



# Effect of hierarchical meso–macroporous alumina-supported copper catalyst for methanol synthesis from CO<sub>2</sub> hydrogenation



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## ABSTRACT

Effects of pore structures of alumina on the catalytic performance of copper catalysts for CO<sub>2</sub> hydrogenation were investigated. Copper-loaded hierarchical meso–macroporous alumina (Cu/HAl) catalyst exhibited no significant difference in terms of CO<sub>2</sub> conversion with copper-loaded unimodal mesoporous alumina (Cu/UAl) catalyst. However, the selectivity to methanol and dimethyl ether of the Cu/HAl catalyst was much higher than that of the Cu/UAl catalyst. This was attributed to the presence of macropores which diminished the occurrence of side reaction by the shortening the mesopores diffusion path length. The Cu/HAl catalyst also exhibited much higher stability than the Cu/UAl catalyst due to the fast diffusion of water out from the catalyst pellets, alleviating the oxidation of metallic copper to CuO.

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## 1. Introduction

Concerns over depletion of fossil fuels and rising CO<sub>2</sub> emissions are driving the need for recycling CO<sub>2</sub> into alternative fuels. The catalytic hydrogenation of CO<sub>2</sub> to methanol is considered one of the most promising processes because methanol can be used as an energy carrier for fuel cell application [1–3]. Moreover, methanol can be converted to dimethyl ether (DME) [4,5] which is considered as a feasible fuel for diesel engines [6,7], or into higher hydrocarbons according to methanol-to-olefins (MTO) process [8–11].

The catalysts contained Cu as a main component together with different promoters such as Zn, Zr, Ga, Al, Si and Mg [12–14] were found to be active for CO<sub>2</sub> hydrogenation toward methanol. Along with main component, an appropriate support is of imperative importance because it can act not only as dispersant but also as stabilizer for the main component. Moreover, the interface contact between the main component and the support can cause synergistic effect which provides the active centers for adsorption of reactants and products, enhancing the catalytic performance. As a consequence, most of recent studies have focused on the

development of Cu-based catalysts at the nanoscale by means of incorporating promoters [12–15], fine tuning catalyst compositions [12,16] and improving preparation procedure [13,17,18].

Another important impact of supports is the transport of reactants and products. Although the nanoporous catalysts have a large internal surface area which contributes to their high intrinsic catalytic activity per unit catalyst weight, they usually contain small pore size, limiting the molecules' accessibility to the active sites [19–21]. It was reported that the hierarchical meso–macropore structure could diminish diffusion limitations [19,22,23] and extend catalyst lifetime [24–26]. In addition to the activity, the transport of reactants and products within the catalyst pellets might also influence the product selectivity [19,27]. Iglesia [27] proposed that, for Fischer–Tropsch synthesis reaction, the long chain hydrocarbon selectivity was increased by diffusion-enhanced  $\alpha$ -olefin re-adsorption phenomena. Despite the significant number of papers reporting the beneficial effect of the hierarchical porous material, its application as supported copper catalyst for methanol synthesis from CO<sub>2</sub> hydrogenation has not yet been studied.

Herein, we report the diffusion-enhanced effects of the hierarchical meso–macroporous structure of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst for CO<sub>2</sub> hydrogenation reaction. Cu-loaded unimodal porous alumina catalyst was employed for the purpose of comparison. The physicochemical properties of the catalysts were characterized by means of scanning electron microscope (SEM), N<sub>2</sub>-physisorption, mercury porosimetry, X-ray diffraction (XRD), N<sub>2</sub>O chemisorption,

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H<sub>2</sub>-temperature-programmed reduction, pyridine-temperature-programmed desorption.

## 2. Experimental

### 2.1. Preparation of alumina supports

Hierarchical meso–macroporous alumina (HA1) was prepared following the method described by Tokudome et al. [28]. In brief, 0.08 g poly(ethylene oxide) (PEO), having viscosity-averaged molecular weight of  $1 \times 10^6$ , was dissolved in a mixture of 4.0 mL ethanol and 5.5 mL deionized water at room temperature for 12 h. Then 4.32 g aluminum chloride hexahydrate (AlCl<sub>3</sub>·6H<sub>2</sub>O) was added to the PEO–water–ethanol solution that was being stirred at room temperature until the homogeneous solution was achieved. 3.75 mL propylene oxide (PO) was added into the solution in order to initiate the hydrolysis–condensation reaction. After stirring for 1 min, the resultant homogeneous solution was transferred into the glass tube, sealed and kept at 40 °C for gelation. Subsequently, the wet gel was aged for 24 h and dried at 40 °C. The obtained alumina monolith was calcined at 600 °C in air at heating rate of 10 °C/min for 12 h. Unimodal mesoporous alumina (UA1) was prepared using the similar procedure as mentioned above except the addition of PEO.

### 2.2. Preparation of copper-loaded alumina catalysts

In order to clearly distinguish the effects of the presence of macropores, the alumina supports were ground and sieved into two fractions, 0.075–0.090 mm and 0.850–2.000 mm denoted as -S and -L, respectively. 10 wt% copper-loaded alumina catalysts were prepared by incipient wetness impregnation method. The calcined unimodal and hierarchical porous alumina supports were impregnated with the desired amount of copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) in aqueous solution. The slurry mixture was stirred at 60 °C for 2 h, dried at 100 °C for 12 h and calcined at 600 °C and a heating rate of 2 °C/min for 2 h. The copper-loaded unimodal and hierarchical alumina catalysts were designated as Cu/UA1 and Cu/HA1, respectively.

### 2.3. Characterization of copper-loaded alumina catalysts

The surface morphology of the alumina supports was assessed with the application of a scanning electron microscope (SEM; FEI Quanta 450) equipped with energy-dispersive X-ray spectroscopy (EDS). The SEM measurement was taken at 20.0 kV. The samples were sputter-coated with gold prior to analysis.

The elemental analysis of the catalysts was tested with inductively coupled plasma–optical emission spectroscopy (ICP–OES, Optima 4300 DV, Perkin-Elmer).

The macropores size distribution was measured with a mercury porosimetry (PoreMaster 33). The BET surface area, mesopores size distribution and pore volume of the alumina supports and the Cu-loaded alumina catalysts were determined by N<sub>2</sub>-sorption measurement with a Quantachrome Autosorb-1C instrument at –196 °C. The copper (Cu<sup>0</sup>) surface area of the catalysts was obtained by N<sub>2</sub>O-titration measurements as described elsewhere [12].

X-ray diffraction (XRD) patterns of the alumina supports and the Cu-loaded alumina catalysts were attained on a diffractometer (Bruker D8 Advance) with Cu K $\alpha$  radiation. The measurements were made at temperatures in a range of 15–75° on  $2\theta$  with a step size of 0.05°. The diffraction patterns were analyzed according to the Joint Committee on Powder Diffraction Standards (JCPDS).

Temperature programmed reduction (TPR) experiments were conducted using a DSC–TGA 2960 thermal analyzer. A 10 mg

sample was pretreated in a flow of N<sub>2</sub> (100 mL/min) at a rate of 10 °C/min until 400 °C was achieved; the 400 °C temperature was maintained for 30 min, then the sample was cooled to 100 °C. Once the 100 °C temperature was reached and stabilized, the sample was heated under flowing 10% v/v H<sub>2</sub> (He as a balance gas) at a heating rate of 4 °C/min from 100 °C to 400 °C.

Temperature programmed desorption (TPD) experiments were performed with the same apparatus as the TPR measurement using pyridine as a probe molecule following the method described by Mohamed and Abu-Zied [29]. Prior to pyridine adsorptions, the alumina supports and the Cu-loaded alumina catalysts were calcined at 400 °C to remove physically and chemically adsorbed water from their surface. Then the samples were transferred into desiccator containing liquid pyridine. The samples were maintained in contact with pyridine vapor at room temperature for a week, prior to acidity measurements. The pyridine desorption measurement was conducted in a flow of N<sub>2</sub> (100 mL/min) at a heating rate of 4 °C/min from room temperature to 600 °C. The amount of acidity was determined from the weight loss due to the desorption of pyridine.

### 2.4. Catalytic activity test

CO<sub>2</sub> hydrogenation was carried out in a fixed-bed stainless steel reactor (7.75 mm inner diameter). In a typical experiment, 0.5 g catalyst was diluted with 0.5 g inert silica sand. The catalyst was reduced in situ under atmospheric pressure with flowing H<sub>2</sub> (60 mL/min) at 350 °C and a heating rate of 2 °C/min for 4 h. After the reduction, the temperature was cooled to 200 °C under flowing N<sub>2</sub>; subsequently a flow of CO<sub>2</sub> and H<sub>2</sub> mixture (CO<sub>2</sub>:H<sub>2</sub> molar ratio of 1:3) was fed through the reactor. The feed flow rate was set at 60 mL/min. The reactor pressure was slowly raised to 30 bars, and the reactor was heated to a variety of temperatures (240, 260, 280, 300 and 320 °C). The effluent gaseous products were analyzed by using gas chromatography. Analysis of H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub> was performed using GC–2014 gas chromatography equipped with a thermal conductivity detector (TCD) and a Unibead-C column. Methanol, DME and other hydrocarbon products were analyzed by using GC 8A equipped with a flame ionization detector (FID) and a Chromosorb WAW (20% PEG) column. The activity–selectivity data were calculated by mass balance from an average of three independent measurements. The selectivity has been calculated taking into account three major products, including methanol, CO and DME, i.e. only a trace amount of methane was observed at 320 °C which was excluded for selectivity calculation. The errors were within  $\pm 3\%$ . CO<sub>2</sub> conversion, selectivity to methanol, CO and DME are defined as follows:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{(\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}) \times 100}{\text{moles CO}_{2,\text{in}}}$$

$$\text{Methanol selectivity (\%)} = \frac{\text{moles methanol} \times 100}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}}$$

$$\text{CO selectivity (\%)} = \frac{\text{moles CO} \times 100}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}}$$

$$\text{DME selectivity (\%)} = \frac{2 \times \text{moles DME} \times 100}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}}$$

## 3. Results and discussion

The apparent morphology of alumina supports was examined by means of SEM. Hierarchical meso–macroporous alumina (HA1) sample (Fig. 1a) exhibited the presence of 3-dimensionally

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