

Synthesis of methanol and dimethyl ether from the CO₂ hydrogenation over Cu-ZnO supported on Al₂O₃ and Nb₂O₅



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ABSTRACT

We report the synthesis, characterization and catalytic evaluation of Cu-ZnO catalysts supported on Al₂O₃ and Nb₂O₅, as acidic materials, to study the CO₂ hydrogenation to methanol and dimethyl ether. The catalysts were prepared by precipitation or impregnation of the metals over the supports. They were characterized by different techniques, such as XRF, BET area, TPD of *n*-butylamine, XRD and TPR. Catalytic tests were performed in an automated catalytic unit coupled to a gas chromatograph with FID and TCD detectors. Different conditions of temperature and pressure were studied. It could be observed that the choice of the synthesis method affects the activity and selectivity of the CO₂ hydrogenation, at the conditions used in this work. The catalyst prepared by impregnation of the metals over the Al₂O₃ support was the most active and selective to dimethyl ether. This result can be explained by the better and lower temperature reducibility of CuO particles along with higher density of acid sites and strength of the alumina support.

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1. Introduction

Carbon dioxide (CO₂) capture and utilization for the manufacture of high value-added products is gaining increased importance, due to the necessity to reduce the emissions of this greenhouse gas in the atmosphere [1–8]. The hydrogenation of CO₂ is a synthetic route of special interest, as it may be used to synthesize fuels and chemicals, thus constituting an important area of research widely explored in recent years [9,10]. In this context, the hydrogenation of CO₂ to methanol and dimethyl ether (DME) appears as an excellent option, as these products might find applications either as fuels or chemicals [11–14].

Methanol is an important raw material [12,15,16]. It can be used directly as fuel or in the production of biodiesel [17]. The Methanol to Gasoline (MTG) process [18] has been commercialized in the 1980's. Nevertheless, the process was adapted to produce ethene and propene, the so-called, Methanol to Olefins (MTO) [19,20], due to the higher added-value of the olefins compared with gasoline. Methanol is also used in the production of important chemical

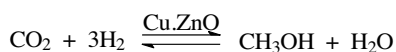
commodities such as formaldehyde and acetic acid [15,16]. DME may be used in diesel engines to replace the petrodiesel. Furthermore, it is considered greener than diesel, because it is virtually free from sulfur and aromatics, emitting less CO, SO_x and particulates. Presently, methanol is synthesized from syngas, a mixture of CO and H₂, which in turn is produced from natural gas or coal. DME may be produced through the acid-catalyzed dehydration of methanol or directly from syngas, using bifunctional catalysts [13]. Additionally, methanol and DME can also be produced from the catalytic hydrolysis of chloromethane over metal-exchanged zeolites [21–23], thus avoiding the production of syngas, which is highly energy demanding.

There are many studies on the CO₂ hydrogenation to methanol [13]. An industrial plant has been built in Iceland producing hydrogen from geothermal energy. On the other hand, the direct conversion of CO₂ to DME is still poorly studied compared with its direct production from syngas [10,24]. The synthesis of methanol from CO₂ often uses Cu-ZnO unsupported catalysts, together with different promoters [10,25–29]. The commercial catalyst for the methanol synthesis from syngas is constituted of 50–70% CuO, 20–50% ZnO, and 5–20% of promoter, in this case, Al₂O₃ [28]. Other oxides, such as chromium, magnesium, rare earths, gallium or zirconium can be used as promoters too [26,30,31].

The CO₂ hydrogenation to methanol is limited by thermodynamics [32], with the equilibrium being favored to the products at

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Scheme 1. Synthesis of methanol from CO₂ hydrogenation.

high pressures and low temperatures (Scheme 1). We have shown that the traditional Cu-ZnO catalyst, promoted with Al₂O₃, operates on the thermodynamic limit at 270 °C and 50 bar [33,34]. However, the catalytic activity is significantly reduced when lower temperatures are used, which suggests the existence of kinetic limitations for this type of catalysts [33,34].

Cu-ZnO supported on different solid acids, such as γ-alumina, ZSM-5 or other zeolites have been used in the direct synthesis of DME from syngas [35,36]. A bifunctional catalyst must be used to perform the hydrogenation of CO₂ to methanol and, in the sequence, the dehydration of methanol to DME (Scheme 2), which is performed by the acid sites of the catalyst [37–39]. Although it is of great importance to control the temperature of the system, the production of DME from methanol does not have severe thermodynamic limitations [24].

Here, we report the synthesis and characterization of Cu-ZnO catalyst supported on acidic materials (Al₂O₃ an Nb₂O₅) to study the CO₂ hydrogenation to methanol and DME.

2. Experimental

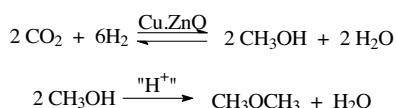
The catalysts were prepared by precipitation or impregnation of Cu(NO₃)₂·3H₂O (99% purity) and Zn(NO₃)₂·6H₂O (98% purity), both from Sigma–Aldrich, over γ-alumina (Al₂O₃), Puralox MP2218 from Evonik, and calcined niobium oxide (Nb₂O₅), obtained from amorphous hydrated niobium pentoxide (Nb₂O₅·nH₂O–72.6% Nb₂O₅) supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração, Brazil), as solid acid supports. Prior to impregnation or precipitation of the metal precursors, the hydrated niobium pentoxide was calcined at 550 °C for 2 h in order to stabilize the structure and avoid the possible formation of metal niobates, due to strong metal-support interaction [40]. The alumina support was used without any previous thermal treatment.

In the precipitation method, 1.9 g of copper nitrate and 2.3 g of zinc nitrate (metal atomic ratio of 1:1) were dissolved in 500 mL of deionized water and put in contact with 10 g of alumina or the calcined niobium oxide. The system was subjected to stirring and 1 mol L^{−1} solution of NaOH (99% purity) was added dropwise until pH 7. At the end, the system was aged for one hour at room temperature before filtration, washing and drying. The catalysts prepared by precipitation are denoted with (p).

In the impregnation method, the solution containing the copper and zinc cations was put in contact with the alumina or niobium oxide support and vigorously stirred for 24 h at room temperature. Then, the water was carefully evaporated on a rotary evaporator at 60 °C and reduced pressure. The catalysts prepared by impregnation are denoted with (i).

All catalysts prepared, either, by precipitation or impregnation were calcined at 550 °C for 2 h prior to the catalytic runs.

The catalyst composition was obtained by X-ray fluorescence (PW2400 Philips equipped with Rh tube 3 KW). The textural characterization was carried out by N₂ physisorption on a Micromeritics ASAP 2020 equipment. X-ray diffraction was performed on a Shimadzu 6000 instrument equipped with a Cu



Scheme 2. Synthesis of DME from CO₂ hydrogenation over bifunctional catalyst.

Kα target, operating at 40 kV and 30 mA. Standard powder diffraction patterns were gathered for 2θ angles ranging from 5 to 80° at a scanning speed of 4°/min. Temperature Programmed Reduction (TPR) was carried out at a home-made system, using a mixture of 1.7 mol% of H₂ in Argon. The acidity of the catalyst was determined by temperature programmed desorption of *n*-butylamine, following a procedure described elsewhere [41].

CO₂ hydrogenation reactions were carried out in a PID high pressure automatic flow unit, coupled with an Agilent 7890A gas chromatograph equipped with Flame Ionization (FID) and Thermal Conductivity (TCD) detectors. An on-line system was used to analyze the products of the reaction on a Plot/Q column (30 m × 0.320 mm × 20 μm). A stainless steel reactor was loaded with 500 mg of catalyst and 500 mg of inert SiC, both sieved to 32–115 mesh, to form a fixed bed. The catalysts were initially reduced under a mixture of 10 mol% H₂ in N₂ in two steps. Initially, the temperature was increased to 140 °C at a rate of 1 °C min^{−1}, remaining at this temperature for 5 h. Then, the temperature was set to 270 °C, using the same previous rate of 1 °C min^{−1}, and remaining at this temperature for 2 h. After reduction, the temperature was set to the desired value (250 or 270 °C) and the system was pressurized (30 or 50 bar) with a 1:3 molar mixture of CO₂ and H₂ (25 vol.% CO₂ and 75 vol.% H₂), respectively. The space velocity was kept constant at 10 h^{−1} and the reaction was monitored for 8 h, without presenting any significant deactivation.

3. Results and discussion

Table 1 shows the results of chemical and textual characterizations of the prepared catalysts. Except for the Cu-ZnO/Nb₂O₅ (p), mostly catalysts presented atomic ratios of these metals close to 1. The BET area of the supported catalysts was lower than the original alumina and calcined niobium oxide supports. Calcined niobium oxide showed a much lower BET area, which is attributed to the high temperature thermal treatment used to stabilize it from an amorphous hydrated niobium pentoxide [42]. However, there was no significant difference in the areas for the precipitated or impregnated catalysts considering the same support.

Table 2 shows the results of total acidity and acid strength distribution of the catalysts in comparison to the original supports. The alumina support has more acid sites than the calcined niobium oxide and this property was reflected on the prepared catalysts. Except for the Cu-ZnO/Nb₂O₅ (p) catalyst, the total acidity increased with the presence of the metals. This may be explained in terms of the adsorption of the probe molecule onto the metals surface.

XRD analyses show that the synthesized catalysts present the same diffraction patterns exhibited by the original supports (Figs. 1 and 2). Prior to calcination, Nb₂O₅ is an amorphous hydrated niobium pentoxide (Nb₂O₅·nH₂O). Its thermal treatment

Table 1
Chemical and textual characterization of the catalysts.

Catalyst	Metal (wt%) ^a		BET area (m ² /g) ^b
	Cu	Zn	
Cu-ZnO/Al ₂ O ₃ (p)	3.7	3.0	171
Cu-ZnO/Al ₂ O ₃ (i)	3.7	3.2	168
Cu-ZnO/Nb ₂ O ₅ (p)	3.1	4.7	30
Cu-ZnO/Nb ₂ O ₅ (i)	2.6	2.8	32
Nb ₂ O ₅ ^c	–	–	42
Al ₂ O ₃	–	–	206

^a Determined by XRF.

^b Determined by N₂ Physisorption.

^c Calcined at 550 °C.

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