Preparation and CO$_2$ hydrogenation catalytic properties of alumina microsphere supported Cu-based catalyst by deposition-precipitation method

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ABSTRACT

A series of Cu/ZnO/Al$_2$O$_3$ catalysts with the total weight percentage of Cu and ZnO from 9.94 wt.% to 44.5 wt.% have been prepared by ammonia deposition –precipitation method and tested for methanol synthesis from CO$_2$ hydrogenation. A Cu/Zn/Al layered double hydroxides (LDHs) precursor can be formed in situ on the surface of microspherical Al$_2$O$_3$ which acts as both support and sole source of Al^{3+} cations. With increase of total Cu and ZnO loading, the dispersion of copper and reducibility of CuO decline continuously, while the exposed copper surface area increases gradually. In addition, the formation of LDHs results in a stronger both basicity and acid strength on the catalyst surface. It is found that the CO$_2$ conversion increases linearly with increase of the Cu and ZnO loading. The methanol selectivity for the catalyst with low total metal loading (9.94 wt.%) is much lower than those for other catalysts, though it increases with increasing loading, which can be mainly assigned to the much smaller Cu particle size (<5 nm) and the higher ratio of isolated CuO phase. Moreover, the Cu/ZnO/Al$_2$O$_3$ catalyst with relatively high total metal loading (44.50 wt.%) still exhibits a considerable stable catalytic performance due to the formation of LDH structure.

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1. Introduction

As a cheap, safe, and renewable carbon source for C1 feedstock, chemical utilization of CO$_2$ is very attractive for contributing to mitigate the impact of excess CO$_2$ in the natural environment [1,2]. Particularly, catalytic hydrogenation of CO$_2$ to methanol is the subject of much research interest, because methanol is an easily transportable fuel and it can be used as direct methanol fuel cells [2–4]. Methanol is also a hydrogen storage medium (12.5 wt.% H$_2$) and a common feedstock to produce a wide variety of chemicals and products including high-octane gasoline, aromatics, ethylene and propylene. Moreover, the needed H$_2$ can be generated by electrolysis of H$_2$O using renewable energy sources such as wind, solar, hydroelectric, geothermal, or atomic energy, which may also support this green integrated process.

The majority of research on CO$_2$ hydrogenation to methanol was conducted over Cu/ZnO/Al$_2$O$_3$ catalysts which have been commercially used for methanol synthesis from syngas (CO + H$_2$), however, they exhibited a poor activity and stability for the hydrogenation of CO$_2$ due to the Cu sintering accelerated by the presence of the water vapor byproduct [5–9]. The formation of catalysts with effective control over small particle size and their subsequent immobilization onto a suitable support have both been found to be effective ways of increasing catalytic activity and stability [10]. Spherical alumina has been extensively used as a catalyst support because of its microporosity, large specific surface area, high crush strength, and resistance against acid and alkali. For the preparation of highly loaded and highly dispersed oxide supported metal catalysts, the homogeneous deposition-precipitation (DP) technique has been developed [11–15]. With DP the metal particles obtained after reduction are smaller and exhibit narrower size distribution compared with the impregnation method. In addition, metal particles do not easily sinter due to their strong interaction with the support.

Layered double hydroxide (LDH) is synthetic or natural lamellar hydroxides with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are the di- and trivalent cation distributed in a uniform manner in the hydroxide layers, and A^{n-} represents an exchangeable interlayer anion [10]. By virtue of the wide versatility of LDH composition and architecture, the metal nanoparticles with high dispersion, enhanced synergetic effects among different elements, high stability against sintering and strongly basic properties can be fabricated via calcination and reduction of LDH precursors [7,10,16,17]. Therefore, LDH can be used as precursors for the formation of nanocatalysts with specific morphology/surface structure as well as high dispersion and stability.

In this work, we used the new DP method developed by Lok et al. [18] in which the pH is homogeneously decreased from moderately basic to neutral values by controlled evaporation of ammonia from an ammonia/carbonate buffer solution at 363 K to deposit Cu^{2+} and Zn^{2+} ions on microspherical Al_2O_3. During this procedure, the Cu/Zn/Al-LDH can be formed in situ on the surface of Al_2O_3 particles which act as both support and sole source of Al^{3+} cations. After calcination and reduction, the highly dispersed Cu/ZnO/Al_2O_3 catalysts were obtained and tested for methanol synthesis from CO_2 hydrogenation. In addition, we investigated the effect of the total Cu and ZnO loading on the physicochemical and catalytic properties of the Cu/ZnO/Al_2O_3 catalyst.

2. Experimental

2.1. Preparation of catalysts

CuO/ZnO/Al_2O_3 catalysts were prepared by ammonia deposition-precipitation (ADP) method as follows. An aqueous solution (500 mL) containing $CuCO_3\cdot Cu(OH)_2\cdot H_2$ (AR, 54–57% Cu basis, Aladdin), $3Zn(OH)_2\cdot 2ZnCO_3$ (AR, Aladdin) (Cu/Zn molar ratio of 7/3) and ammonia solution of required amount was placed in a three-necked flask. Then, γ-Al_2O_3 (10 g, 100–200 mesh) was added with vigorous stirring for 1 h to obtain a homogeneous suspension, and the initial pH of the suspension was 11–12. Subsequently, the mixture was kept under stirring at 368 K for 12 h to allow for the evaporation of ammonia and the deposition of metal species on γ-Al_2O_3, and nitrogen was flushed through the system at a rate of 200 mL min^{-1}. After the precipitation was complete, the precipitate was obtained by centrifugation, washed several times with distilled water and dried at 373 K for 12 h. The dried samples were calcined at 623 K in air for 4 h. Metal compositions and nominations of the prepared catalysts are listed in Table 1.

2.2. Characterization of catalysts

The actual metal loading of the catalysts was analyzed by a PE Optima 2100 DV inductive coupled plasma emission spectrometer (ICP).

Crystal and structural characteristics of the samples were investigated by powder X-ray diffraction (XRD) performed on a Rigatku Ultima 4 X-ray diffractometer with Cu Ka radiation (40 kV, 40 mA) in the range of 5°–80° and scanning step length of 0.0167°.

Surface area and pore size of all the samples were determined by N_2 adsorption-desorption at 77 K, using the multipoint BET analysis method, with a TriStar II 3020 instrument. Prior to the measurements, the samples were treated in vacuum at 473 K for 6 h.

Thermal decomposition of the precursors was investigated by the thermogravimetric (TG) method using a STA449-QMS thermal analyzer. Measurements were performed in the temperature range of 313–1073 K with a linear heating rate of 10 K min^{-1} in a continuous flow of synthetic air (30 mL min^{-1}).

The morphology of the samples was observed by a SUPRRATM 55 Scanning electron microscopy (SEM) with an accelerating voltage of 2.0 kV and a Tecnai G220 high-resolution transmission electron microscope (TEM) operated at 200 kV.

Copper dispersion (D_{Cu}) and the specific surface area of metallic copper (S_{Cu}) of catalysts were measured by dissociative N_2O adsorption and carried out on a Micromeritics AutoChem 2920 instrument. In a typical experiment, the catalyst (100 mg) was placed in a U-shaped quartz reactor and reduced by raising the temperature to the reduction temperature (513 K) with a ramp rate of 5 K min^{-1} in 5% H_2/Ar flow (30 mL min^{-1}) for 2 h, followed by cooling to 338 K and isothermally purged with Ar for 30 min. Then the sample was exposed to 30 mL min^{-1} of N_2O flow for 1 h at 338 K, in order to oxidize the surface Cu^0 to Cu^+ by adsorptive decomposition of N_2O. The sample was then flushed with Ar to remove the N_2O and cooled to 323 K. Finally, TPR was carried out on the freshly oxidized Cu_2O surface in order to reduce the Cu_2O to metallic Cu by increasing the temperature to 513 K with 10 K min^{-1} for 1.5 h using 5% H_2/He flow (30 mL min^{-1}). By quantifying the amount of consumed H_2, S_{Cu} of the catalyst was calculated by Eq. (1) [19]. D_{Cu} is defined as the ratio between the surface Cu atoms and the total Cu atoms present in the catalyst. Eq. (2) [20] was used to calculate D_{Cu} from the same experiment.

$$S_{Cu} = \frac{2n_{H_2} \times N}{1.4 \times 10^{19} \times W} (m^2 g^{-1}) \tag{1}$$

$$D_{Cu} = \frac{(2n_{H_2} \times M_{Cu}/W) \times 100\%}{X} \times 100\% \tag{2}$$

where n_{H2} is the molar number of consumed H_2, M_{Cu} is relative atomic mass (63.546 g mol^{-1}), W is the weight of the catalyst, X is the composition of Cu (wt.%) determined by inductive coupled plasma emission spectrometer (ICP), N is Avogadro's constant (6.02×10^{23} atoms mol^{-1}), and 1.4×10^{19} is the number of copper atoms per square meter.

X-ray photoelectron spectroscopy (XPS) was performed using a Quantum 2000 Scanning ESCA Microprobe instrument equipped

Table 1
Physicochemical properties of Cu/ZnO/Al_2O_3 catalysts with different Cu and ZnO loadings.

Samples	Cu/Zn (molar ratio)	Cu + ZnO (wt.%)	Crystallite sizes[a] (nm) CuO	Crystallite sizes[a] (nm) Cu	S_{BET}[b] (m² g⁻¹)	V_P[b] (cm³ g⁻¹)	D_P[b] (nm)	S_{Cu}[c] (m² g⁻¹)	D_{Cu}[c] (%)
Al_2O_3	/	/	/	/	168	0.49	8.94	/	/
CZA-1	2.30	9.94	/	/	141	0.26	6.25	16.3	47.2
CZA-2	2.38	22.76	11.6	12.5	126	0.21	5.17	22.9	34.7
CZA-3	2.37	33.61	12.3	13.3	90	0.19	5.67	31.6	21.1
CZA-4	2.32	44.50	13.8	14.4	93	0.21	7.01	33.5	17.3

[a] Determined from full width at half maxima of CuO (0 0 2) or Cu (1 1 1) XRD peak.
[b] Tested by N_2 adsorption-desorption at 77 K.
[c] Calculated from N_2O dissociative adsorption.