



Correlation between synthesis pH, structure and Cu/MgO/Al₂O₃ heterogeneous catalyst activity and selectivity in CO₂ hydrogenation to methanol

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ABSTRACT

Cu/MgO/Al₂O₃ catalysts were synthesized by a co-precipitation preparation method, varying pH, while their catalytic performance was evaluated in a continuous-flow packed-bed reactor to relate the catalytic material activity, selectivity and stability with its surface structure. The major reaction products were methanol and water with CO as a sole process by-product. Alkaline synthesis conditions (pH = 8) positively affected CO₂ conversion and CH₃OH yield (< 250 °C), as CuO and Cu₂O phases were present, since Cu²⁺ was only partially reduced. The hydrogen consumption variation also indicated that these different Cu species changed the interaction with magnesium and alumina. An increase in active basic sites was ascribed to the formation of spinel CuAl₂O₄ and MgAl₂O₄. Alongside with H₂ TPD, XRD and SEM data suggested that a higher precursor solution pH enhanced the dispersion of CuO, enlarged Cu and BET areas, and improved the adsorption of H₂. The XPS profiles of fresh, pre-treated and spent heterogeneous catalysts indicated that the dispersed copper moieties were reduced (to Cu⁰ or Cu⁺) during CO₂ hydrogenation. CO₂ turnover was consistent with metallic atom distribution, derived from N₂O measurements. A maximum TOF of 13.2 × 10⁻⁴ s⁻¹ was obtained over the catalyst, prepared at the pH of 8, whereas a minimum TOF of 5.5 × 10⁻⁴ s⁻¹ corresponded to the pH of 5. A volcano plot-type shape of the productivity and basicity *versus* pH was observed as well, as the highest methanol productivity was attained using the precipitation pH of 8 (200 °C operation).

1. Introduction

The greenhouse effect from CO₂ emissions is considered as one of the most serious environmental problems [1]. On the other hand, CO₂ is a valuable carbon resource that can be transformed into useful chemicals such as methanol, methane, and dimethyl ether etc. [2]. Chemical utilisation of CO₂ is believed to be an effective method for prevention of a further increase in atmospheric CO₂ concentration. Although most of the research focuses on CO₂ hydrogenation to methanol, CO₂ conversions remain low (< 20%) due to difficulties in activating CO₂ [2,3]. Thus, a pressing need for the development of new efficient catalysts with greater activity and methanol selectivity exists. Industrial catalysts, which are active for feed with high CO concentrations are not active with the feed with high CO₂ concentrations [4]. It is well established, however, that copper-based catalysts are typically used for methanol synthesis from CO₂ [5]. Also due to feedstock differences, Cu-ZnO catalysts along with a wide range of metal oxides are investigated for the production of methanol through hydrogenation of CO₂ [1,6,7].

In literature, there are a numerous number of highly active catalysts for CO₂ hydrogenation have been reported, containing copper with various modifiers and supports [5,8,9].

The investigated catalysts were prepared by a conventional co-precipitation method, which is a standard preparation technique for catalyst precursors [10]. Through modification of precipitation parameters, a homogenous dissemination of diverse metal cations in a mixed solution followed by a rapid solidification could result in a multi-catalyst precursor [11]. Upon decomposition and reduction of these precursors, a well mixed and homogeneous metal oxide catalysts with a high dispersion can be formed. A noticeable example is the preparation of Cu/Zn/Al₂O₃ catalysts by the co-precipitation method [12,13]. The final active catalysts are obtained by reduction of CuO to metallic copper under in a hydrogen gas flow. This synthesis route has been previously shown to yield highly active catalysts but is rather complex. [4,10,14]. The synthesis parameters have been well studied and their critical influence termed the “chemical memory of the CuZnAl system” [7,15,16].

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Table 1

Surface area, pore volume, crystallite size, hydrogen consumption (in TPR) and amount of hydrogen desorbed from different Cu/Mg/Al catalysts, prepared under varying pH conditions.

Catalyst preparation pH	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Crystallite Size (nm)	H ₂ consumption (mmol g ⁻¹)	H ₂ -TPD (mmol g ⁻¹)	
					Peak α	Peak β
3	98	0.32	12	5.8	1.1	1
5	65	0.21	18	6.1	1.8	0.9
7	59	0.19	25	6.3	2.3	1.1
8	55	0.18	29	7.8	2.8	1
9	61	0.20	30	8.5	3.5	0.8
11	64	0.21	31	8.6	3.7	1.1

Numerous studies have tried to cover a limited part of full catalyst synthesis and these studies are mainly focused on the binary Cu-Zn systems [17–19]. For the preparation of Cu/ZnO/Al₂O₃ catalysts via co-precipitation through nitrate route, a constant pH is required for the sequential hydrolysis of Cu²⁺ and Zn²⁺, which results in a non-homogenised precipitate [16,20]. A careful monitoring of acidity during the co-precipitation and aging is necessary for this process. At a too low pH some Zn may not be solidified and remains in the mother liquor which cannot be incorporated into zincian malachite precursor phase [7,17]. This can be achieved with increased temperature, but it still influences the tendency of the initial Cu precipitate towards oxidation [4,18].

The active sites in Cu-based catalysts for CO₂ hydrogenation are believed to be Cu⁰, Cu⁺ or both [21]. Many researchers [7,19,21,22] have pointed out that metallic Cu is the active site and that the activity is directly proportional to the Cu surface area. It could be strongly influenced with varying pH during the catalyst preparation [23]. It is widely reported [10,11,23] that the pH of catalyst synthesis affects the surface area, dispersion and morphology of the active metal in the catalyst. There is some doubt whether the catalytic activity increases linearly with the copper surface or differently [3,24]. In addition to the copper surface area, the reducibility of CuO in the catalyst also shows a large effect on the catalytic activity. These properties of copper depending on the basic metal present in the catalyst, e.g. Zn. Methanol selectivity is correlated with the strength and number of basic sites [13,25]. Recently, Zhong et al. [24] have investigated the influence of alkaline earth oxides on the activity of CuO-ZrO₂ catalyst for CO₂ hydrogenation to methanol. They showed that both the surface basicity and copper surface area upraises the catalyst activity. The nature of the metal in Cu/M/Al structure strongly influences the catalytic activity.

Ren et al. [26] have shown that the addition of MgO to Cu-Al catalyst increased the formation of small Cu⁰ particles with a high dispersion and improved the catalytic performance of Cu-based catalysts in methanol synthesis. This is probably due to the synergistic effect of Cu and MgO, and the catalyst basicity. Asthana et al. [27] showed that the presence of MgO increased the selectivity in the Cu-based methanol synthesis. In addition to this, Cu/MgO catalysts are used for low-temperature methanol synthesis using ethanol as a promoter [28].

In our paper, CO₂ hydrogenation to methanol was examined over a series of Cu/Mg/Al catalysts prepared by co-precipitation method at various pH conditions, in a continuous flow fixed-bed reactor to evaluate the catalyst performance. The effect of preparation pH on the performance of Cu/Mg/Al catalyst was investigated in detail with an aim of enhancing catalytic activity and improving the stability of the catalyst.

2. Experimental

2.1. Catalyst preparation

The Cu/Mg/Al catalyst with molar metal ratio Cu:Mg:Al = 50:30:20 was prepared by a co-precipitation method [9] at a pH varying 3–11

and constant temperature (60 °C). A solution containing metal nitrates ([Cu²⁺] + [Mg²⁺] + [Al³⁺] = 1.0 M) and a sodium carbonate solution (1.0 M) were simultaneously added to a reaction vessel containing a small amount of deionised water. The suspension was continuously stirred at 600 rpm and kept at desired pH by adjusting the relative flow rates of two solutions. The final suspension was aged under stirring at 60 °C for 1 h. The precipitate was filtered off and repeatedly washed with sufficient amount of deionised water to ensure that there was no sodium content in the slurry. The solid was dried for 12 h at 90 °C and it was further calcined under a positive flow of air at a temperature of 600 °C for 4 h.

2.2. Catalyst characterisation

To obtain a better insight into the differences caused by varying pH during the catalyst preparation, several characterisation techniques were employed. Powder X-ray diffraction (XRD) was used to elucidate the crystal structure of the catalysts. Then, Brunauer–Emmett–Teller (BET) surface area and pore volume studies were performed. From H₂ temperature programmed reduction (TPR) and CO₂ temperature programmed desorption (TPD), surface species nature and surface basicity were determined, respectively. X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDXS) were also used to further characterise the catalyst properties. The procedure for the characterisation techniques is given in **Electronic Supplementary information**.

2.3. Catalytic testing

Catalytic activity for CO₂ hydrogenation of methanol was evaluated carried out in a continuous-flow, high-pressure fixed-bed reactor. A catalyst (1 mL) was placed in a stainless tube reactor with i.d. of 6.35 mm and length 60 cm, packed in the middle of the tube. Prior to the reaction, catalysts were pre-reduced in a flow of H₂ gas (0.04 g/min) for 12 h at 400 °C under atmospheric pressure.

After the reduction, the reactor was cooled down to room temperature. The catalytic testing was done at a GHSV of 2000 h⁻¹ with a mixture of CO₂ and H₂ gases (1 CO₂:2.8 H₂ molar ratio). The pressure of the reactor was kept constant at 20 bar while varying the temperature from 200 °C to 400 °C with increments of 50 °C. The gas products were analysed using Agilent 490 Micro GC TCD with CP-Molsieve and PoraPolt U columns. Reported values are given after 5 h of the reaction under steady-state conditions. The CO₂ conversion and the carbon-based selectivity of CH₃OH were calculated by an internal normalization method, as:

$$\text{CO}_2 \text{ conversion (mol \%)} = \frac{(x_{\text{CO}}^{\text{out}} + x_{\text{MeOH}}^{\text{out}})}{x_{\text{CO}}^{\text{in}}} (1 - 2x_{\text{MeOH}}^{\text{out}}) \cdot 100 \%$$

$$\text{Selectivity of CH}_3\text{OH (mol \%)} = \frac{x_{\text{MeOH}}^{\text{out}}}{x_{\text{MeOH}}^{\text{out}} + x_{\text{CO}}^{\text{out}}} \cdot 100 \%$$

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