub> hydrogenation to methanol. Consequently, the parent catalyst has been often modified by addition of various oxides such as chromium, manganese, zirconium and silica (Wu, 2001). In the present work, small amounts of cerium oxide (10 wt %) and lanthanum oxide (10 wt %) have been added to the Cu-Zn/SiO<sub>2</sub> parent catalyst with the aim to improve the catalytic activity towards CO<sub>2</sub> hydrogenation.

**Catalysts' preparation and characterization** - The oxide precursors of Cu-Zn-La/Si<sub>2</sub>O and Cu-Zn-Ce/Si<sub>2</sub>O were prepared by conventional co-precipitation method. Aqueous solutions of metal nitrate and sodium carbonate were simultaneously added under vigorous stirring, to a suspension of the SiO<sub>2</sub> support. The precipitation was carried out at 90°C and at constant pH of 7. After calcinations at 450 °C, the catalysts were widely characterized by different physico-chemical techniques.

The surface areas of the calcined materials were 51 and 60 m<sup>2</sup>.g<sup>-1</sup> respectively for the Cu-Zn-La/SiO<sub>2</sub> and Cu-Zn-Ce/SiO<sub>2</sub> catalysts (Table 1). XRD spectra show well defined peaks assigned to the expected phases: CuO, ZnO, SiO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub>. Thermogravimetric analysis showed that both catalysts were stable up to 600°C. The SEM images displayed that the catalysts were constituted of aggregated of spherical particles with diameter in the 40-200 nm ranges. The EDX cartographies confirmed a good dispersion of the ceria on the surface of the catalysts, while the lanthanum-containing phase was less well dispersed with the presence of bigger aggregates.

Table 1. BET surface area, pore diameter, and pore volume of the prepared catalysts and support.

Simples	Surface BET (m <sup>2</sup> .g <sup>-1</sup> )	Ø pores (nm)	V pore (cm <sup>3</sup> .g <sup>-1</sup> )
SiO <sub>2</sub> *	405.85	459.71	0.99
Cu-Zn-La/ SiO <sub>2</sub>	51.07	11.82	0.12
Cu-Zn-Ce/ SiO <sub>2</sub>	60.61	19.12	0.23

**Catalytic activity** - The catalytic results are summarized in Table 2 and in Figures 1 and 2. The CO<sub>2</sub> hydrogenation tests were carried out in a stainless steel tubular reactor, at atmospheric pressure and at different temperatures (250-600 °C). Previously to reaction, the catalysts were reduced in diluted H<sub>2</sub> at 350 °C and atmospheric pressure

for 3h. The reaction products, carbon monoxide, methanol and methane were analyzed by Shimadzu GC chromatographs.

Table 2: CO<sub>2</sub> conversion and CH<sub>3</sub>OH, CH<sub>4</sub> selectivity at T=290°C.

Samples	CO <sub>2</sub> conversion (%)	CH <sub>4</sub> selectivity (%)	CH <sub>3</sub> OH selectivity (%)
SiO <sub>2</sub> *	-	-	-
Cu-Zn/ SiO <sub>2</sub>	0.2	traces	traces
Cu-Zn-La/ SiO <sub>2</sub>	8.8	8	92
Cu-Zn-Ce/ SiO <sub>2</sub>	12.0	7	93

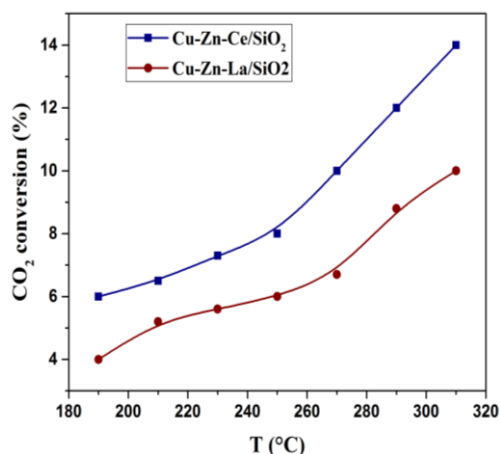


Fig.1. CO<sub>2</sub> conversion as a function of temperature (190–310°C) (P=1bar, CO<sub>2</sub>/H<sub>2</sub>= 1/9).

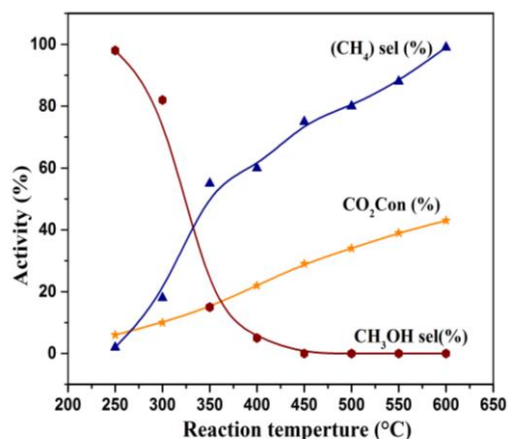


Fig.2. CO<sub>2</sub> conversion, and CH<sub>3</sub>OH and CH<sub>4</sub> selectivity, as function of the temperature (250–600°C) over Cu-Zn-La/SiO<sub>2</sub> catalyst, (P=1bar, CO<sub>2</sub>/H<sub>2</sub>= 1/9).

In each case the conversion of CO<sub>2</sub> and CH<sub>4</sub> selectivity increased with the reaction temperature, while CH<sub>3</sub>OH selectivity diminished by increasing the reaction temperature. This results are due to the competition between the methanol synthesis reaction (2) and the methanation reaction (3), both involved in the CO<sub>2</sub> hydrogenation process. Clearly, the increasing of the temperature is beneficial to methanation being an endothermic reaction.

The Cu-Zn-Ce/SiO<sub>2</sub> was found to be the most active catalysts in carbon dioxide hydrogenation; such a behaviour can be related to the slightly higher surface area, to the higher dispersion of ceria on the catalyst surface, and to higher reducibility characteristic of ceria.

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## References

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