



Catalytic hydrogenation of CO₂ into methanol and dimethyl ether over Cu-X/V-Al PILC (X = Ce and Nb) catalysts



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ABSTRACT

The production of methanol (MeOH) and dimethyl ether (DME) through CO₂ hydrogenation is an attractive route to recycle CO₂ and control its emission to the atmosphere. In the present work, the hydrogenation of CO₂ into MeOH and DME over Al-pillared clays impregnated with different metals (Cu-X/V-Al PILC, where X = Ce and Nb) was investigated in the temperature range 200–300 °C. The influence of additives on the physico-chemical properties of the catalysts was evaluated by N₂ adsorption, *ex situ* XRD, TPR analysis, and *in situ* XANES and XRD. The acid sites were analyzed by FTIR analysis after adsorption of pyridine and NH₃-TPD. The basic and metallic sites were analyzed by CO₂-TPD and N₂O-TPD, respectively. *In situ* XANES was used to investigate the Cu⁺ and CuO species. MeOH and DME selectivities were directly related to the presence of acid, basic and metallic sites and with the reaction temperature. The results indicated that the CuCe/V-Al PILC catalyst was the most promising catalyst for DME synthesis from CO₂.

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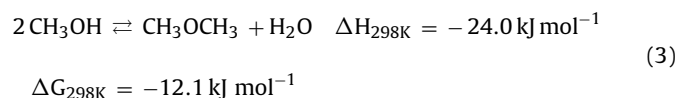
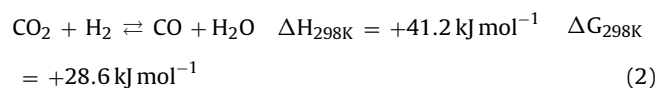
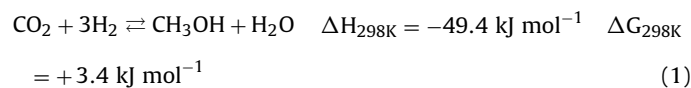
1. Introduction

Nowadays, the relationship between carbon dioxide (CO₂) emission and environmental impact is well recognized and the development of technologies for converting CO₂ into useful compounds has been of high interest. Various studies on catalysis have been aimed at obtaining methanol (MeOH) and dimethyl ether (DME) by CO₂ hydrogenation [1–10].

The synthesis of MeOH (MS) from catalytic CO₂ hydrogenation is an environmentally friendly process, whose the main product is methanol, (Eq. (1)) [6,11]. Other products of parallel reactions can also be formed, such as DME, H₂O, CO, hydrocarbons and long chain alcohols [11].

The synthesis of DME is usually performed according to two approaches: (i) two reactors: MeOH synthesis on metallic sites followed by dehydration on solid acid catalysts (Eqs. (1) and (3)), or (ii) single step, which comprises bifunctional catalysts constituted by acid and metallic sites. The one-step DME synthesis involves numerous competing reaction pathways, for example, the reverse water-gas-shift (RWGS), which can occur in parallel with MeOH synthesis, Eqs. (2) and (1), respectively [12]. The main reactions

involved in the synthesis of MeOH and DME are represented by Eqs. (1)–(3) [12–15].



Typically, Cu–ZnO–Al₂O₃ is the most employed catalysts for industrial MeOH synthesis, in which metallic copper is the active phase. ZnO is used to increase the Cu dispersion on the support, thus providing a high number of active sites exposed to gaseous reactants [7,8,16]. On the other hand, acid-catalysts such as Al₂O₃ and HZSM-5 are responsible for methanol dehydration into DME [14,17–20]. Pillared clays (PILCs) have been studied as acid-solid catalysts due to their valuable applicability and low cost. The inclusion of aluminum polycations in the clays leads to significant modifications in their acidity, which is due to the increase of specific surface area and formation of new acid sites [21–24].

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Therefore, the resulting product distribution obtained from CO₂ conversion is directly related to the catalyst composition and reaction conditions. Many types of catalysts have been tested in the CO₂ hydrogenation into MeOH and DME, for instance Cu-based catalysts with different promoters such as Zn, Zr, Ce, Al, Si, V, Ti, Ga, B and Cr [4,11].

Cu-CeO₂-based catalysts have displayed promising performance on MeOH synthesis because of their redox properties and ability to store oxygen [9]. According to Liu et al. [25], the interaction between Ce and Cu may promote electron transfer effects between CeO₂ and Cu particles, leading to formation of Cu⁺ species, Eq. (4).



Gao et al. [26] studied copper catalysts and observed that the formation of Cu⁺ and CuO species was essential to the synthesis of MeOH, and the Cu⁺/CuO relationship determined the specific activity of the catalysts.

Nb-based catalysts have exhibited high catalytic activity and selectivity for dehydration of alcohols. This behavior has been associated to the presence of strong Lewis and Brønsted acid sites [27–29]. Ladera et al. [27] studied a series of NbOx-based catalysts and observed that their catalytic performance on MeOH dehydration into DME was favored by high Nb contents.

In light of the above, the goal of this study was to evaluate the performance of Cu-X/V-Al PILC (X = Ce or Nb) catalysts on the production of MeOH and DME from catalytic CO₂ hydrogenation.

2. Experimental

2.1. Preparation of catalysts

A V-Al PILC (Volclay Al-pillared) support was prepared by pillaring montmorillonite (V) with Keggin ion (Al13), as reported in details elsewhere [30]. Chemical analysis of the support by EDS showed the presence of O, Mg, Al, Si, K and Fe at contents of 52.9, 1.4, 15.5, 26.8, 0.4 and 3.0 wt.%, respectively [30].

The Cu-X/V-Al PILC catalysts were prepared by simultaneous impregnation of the support with aqueous solutions of copper and cerium nitrates, or copper and niobium nitrate. The Cu and additives (Ce and Nb) loadings in the support were adjusted to 10 wt.% and 5 wt.%, respectively. The resulting precursors were dried at 80 °C for 24 h and then calcined in air at 500 °C for 3 h. Additionally, one catalyst sample containing only Cu on pillared clay was synthesized under similar conditions. The catalysts samples were designated as CuCe/V-Al PILC, CuNb/V-Al PILC and Cu/V-Al PILC.

2.2. Characterizations

The crystalline structures of catalysts were analyzed by powder X-ray diffraction (XRD). *Ex situ* diffraction patterns (XRD) were obtained on a Rigaku Multiflex diffractometer using Cu K α (1.5406 Å) radiation source. The scan was performed from 10° to 80° at 2° min⁻¹. *In situ* X-ray diffraction patterns were recorded in a D10B-XPB beamline at the National Laboratory of Synchrotron Light (LNLS) in Campinas-Brazil using a Huber diffractometer, Arara furnace and Cyberstar detector. The parameters were: 2 θ range from 30° to 55°, step of 2.51° and 10 s acquisition time per point, with radiation of $\lambda = 1.54996$ Å selected with a Si (111) monochromator. After performing XRD measurements at 25 °C, the samples were heated in a hydrogen-rich atmosphere (5% H₂/He) at flow rate of 100 mL min⁻¹–300 °C (reduction temperature) at 5 °C min⁻¹ for 1 h and new XRD pattern acquisitions were performed.

Temperature programmed reduction (TPR) tests were performed in a Micromeritics Pulse ChemSorb 2750 equipped with a thermal conductivity detector (TCD). The hydrogen consumption

was measured in-line with a TCD. 100 mg of sample were placed in the TPR reactor and reduced with a H₂/Ar mixture (10% v/v) flowing at 30 mL min⁻¹. The temperature was raised to 1000 °C at a heating rate of 5 °C min⁻¹.

The metallic surface area of copper (S_{Cu}) was determined using a N₂O decomposition method [31] in an analytical multipurpose system. Firstly, 100 mg of sample were reduced in a mixture of 1.96% H₂/Ar (flow 30 mL min⁻¹) at 300 °C for 1 h. After, the sample was cooled to 60 °C and a gas mixture (10% N₂O/He) was carried out at flow rate of 30 mL min⁻¹ for 30 min to oxidize the surface CuO atoms producing Cu₂O. Physically adsorbed N₂O was removed by N₂ purging (flow 30 mL min⁻¹) for 1 h. After this step, the sample was cooled to room temperature under N₂ flow and a new reduction cycle was performed to reduce the surface Cu₂O to CuO.

The chemical composition of the catalysts was determined by energy dispersive X-ray spectroscopy (EDS) using a LEO 440 scanning electron microscope equipped with a tungsten filament and coupled to an energy dispersive X-ray detector.

The specific surface area was calculated by the B.E.T method. The area and volume of micropores were determined by t-plot analysis. The data were obtained on a Quantachrome Nova 1000 gas adsorption analyzer. All samples were previously degassed at 250 °C for 4 h.

XANES spectra at the Cu K-edge were recorded *in situ* by transmission mode and under activation condition in the XAFS2 beamline of the LNLS. Initially, XANES spectra were obtained at 25 °C and then from 25 °C to 300 °C at 5 °C min⁻¹ for 1 h in a hydrogen-rich atmosphere (5% H₂/He) with a flow rate of 100 mL min⁻¹.

The quantification of copper species in the Cu K-edge was performed by linear combination analysis (LCA) and principal component analysis (PCA) of XANES spectra, including three model compounds, namely, CuO, Cu₂O and Cu. All analyses were carried out in the MAX-StraightNoChaser XAFS data analysis code [32–34].

The acidity of catalysts was characterized by means of temperature programmed desorption of ammonia (NH₃-TPD) and Fourier transform infrared spectroscopy after pyridine adsorption (Py-FTIR). NH₃-TPD analyses were conducted on an AutoChem II 2920 Micromeritics chemisorption analyzer. 100 mg of sample were pretreated at 550 °C in a He atmosphere (50 mL min⁻¹) for 30 min, cooled to room temperature and reduced at 300 °C for 1 h under flow of 10% H₂/He. Next, the sample was cooled to 120 °C under He flow for 30 min. NH₃ adsorption was carried out at 20 kPa for 30 min with a 15% NH₃/He mixture. Physically adsorbed NH₃ was removed by He purging for 1 h, and the sample was heated at 10 °C min⁻¹ from 50 °C to 900 °C under a He flow (30 mL min⁻¹).

The Py-FTIR spectra were recorded on a Prestigi-21 spectrophotometer in the range of 1800–1400 cm⁻¹. For acidity determinations by FTIR, 50 mg of sample were pretreated in a tubular furnace at 300 °C under N₂ flow of 100 mL min⁻¹ for 1 h. Afterwards, gaseous pyridine (Py) was adsorbed on the sample for 1 h at 150 °C using N₂ gas carrier flowing at 100 mL min⁻¹. The temperature and N₂ flow were maintained for 1 h to eliminate the physically adsorbed pyridine molecules [35].

Temperature programmed desorption of CO₂ (CO₂-TPD) procedure was similar to the NH₃-TPD analysis. Firstly, the sample was reduced at 300 °C for 1 h in a flowing of mixture 10% H₂/He and then cooling down to 50 °C under He flow (30 mL min⁻¹). After that, the catalyst was saturated with CO₂ (30 mL min⁻¹) during 30 min. Afterward, the CO₂-TPD experiment was performed with a heating rate of 10 °C min⁻¹ under He flow (30 mL min⁻¹) until 900 °C.

2.3. Catalytic evaluation

The CO₂ hydrogenation reactions were carried out in a high-pressure reactor (Parr Instruments) at 40 bar containing 0.2 g of

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