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Highly efficient Cu-based catalysts via hydrotalcite-like precursors for CO_2 hydrogenation to methanol

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ABSTRACT

A series of Cu–Zn–Al–Zr precursor materials are prepared by coprecipitation at different pH values (6.0–11.0) and treated under hydrothermal condition. Zincian malachite is formed as the main phase at the low pH of 6.0 and 7.0, and is replaced by hydrotalcite-like phases with increasing the pH. After calcination and reduction of precursors, $Cu/ZnO/Al_2O_3/ZrO_2$ catalysts are obtained and tested for methanol synthesis from CO_2 hydrogenation at the reaction temperature of 463 K. With increasing pH, the Cu particle size first increases until pH 9.0 and then decreases. Compared with the sample resulting from well-crystallized zincian malachite (pH 7.0), the catalysts derived from phase-pure hydrotalcite-like precursors ($pH \geq 9.0$) exhibit lower BET specific surface area and lower specific Cu surface area. In addition, due to the smaller of Cu particle size and the stronger interaction among Cu and ZnO, the catalytic activity for the $Cu/ZnO/Al_2O_3/ZrO_2$ catalysts via the hydrotalcite-like precursors is higher than that for the catalysts derived from zincian malachite precursors at low reaction temperature. A maximum CH_3OH yield of 0.087 g $gcat^{-1}$ h^{-1} with the CO_2 conversion of 10.7% and the CH_3OH selectivity of 81.8% at 463 K and 5.0 MPa is obtained over the $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst prepared at pH 9.0.

1. Introduction

Catalytic conversion of CO_2 to useful chemicals and fuels is a promising route that may offer a solution to the issues of greenhouse gas control and fossil fuel substitution. Methanol is a common feedstock for several important chemicals and can be used as a fuel additive or clean fuel. It can also be converted to high-octane gasoline, aromatics, ethylene, propylene as well as other useful petrochemicals which now are derived from crude oil [1,2]. In this context, hydrogenation of CO_2 to methanol has attracted much attention from both industry and academia.

The $Cu/ZnO/Al_2O_3$ catalyst, used for methanol synthesis from syngas in industry, is also widely investigated for CO_2 hydrogenation to methanol [3–7]. However, the low activity of industrial $Cu/ZnO/Al_2O_3$ catalysts creates major barriers toward direct application to CO_2 hydrogenation. Especially, at low reaction temperature, their behavior is the deactivation of Cu-based catalysts due to the high activation energy of hydrogen dissociation [8,9]. It has been suggested that the high activity for CO_2 hydrogenation was generated by the presence of surface defects of metallic Cu surface which could reduce the activation energy of hydrogen dissociation [10,11]. In addition, rich surface defects can be achieved by decreasing the size of Cu nanoparticles with a simultaneous high dispersion. Great efforts have been made to decrease the copper particle size for Cu/ZnO-based catalysts by addition of various promoters such as Zr, Ti, Ga, Y, Ce and B [5,12–14]. The influences of synthesis conditions and pre-treatment process on the copper crystallite size of Cu/ZnO-based catalysts were also investigated [15–18].

With the use of Cu–Zn–Al hydrotalcite-like (HTl) precursors, small Cu clusters are generated as the active sites for methanol synthesis from syngas or CO_2 hydrogenation [19–22]. The composite oxides derived from hydrotalcite-like compounds (HTlcs) possess homogeneous dispersion of metal at an atomic level, enhanced synergetic effects among different elements, strong basic properties

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and high stability against sintering [23–25]. Moreover, by virtue of the wide versatility of HTlcs composition and architecture, metal nanoparticles with high dispersion, high density, and good thermal stability for catalysis can be fabricated via reduction of HTl precursors [26]. In our previous work, we presented Cu/ZnO/Al_2O_3/ZrO_2 catalysts with promising catalytic performance in the CO_2 hydrogenation to methanol obtained from HTl precursors [19,27,28], and found that the catalytic activity decreased with significant decrease of the yield of HTl phase in precursors [19]. HTlcs are conventionally synthesized through coprecipitation methods. However, such process suffers from a product with a low crystallinity. Especially, much amorphous phases were formed with the introduction of large radius of metal cations (such as Y^{3+}, Ce^{3+} and Zr^{4+}) into HTl structures [14,19]. The product crystallinity can be affected by various reaction parameters (pH, temperature, concentration and rate of added solutions, and the aging temperature and time) and/or post-synthesis operations (for example, aging of the precipitate) [29]. A substantial improvement of the product crystallinity can be achieved by hydrothermal treatment and the hydrothermal treatment was applied to improve the crystallinity of many kinds of HTlcs [29–31].

Furthermore, the typical hydroxy carbonate precursor phases for industrial Cu/ZnO/Al_2O_3 catalysts are zincian malachite, aurichalcite, or a phase mixture of zincian malachite and aurichalcite [32]. The crystal phase of the precursor was mainly depended on the metal composition, for example, high Al content was favourable for the formation of HTl phase [28] and zincian malachite or aurichalcite phases were formed as a main phase at the low Al content [17]. Al_2O_3 has been pointed out to work as the promoter to increase the stability and the activity [33], thus the Al content will affect the catalytic performance for CO_2 hydrogenation to methanol. So far, few comparative studies on the influences of different precursors with the same metal composition on the catalyst activity exist.

In the present work, a series of Cu–Zn–Al–Zr precursors (Cu^{2+}:Zn^{2+}:Al^{3+}:Zr^{4+} = 2:1:1.2:0.1) were synthesized by coprecipitation method at different pH values (6.0–11.0) and treated under hydrothermal conditions at 293 K. The Cu/ZnO/Al_2O_3/ZrO_2 catalysts were then obtained by calcination and reduction of precursors and tested for methanol synthesis from CO_2 hydrogenation at 463 K. The main focus is to study the effect of pH conditions on physicochemical properties of precursor materials, related mixed oxides, and reduced samples. In addition, the effects of pH of preparation on the catalytic performance were investigated for the structure–activity relationship. This work also allowed us to investigate how different precursors can affect the catalytic activity for CO_2 hydrogenation to methanol.

2. Experimental

2.1. Preparation of catalysts

Cu/ZnO/Al_2O_3/ZrO_2 catalysts with Cu^{2+}:Zn^{2+}:Al^{3+}:Zr^{4+} = 2:1:1.2:0.1 were synthesized by a co-precipitation method at 293 K. Typically, two aqueous solutions, a solution of the metal nitrates and a mixed solution of NaOH and Na_2CO_3 precipitant, were added dropwise to 200 mL of deionized water under vigorous stirring. The mixed solution was conducted at pH range of 6.0–11.0. The product was then transferred into the Teflon coated stainless steel autoclave for hydrothermal treatment at 373 K for 16 h under autogenous water vapor pressure. After the hydrothermal treatment, the precipitate was filtered and washed with deionized water. The filter cakes were dried overnight at 353 K. The samples were calcined in air at 773 K for 5 h, and the obtained samples were crushed and sieved to particles in the range of 40–60 mesh. The as-obtained precursors with different pH were denoted as HT-*n* (*n* is pH during precipitation), and the corresponding calcined and reduced samples were denoted as CHT-*n* and RHT-*n*, respectively.

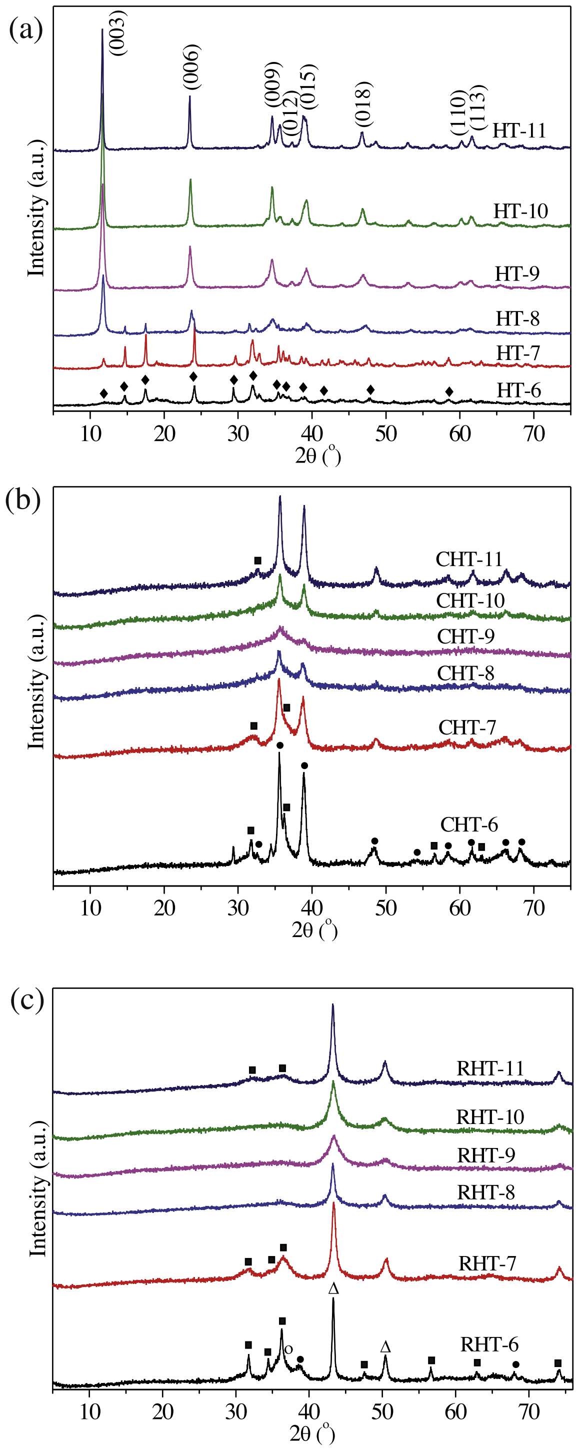

Fig. 1. XRD patterns of (a) uncalcined materials, (b) calcined samples and (c) reduced Cu/ZnO/Al_2O_3/ZrO_2 catalysts preapred at various pH conditions. (♦) Zincian malachite, $(Cu,Zn)_2(OH)_2CO_3$; (Δ) Cu; (○) Cu_2O; (●) CuO; (■) ZnO.

2.2. Characterization of catalysts

The chemical composition of the calcined samples was determined by X-ray fluorescence (XRF) spectroscopy (PW2404 X-ray wavelength dispersive spectrometer).

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