available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013))

Selective hydrogenolysis of glycerol to propylene glycol on hydroxycarbonate-derived Cu-ZnO-Al₂O₃ catalysts

Shuai Wang, Haichao Liu*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:

Received 20 March 2014

Accepted 27 March 2014

Published 20 May 2014

Keywords:

Glycerol

Selective hydrogenolysis

Propylene glycol

Copper

Zinc oxide

Alumina

Hydroxycarbonate precursor

Structure-activity relationship

Stability

ABSTRACT

Three Cu-ZnO-Al₂O₃ catalysts with similar compositions were prepared by homogeneous coprecipitation (CZA-HP), deposition-precipitation (CZA-DP), and conventional coprecipitation (CZA-CP). A Cu-ZnO catalyst was also prepared by homogeneous coprecipitation (CZ-HP) for reference. X-ray diffraction results showed that the degree of mixing of Cu²⁺, Zn²⁺, and Al³⁺ ions in the Cu-Zn-Al hydroxycarbonate precursor followed the order of CZA-DP < CZA-HP < CZA-CP. A more homogeneous aluminum distribution and intimate contact between Al₂O₃ and ZnO led to smaller CuO and ZnO crystallites in the CuO-ZnO-Al₂O₃ composite oxides, and consequently smaller Cu and ZnO crystallites in the final Cu-ZnO-Al₂O₃ catalysts. However, the intimate ZnO-Al₂O₃ contact hindered the interaction between Cu and ZnO in the Cu-ZnO-Al₂O₃ catalysts. As a result of these effects of Al₂O₃, for the samples other than CZA-CP, the Cu particles on CZA-HP showed the highest redox activity, which was characterized by N₂O chemisorption-H₂ temperature-programmed reduction. These catalysts catalyzed glycerol hydrogenolysis to propylene glycol with high selectivities above 90% at 30% glycerol conversion (473 K and 6.0 MPa H₂). Their activities normalized per exposed surface Cu atom to give turnover frequencies increased in the order CZA-DP < CZA-CP < CZ-HP < CZA-HP, which was the order of the redox ability of the Cu particles. The addition of alumina increased the stability of Cu-ZnO catalysts. After six cycles (6 h per run), the activity of CZ-HP decreased by 45% accompanied by an increase of Cu crystallite size from 13.2 to 45.2 nm, while that of CZA-HP decreased only by 10% with an increase of the Cu crystallite size from 8.3 to 19.0 nm. These results demonstrated the promoting effects of Al₂O₃ on the activity and stability of Cu-ZnO catalysts derived from the hydroxycarbonates.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Glycerol hydrogenolysis to propylene glycol has been intensively studied in the past decade as an alternative route for the efficient utilization of surplus glycerol, an inevitable byproduct of biodiesel processes [1–5]. Cu-based catalysts, such as Cu-ZnO [6], Cu-SiO₂ [7,8], Cu/Al₂O₃ [9], Cu-ZnO-Al₂O₃ [10,11], and

Cu/MgO-Al₂O₃ [12], exhibit high selectivity for propylene glycol (above 90%) even at high glycerol conversions (> 75%). In contrast, catalysts containing Group VIII metals, such as Ru, Rh, Pt, and Ni, tend to cleave the C–C bonds of glycerol leading to the formation of ethylene glycol and even methane [13–16]. Despite the superior selectivity of Cu-based catalysts, they possess inferior intrinsic activity and especially hydrothermal

* Corresponding author. Tel/Fax: +86-10-62754031; E-mail: hcliu@pku.edu.cn

This work was supported by the National Basic Research Program of China (973 Program, 2011CB201400, 2011CB808700) and the National Natural Science Foundation of China (21173008, 21373019, 51121091).

DOI: 10.1016/S1872-2067(14)60094-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 5, May 2014

stability compared with the Group VIII metals [1,2]. Therefore, the design of novel Cu-based catalysts is focused on how to improve the activity of Cu and its stability under the hydrothermal reaction conditions of glycerol hydrogenolysis [17–20]. Small Cu particles and a strong Cu-support interaction can promote the redox ability of the Cu particles, and consequently their hydrogenolysis activity, according to the proposed mechanism involving glycerol dehydrogenation to glyceraldehyde on the metal surface as the kinetically relevant step [6,13]. The use of a hydrothermally stable support can prevent the agglomeration of the Cu particles during the hydrogenolysis in the aqueous phase [21]. For instance, Bienholz et al. [22] found that the introduction of Ga_2O_3 into Cu-ZnO catalysts remarkably enhanced the stability of the Cu particles, which showed essentially no loss of activity (less than 10%) after four reaction cycles with a total reaction time of 20 h at 473 K and 5.0 MPa H_2 .

Our previous studies have shown that the homogeneous mixing of Cu^{2+} and Zn^{2+} ions in the Cu-Zn hydroxycarbonate prepared by homogeneous coprecipitation using urea hydrolysis favored the formation of small Cu particles with a strong Cu-ZnO interaction in the resulting Cu-ZnO catalyst, and this catalyst gave good activity in glycerol selective hydrogenolysis to propylene glycol [6,23]. In this work, Al_2O_3 was introduced into the Cu-ZnO catalysts in order to increase the activity and stability of the Cu particles, based on the consideration of the much larger surface area and better thermal stability of Al_2O_3 compared with ZnO [24]. The promoting effects of Al_2O_3 were elucidated from a comparison of three Cu-ZnO- Al_2O_3 catalysts prepared by different coprecipitation methods. A correlation between the structure of the Cu-ZnO- Al_2O_3 catalysts and their hydroxycarbonate phase was also revealed.

2. Experimental

2.1. Preparation of the catalysts

Three Cu-Zn-Al hydroxycarbonate precursors with a Cu:Zn:Al molar ratio of 40:40:20 were prepared by homogeneous coprecipitation [25], deposition-precipitation [8], and conventional coprecipitation methods [26]. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were the metal sources (Beijing Chemicals, AR grade). For the homogeneous coprecipitation method, the metal nitrates with the desired Cu:Zn:Al molar ratio and urea (Beijing Chemicals, AR grade) were dissolved together in 100 mL H_2O . The total concentration of the cations was 0.30 mol/L, while the urea concentration was 3.0 mol/L. The aqueous solution was heated to 373 K and maintained at 373 K for 3 h to form the Cu-Zn-Al hydroxycarbonate. A Cu-Zn hydroxycarbonate with a Cu:Zn molar ratio of 50:50 was also prepared by the same method for reference. For the deposition-precipitation method, the procedure was similar to the homogeneous coprecipitation method except that $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was replaced by an $\text{Al}(\text{OH})_3$ gel. The $\text{Al}(\text{OH})_3$ gel was prepared using the same homogeneous coprecipitation method via urea hydrolysis. For the conventional coprecipitation method, a solution of the three metal nitrates and a solution containing NaOH (0.34 mol/L, Beijing Chemicals, AR grade) and

Na_2CO_3 (0.060 mol/L, Beijing Chemicals, AR grade) were placed simultaneously into 50 mL H_2O under vigorous stirring at room temperature. The resulting precipitate was aged overnight in the mother liquor. The pH value was kept at 9–10 during the solution addition and aging. The precipitate from each of the above three methods was filtered and washed with deionized water until the filtrate was neutral. The precipitate was subsequently heated in ambient air at 383 K overnight and at 673 K for 4 h. The Cu-ZnO and Cu-ZnO- Al_2O_3 catalysts were obtained after a treatment in 20% H_2/N_2 flow (Beijing Huayuan, certified mixture) at 623 K for 4 h. Inductively coupled plasma (Vario EL) analysis showed that the average Cu:Zn molar ratio of the Cu-ZnO catalyst prepared from the homogeneous coprecipitation method was 51:49. The Cu:Zn:Al molar ratios in the Cu-ZnO- Al_2O_3 catalysts prepared from the homogeneous coprecipitation, deposition-precipitation, and conventional coprecipitation methods were 39:39:22, 39:42:19, and 40:39:21, respectively. The compositions of these Cu-based catalysts were all close to their nominal values.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) measurements ($2\theta = 10^\circ\text{--}80^\circ$) were carried out on a Rigaku D/MAX-2400 diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 100 mA. The Scherrer equation was applied to calculate the crystallite sizes of ZnO, CuO, and Cu. N_2 physisorption was performed on an ASAP 2010 analyzer (Micromeritics) after the sample was evacuated (< 2.66 Pa) at 393 K for 4 h. The specific surface area was evaluated from the adsorption data using the BET method. Cu dispersion was obtained using a dissociative N_2O adsorption- H_2 temperature-programmed reduction (H_2 -TPR) method on a flow unit (TP5000, Tianjin Xianquan) [6]. A fresh Cu catalyst was exposed to a 5% $\text{N}_2\text{O}/\text{He}$ mixture (40 mL/min, Beijing Huayuan) at 323 K for 0.5 h to oxidize the surface Cu sites to Cu_2O . The resulting sample was cooled to room temperature in He flow (40 mL/min, Beijing Huayuan), and then H_2 -TPR was performed in 5% H_2/N_2 flow (40 mL/min, Beijing Huayuan). H_2 consumption was quantitatively measured by a thermal conductivity detector.

2.3. Glycerol hydrogenolysis reaction

10 wt% glycerol (50 g, AR, Beijing Chemical) aqueous solution and a weighted amount of Cu catalyst were placed in a teflon-lined stainless steel autoclave (100 mL). The glycerol hydrogenolysis reaction was run at 6.0 MPa H_2 and 473 K with a stirring speed of 800 r/min. The used catalyst and liquid product were separated by filtration after the reaction. A gas chromatograph (Agilent 7890A GC) with a capillary column (AT-Aquawax: 30 m $\times$ 0.25 mm $\times$ 0.25 μm) connected to a flame ionization detector was used to analyze the liquid product. Volatile compounds such as methanol and 1-propanol were quantified with an internal standard of 1-butanol, while high boiling point compounds such as glycerol, propylene glycol, and ethylene glycol were quantified with an internal standard of 1,4-butanediol. The gas product, which was mainly methane

and CO₂, was analyzed using a Porapak Q column and a thermal conductivity detector. Good carbon balances were achieved in the product analysis (100% ± 5%). As with our previous reports [6,13,20], the activity was described by the molar glycerol conversion per mole of exposed Cu atoms (obtained from the measurement of Cu dispersion) and product selectivities were calculated on the carbon basis.

3. Results and discussion

3.1. Synthesis of the Cu-Zn-Al hydroxycarbonate precursor

The catalytic activity of Cu-ZnO-based catalysts synthesized by coprecipitation methods is closely related to their hydroxycarbonate precursor [27–29]. For instance, aurichalcite (Cu_xZn_{1-x})₅(OH)₆(CO₃)₂ and rosasite (Cu_xZn_{1-x})₂(OH)₂CO₃ (0 < x < 1) are both made of MO₆ octahedral units (M = Cu and Zn), with the CuO₆ and ZnO₆ units being distributed more homogeneously and intimately in the former crystalline phase [30]. In line with their structural difference, Cu-ZnO catalysts derived from the aurichalcite precursor showed smaller Cu cluster sizes and a stronger interaction between Cu and ZnO than those derived from the rosasite precursor [27]. It has been consistently found that aurichalcite is a superior Cu-ZnO precursor compared with rosasite in glycerol hydrogenolysis [6]. By following the same rule, the effects of aluminum in the ternary Cu-ZnO-Al₂O₃ catalysts can be traced back to the connections between the CuO₆, ZnO₆, and AlO₆ octahedral units in the hydroxycarbonate precursors [28,31].

Homogeneous coprecipitation by urea hydrolysis was applied here to prepare a Cu-ZnO-Al₂O₃ catalyst with a Cu:Zn:Al molar ratio of 40:40:20. A Cu-ZnO catalyst (Cu:Zn = 50:50 in molar units) was also prepared using the same method for comparison. These were labeled as CZA-HP and CZ-HP in this work, respectively. Figure 1 shows the XRD patterns for the hydroxycarbonate precursor of the two catalysts. The hy-

droxycarbonate precursor of CZ-HP consists of a pure aurichalcite crystalline phase with the characteristic diffraction peaks at 13.0°, 24.2°, and 34.3° (JCPDS 17-074). In contrast, the diffraction peaks for CZA-HP were broadened with several new peaks at 14.6°, 17.5°, and 19.4°. The peaks at 14.6° and 17.5° were assigned to rosasite (JCPDS 36-1475), while the peak at 19.4° was assigned to an undefined Zn-Al hydroxycarbonate crystalline phase [32]. The introduction of aluminum has decreased the degree of crystallization and produced a new phase in the Cu-Zn-Al hydroxycarbonate formation.

It is known that Al³⁺ ions do not easily coprecipitate with Cu²⁺ ions to form a single Cu-Al hydroxycarbonate phase because of the distorted coordination of Cu²⁺ ions due to the Jahn-Teller effect [26]. Therefore, during the coprecipitation of the three cations, the Al³⁺ ions were partly replaced by the Zn²⁺ ions in the aurichalcite phase, leading to the broadening of the diffraction peaks, and the other Al³⁺ ions coprecipitated with Zn²⁺ ions to form a separate Zn-Al hydroxycarbonate phase. These two effects drove the expulsion of Zn²⁺ ions from the Cu-Zn hydroxycarbonate. According to our previous study, aurichalcite is thermodynamically favored when the Cu/Zn molar ratio is below one, while rosasite is thermodynamically favored when the Cu/Zn molar ratio is above one [6]. As a consequence, the decrease of the Zn²⁺ content in the Cu-Zn hydroxycarbonate caused part of the aurichalcite precursor to transform to rosasite, as shown by the XRD results (Fig. 1). It indicated that the homogeneous coprecipitation of the Cu²⁺, Zn²⁺, and Al³⁺ ions by urea hydrolysis actually produced a mixture of different Cu-Zn-Al hydroxycarbonates.

Cu-ZnO-Al₂O₃ catalysts with the same Cu:Zn:Al molar ratio of 40:40:20 were also prepared by deposition-precipitation and conventional coprecipitation to modify the structure of the Cu-Zn-Al hydroxycarbonates. For the deposition-precipitation method, Cu²⁺ and Zn²⁺ ions were coprecipitated by urea hydrolysis from a well-dispersed Al(OH)₃ gel in an aqueous solution [8]. The effect of aluminum introduction on Cu-Zn hydroxycarbonate formation is minimized in the deposition-precipitation method because the Al³⁺ ions are precipitated in the form of amorphous Al(OH)₃ before the coprecipitation of the Cu²⁺ and Zn²⁺ ions. In line with this hypothesis, the Cu-Zn-Al hydroxycarbonate prepared by deposition-precipitation (denoted as CZA-DP) presented a similar XRD pattern for the binary Cu-Zn hydroxycarbonate (CZ-HP), except that there were the additional weak diffraction peaks at 14.6° and 17.5° of rosasite (Fig. 1) as a result of the Ostwald ripening of the Al(OH)₃ gel and Cu-Zn hydroxycarbonate in the mother liquor. It was clear that CZA-DP contained a physical mixture of amorphous Al(OH)₃ and aurichalcite. In contrast, a monophasic hydrotalcite-like Cu-Zn-Al hydroxycarbonate ((Cu,Zn)_{1-x}Al_x)(OH)₂(CO₃)_{x/2} (0 < x < 1), denoted as CZA-CP, was obtained by the conventional coprecipitation method using NaOH and Na₂CO₃ as precipitants [26]. As shown in Fig. 1, a pure hydrotalcite-like pattern with characteristic diffraction peaks at 11.7°, 23.4°, 34.6°, and 38.9° (JCPDS 37-629) was observed for CZA-CP, in which Cu²⁺, Zn²⁺, and Al³⁺ ions were distributed homogeneously at an atomic level.

In summary, structural control of the Cu-Zn-Al hydroxycar-

Fig. 1. XRD patterns of the Cu-Zn-Al hydroxycarbonate precursors prepared via homogeneous coprecipitation (CZA-HP), deposition-precipitation (CZA-DP), and conventional coprecipitation (CZA-CP), and for comparison a pure aurichalcite Cu-Zn hydroxycarbonate precursor prepared via homogeneous coprecipitation (CZ-HP).

bonate precursor was achieved in the different coprecipitation methods. The degree of mixing of the Cu^{2+} , Zn^{2+} , and Al^{3+} ions for the three samples followed the order of $\text{CZA-DP} < \text{CZA-HP} < \text{CZA-CP}$. We envisage that the difference in the distribution of the three cations in the hydroxycarbonate precursors will result in different activities for the $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts in glycerol hydrogenolysis.

3.2. Structural characterization of the hydroxycarbonate-derived $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts

Calcination of the Cu-Zn-Al hydroxycarbonate precursors in air at 673 K led to ternary $\text{CuO-ZnO-Al}_2\text{O}_3$ composite oxides. Their XRD patterns were similar to that for the binary CuO-ZnO sample formed from the Cu-Zn hydroxycarbonate (CZ-HP). As shown in Fig. 2, only monoclinic CuO ($2\theta = 32.5^\circ, 35.7^\circ, 38.9^\circ$, and 49.0°) and hexagonal ZnO ($2\theta = 31.8^\circ, 34.4^\circ, 36.3^\circ$, and 47.5°) appeared in the three $\text{CuO-ZnO-Al}_2\text{O}_3$ composite oxides. There was neither detectable crystalline Al_2O_3 phase nor new mixed phases of CuO , ZnO , and Al_2O_3 . Compared with the binary CuO-ZnO composite oxide, the introduction of aluminum led to the broadening of the diffraction peaks, and the broadening increased with the degree of mixing of the Cu^{2+} , Zn^{2+} , and Al^{3+} ions in the Cu-Zn-Al hydroxycarbonate precursors ($\text{CZA-DP} < \text{CZA-HP} < \text{CZA-CP}$). More broadening reflects a smaller crystallite size. In line with the broadening trend, the measured crystallite sizes of the CuO in the oxide precursors of CZ-HP, CZA-DP, CZA-HP, CZA-CP were 10.4, 9.3, 4.5, and 3.0 nm, respectively, while the corresponding sizes of ZnO were 11.8, 8.4, 6.0, and 4.1 nm, respectively (Table 1). This supported the observation that the CuO_6 and ZnO_6 octahedral units were dispersed by amorphous alumina during the formation of the hydroxycarbonate precursor, which in turn decreased the crystallite sizes of the CuO and ZnO domains in the composite oxides, due to the much larger surface area and higher thermal stability of the amorphous alumina. In agreement with this, the surface area of the CZ-HP oxide precursor was only $29 \text{ m}^2/\text{g}$, while those of CZA-DP, CZA-HP, and CZA-CP were 65, 101, and 97

Table 1

BET surface area, Cu dispersion, and crystallite sizes for the Cu-ZnO catalysts before and after H_2 reduction at 623 K.

Catalyst	S_{BET} (m^2/g)		D_{Cu}^a	d_{CuO}^b	d_{Cu}^b	d_{ZnO}^b (nm)	
	Oxide	Reduced	(%)	(nm)	(nm)	Oxide	Reduced
CZ-HP	29	27	9.8	10.4	13.2	11.8	17.0
CZA-DP	65	65	13.8	9.3	10.9	8.4	9.1
CZA-HP	101	84	15.1	4.5	8.3	6.0	6.9
CZA-CP	97	88	20.7	3.0	7.4	4.1	4.9

^a Dispersions of Cu particles determined by the N_2O decomposition method.

^b Crystallite sizes calculated from XRD.

m^2/g , respectively (Table 1).

The $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts were obtained by reduction of the $\text{CuO-ZnO-Al}_2\text{O}_3$ composite oxides in H_2 at 623 K. Figure 3 shows that the diffraction peaks of CuO in the oxide samples ($2\theta = 32.5^\circ, 35.7^\circ, 38.9^\circ$, and 49.0°) were replaced by the peaks at 43.4° and 50.6° of a cubic Cu phase, while no change was detected for the diffraction peaks of the ZnO phase. This demonstrated the complete reduction of CuO to metallic Cu by H_2 . After reduction, the Cu and ZnO crystallite domains became larger compared to CuO and ZnO in the oxide precursors (Table 1). The crystallite sizes of Cu for CZ-HP, CZA-DP, CZA-HP, and CZA-CP were 13.2, 10.9, 8.3, and 7.4 nm, and these of ZnO for them were 17.0, 9.1, 6.9, and 4.9 nm, respectively. It was clear that the more homogeneous distribution of the Cu^{2+} , Zn^{2+} , and Al^{3+} ions in the Cu-Zn-Al hydroxycarbonate precursor led to better dispersion and thermal stability of the Cu and ZnO domains in the resulting $\text{Cu-ZnO-Al}_2\text{O}_3$ catalyst. The thermal stability of the ZnO domains was improved significantly by the introduction of aluminum. The size of the ZnO domains for the three $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts was increased slightly (but remained below 1.0 nm), but the ZnO size in the binary CZ-HP sample was increased from 11.8 to 17.0 nm (by 5.2 nm) after the treatment in H_2 at 623 K. In contrast, no difference was observed in the stability of Cu for these catalysts. This indicated that Al_2O_3 likely had much closer contact with ZnO than with Cu in the $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts, which is consistent with the co-

Fig. 2. XRD patterns of the CuO-ZnO and $\text{CuO-ZnO-Al}_2\text{O}_3$ composite oxides prepared by different methods.

Fig. 3. XRD patterns of the Cu-ZnO and $\text{Cu-ZnO-Al}_2\text{O}_3$ catalysts prepared by different methods.

precipitation procedure for the preparation of the Cu-Zn-Al hydroxycarbonates. As discussed above, Al^{3+} ions are favored to coprecipitate with Zn^{2+} rather than Cu^{2+} because of the Jahn-Teller effect of Cu^{2+} ions.

The catalytic activity of the Cu-ZnO- Al_2O_3 catalysts was related to the dispersion of the Cu particles and their redox ability. The Cu dispersion was measured by the titration of surface Cu atoms with N_2O at 323 K assuming a $\text{N}_2\text{O}/\text{Cu}_{\text{surface}}$ stoichiometry of 0.5 [33]. Table 1 shows that the Cu dispersion for CZ-HP, CZA-DP, CZA-HP, and CZA-CP was 9.8%, 13.8%, 15.1%, and 20.7%, respectively. The good correlation between the Cu dispersion and Cu crystallite size in the Cu-ZnO- Al_2O_3 catalysts implied that most of the Cu particles were accessible on the catalyst surface. In addition, the redox ability of the surface Cu atoms was examined by H_2 TPR of the surface Cu_2O species, which were formed by N_2O oxidation of the pre-reduced Cu-ZnO- Al_2O_3 catalysts. According to our previous study, a lower reduction temperature of the surface Cu_2O species reflects a higher redox activity of the Cu particles [6]. As depicted in Fig. 4, a single TPR peak at 436 K was detected on CZ-HP, which was consistent with the uniformly sized Cu particles derived from the monophasic aurichalcite of the binary Cu-Zn hydroxycarbonate precursor. In contrast, two TPR peaks of Cu_2O species were observed on CZA-HP (431 and 444 K) and CZA-DP (443 and 454 K), indicating the presence of two kinds of Cu particles on the catalyst surface. These reflect different Cu dispersions or different metal-support interactions. As discussed above, the introduction of aluminum into the Cu-Zn hydroxycarbonate precursors by homogeneous coprecipitation and deposition-precipitation induced a phase transition from aurichalcite to rosasite. The Cu particles derived from the rosasite phase were less active than those from the aurichalcite phase. Therefore, the low temperature peak was correlated with aurichalcite, and the high temperature peak with rosasite. This assignment was confirmed by that the area ratio of the high temperature peak to the low temperature peak on CZA-HP was larger than that on CZA-DP (1.4 vs 0.67), in agreement with that CZA-HP possessed a larger fraction of the rosasite phase in its Cu-Zn-Al hydroxycarbonate precursor. Different from

Fig. 4. H_2 -TPR profiles for the Cu-ZnO and Cu-ZnO- Al_2O_3 catalysts prepared by different methods after exposure to N_2O at 323 K.

CZA-HP and CZA-DP, CZA-CP presented a single TPR peak at 447 K, in line with the pure hydrotalcite-like Cu-Zn-Al hydroxycarbonate precursor formed by the conventional coprecipitation method.

The redox activity of the Cu particles in the Cu-ZnO- Al_2O_3 catalysts was determined by two factors, namely, the size of the Cu particles and the interaction between Cu and ZnO. For instance, the redox activity of the Cu particles derived from aurichalcite followed the order of CZA-DP < CZ-HP < CZA-HP. On one hand, the lower activity of CZA-DP compared with CZ-HP indicated that the introduction of aluminum hindered the interaction between Cu and ZnO although the Cu size was smaller in CZA-DP than in CZ-HP (10.9 vs 13.2 nm). On the other hand, the size effect resulted in the higher activity of CZA-HP because the Cu size in CZA-HP was further decreased to 8.3 nm by a better dispersion by alumina. Similarly, the homogeneous mixing of Al_2O_3 gave the less active Cu particles on CZA-CP than those derived from aurichalcite on CZA-HP (447 vs 431 K), although CZA-CP possessed the smallest Cu particles (7.4 nm) of the four catalysts. The hydrotalcite-like Cu-Zn-Al hydroxycarbonate precursor did not give a strong Cu-ZnO interaction in the final Cu-ZnO- Al_2O_3 catalyst [26].

These structural characterization results for the hydroxycarbonate-derived Cu-ZnO- Al_2O_3 catalysts showed that the structure and properties of the Cu particles of the Cu-ZnO- Al_2O_3 catalysts were dependent on their Cu-Zn-Al hydroxycarbonate precursor. This relationship provides a way to tune the activity of the Cu-ZnO- Al_2O_3 catalysts by changing the degree of mixing of aluminum in the Cu-Zn-Al hydroxycarbonate precursor.

3.3. Activity, selectivity, and stability of Cu-ZnO- Al_2O_3 catalysts in glycerol hydrogenolysis

Table 2 shows the activities and selectivities of the Cu-ZnO- Al_2O_3 catalysts in glycerol hydrogenolysis at 473 K and 6.0 MPa H_2 . The glycerol conversions were kept at about 30% to be in the kinetic controlled regime. The activity of the Cu-ZnO- Al_2O_3 catalysts was evaluated by the glycerol conversion rate normalized to the surface Cu atoms of the fresh catalyst, i.e., the turnover frequencies (TOFs). As shown in Table 2, glycerol was converted to propylene glycol with a high selectivity of above 90% on all these Cu-ZnO- Al_2O_3 catalysts regardless of their preparation methods. Ethylene glycol was the main byproduct with a selectivity of 6%–10%, while trace amounts of methanol, 1-propanol, methane, and CO_2 were also detected in the products. In contrast to the similar selectivities, these Cu-ZnO- Al_2O_3 catalysts showed different TOFs in glycerol hydrogenolysis with the order of CZA-HP (5.7 mmol glycerol/(mol Cu_{surf} s)) > CZ-HP (4.6 mmol glycerol/(mol Cu_{surf} s)) > CZA-CP (4.4 mmol glycerol/(mol Cu_{surf} s)) > CZA-DP (2.8 mmol glycerol/(mol Cu_{surf} s)). It was clear that the homogeneous coprecipitation method provided more active Cu-ZnO-based catalysts than the conventional coprecipitation and deposition-precipitation methods.

Our previous study suggested that glycerol first dehydrogenated to glyceraldehyde on the Cu surface [6,20], which then

Table 2Turnover frequency and selectivity in glycerol hydrogenolysis of the Cu-ZnO and Cu-ZnO-Al₂O₃ catalysts.

Catalyst	Conversion (%)	TOF (mmol glycerol/(mol Cu _{surf} s))	Selectivity (%)			
			Propylene glycol	Ethylene glycol	Methanol	Others*
CZ-HP	28.5	4.6	93.9	6.0	0.1	trace
CZA-HP	31.0	5.7	91.6	8.2	0.2	0.1
CZA-DP	30.2	2.8	91.2	8.8	trace	trace
CZA-CP	31.8	4.4	90.1	9.9	trace	trace

Reaction conditions: 10 wt% aqueous glycerol solution 50 g, 473 K, 6.0 MPa H₂, 6 h, ca. 30% glycerol conversion obtained by varying catalyst amount.* Including 1-propanol, methane, and CO₂.

dehydrates to pyruvaldehyde to cleave a terminal C–O bond, followed by sequential hydrogenation to acetol and ultimately propylene glycol (Scheme 1). Alternately, the glyceraldehyde intermediate can dehydrogenate on the Cu surface to 2-hydroxymalonaldehyde, which then cleaves a terminal C–C bond via the retro-Claisen mechanism to formic acid and 2-hydroxyacetaldehyde. Formic acid further decomposes to CO₂ or hydrogenates to methanol, while 2-hydroxyacetaldehyde hydrogenates to ethylene glycol. Glycerol dehydrogenation to glyceraldehyde was assumed to be the rate limiting step. As a consequence, the activity of the Cu-based catalysts correlates with the redox ability of Cu particles, which is consistent with the studies with binary Cu-ZnO catalysts [6]. It is interesting that the TOFs of the Cu-ZnO-Al₂O₃ catalysts in glycerol hydrogenolysis did not strictly follow the redox ability of the Cu particles revealed from the H₂-TPR of surface Cu₂O species. For instance, CZA-HP and CZ-HP showed similar reduction temperatures around 438 K, but CZA-HP gave higher hydrogenolysis activity than CZ-HP (5.7 vs 4.6 mmol/glycerol/(mol Cu_{surf}s)). CZA-CP and CZA-DP also showed similar reduction temperatures around 447 K, but the TOF of CZA-CP was higher than that of CZA-DP (4.4 vs 2.8 mmol glycerol/(mol Cu_{surf}s)), which was close to CZ-HP. This deviation in the correlation came from the increase of Cu particle size in glycerol hydrogenolysis due to that small Cu particles are more active than large Cu particles [6,23]. The Cu particle size on CZ-HP was increased to 17.0 nm after the reaction, while the presence of alumina stabilized the Cu particle size at 13.4 nm on CZA-HP in the reaction. Similarly, the Cu particle size of CZA-CP and CZA-DP were increased to 12.1 and 17.1 nm, respectively. It was obvious that the

Cu-ZnO-Al₂O₃ catalysts derived from the Cu-Zn-Al hydroxycarbonate precursors with atomic mixing of Cu²⁺, Zn²⁺, and Al³⁺ ions, such as CZA-HP and CZA-CP, exhibited higher stability of the Cu particles, and thus higher activity in glycerol hydrogenolysis. The inferior activity of CZA-CP compared with CZA-HP, considering their similar Cu particle sizes and stability, appeared to be due to its superior dispersion of Al₂O₃, which inhibited the interaction between Cu and ZnO. These results suggested that the roles of alumina in hindering Cu-ZnO interaction and in the improvement of Cu dispersion and stability need to be taken into account to optimize Cu-ZnO-Al₂O₃ catalysts.

The promoting effect of alumina on the catalyst stability was examined by comparing CZ-HP and CZA-HP in recycling experiments at 473 K and 6.0 MPa H₂. During the recycling, the used catalysts were collected from the liquid product by filtration, washed sufficiently with deionized water and then dried under vacuum for the next run. As show in Fig. 5, the activity of the two catalysts gradually decreased and reached constant values after four runs. An activity loss of 45% was observed for CZ-HP in six cycles with a total reaction time of 36 h, while the corresponding loss for CZA-HP was only 10%. ICP measurements of the used catalysts showed negligible leaching of Cu during the recycling. Thus, the agglomeration of the Cu particles would be the main reason for their deactivation, which was confirmed by the XRD results revealing that the Cu particle size in the CZ-HP sample after six cycles was increased to 45.2 nm and was much larger than the size for CZA-HP (19.0 nm). Clearly, the addition of alumina into the Cu-ZnO catalysts not only improved the activity of the catalysts, but also prevented

Scheme 1. Pathways for cleavage of C–O and C–C bonds in glycerol hydrogenolysis on Cu-based catalysts [6].

Fig. 5. Glycerol conversions and selectivities for propylene glycol in six consecutive cycles of glycerol hydrogenolysis on a Cu-ZnO catalyst (CZ-HP) (a) and a Cu-ZnO-Al₂O₃ catalyst (CZA-HP) (b) prepared via homogeneous coprecipitation. Reaction conditions: 10 wt% aqueous glycerol solution 50 g, 473 K, 6.0 MPa H₂, 6 h.

their deactivation.

It is worth mentioning that the selectivities of the catalysts remained essentially unaltered in the recycling reactions (Fig. 5), indicating that unlike the activity, the selectivity was not sensitive to the Cu particle size. The underlying reason needs to be clarified. However, we noticed that the presence of Al₂O₃ in the Cu-ZnO based catalysts slightly decreased the propylene glycol selectivity from 93.9% (CZ-HP) to 91.6% (CZA-HP), with a concurrent increase in the ethylene glycol selectivity from 6.0% to 8.2%. A similar decrease of the selectivity to propylene glycol was also found on CZA-CP (90.1%) and CZA-DP (91.2%). We proposed that the selectivity of propylene glycol to ethylene glycol was mainly determined by the dehydration rate of glyceraldehyde to pyruvaldehyde (Scheme 1), which drives the step of C–O bond cleavage. Glyceraldehyde dehydration was suggested to be catalyzed by basic sites on an oxide support when the reaction was carried out in a neutral aqueous solution [13]. Specifically, the acidic α -H of glyceraldehyde is abstracted by the lattice oxygen on ZnO, which is followed by a nucleophilic attack of the β -OH group to form H₂O and pyruvaldehyde (Scheme 2). It is known that Al₂O₃ is more acidic than ZnO [34]. The mixing of Al₂O₃ with ZnO thus decreased the basicity of the support surface, and consequently decreased the glyceraldehyde dehydration rate and the selectivity to propyl-

ene glycol. This is consistent with that fact that CZA-CP with the highest Al₂O₃ dispersion among the three Cu-ZnO-Al₂O₃ catalysts exhibited the lowest selectivity to propylene glycol (Table 2).

4. Conclusions

The activity and stability of Cu-ZnO catalysts in glycerol hydrogenolysis were improved by the addition of Al₂O₃ during the preparation of the Cu-Zn-Al hydroxycarbonate precursor, such as Al-substituted aurichalcite, with a homogeneous mixing of Cu²⁺, Zn²⁺, and Al³⁺ ions at the atomic level. Cu and ZnO domains were dispersed by amorphous Al₂O₃ that gave enhanced thermal stability through an intimate contact between ZnO and Al₂O₃ in the Cu-ZnO-Al₂O₃ catalysts, which resulted in smaller Cu particles, and consequently higher redox ability and superior hydrogenolysis activity. However, too intimate a ZnO-Al₂O₃ contact hinders the strong interaction between Cu and ZnO, which is unfavorable for the activity of the Cu particles. Furthermore, the addition of Al₂O₃ led to a decrease in the basicity of the Cu-ZnO catalysts, and consequently a slight decline in the selectivity to propylene glycol because the cleavage of the terminal C–O bond of glycerol occurs via base-catalyzed glyceraldehyde dehydration. These results showed the improvement in the activity, selectivity, and stability of Cu-ZnO-Al₂O₃ catalysts in glycerol hydrogenolysis by adding Al₂O₃ and using its interaction with Cu and ZnO.

References

- [1] Ruppert A M, Weinberg K, Palkovits R. *Angew Chem Int Ed*, 2012, 51: 2564
- [2] Besson M, Gallezot P, Pinel C. *Chem Rev*, 2014, 114: 1827
- [3] Nakagawa Y, Tomishige K. *Catal Sci Technol*, 2011, 1: 179
- [4] ten Dam J, Hanefeld U. *ChemSusChem*, 2011, 4: 1017
- [5] Zhou C H, Zhao H, Tong D S, Wu L M, Yu W H. *Catal Rev Sci Eng*, 2013, 55: 369
- [6] Wang S, Zhang Y, Liu H. *Chem Asian J*, 2010, 5: 1100
- [7] Huang Z, Cui F, Kang H, Chen J, Zhang X, Xia C. *Chem Mater*, 2008, 20: 5090
- [8] Huang Z, Cui F, Xue J, Zuo J, Chen J, Xia C. *Catal Today*, 2012, 183: 42
- [9] Zhao L L, Chen J X. *Chin J Catal* (赵兰兰, 陈吉祥. 催化学报), 2012, 33: 1410
- [10] Panyada S, Jongpatiwut S, Sreethawong T, Rirksomboon T, Osuwan S. *Catal Today*, 2011, 174: 59
- [11] Zhou Z M, Li X, Zeng T Y, Hong W B, Cheng Z M, Yuan W K. *Chin J Chem Eng*, 2010, 18: 384
- [12] Yuan Z, Wang L, Wang J, Xia S, Chen P, Hou Z, Zheng X. *Appl Catal B*, 2011, 101: 431
- [13] Wang S, Yin K, Zhang Y, Liu H. *ACS Catal*, 2013, 3: 2112
- [14] Feng J, Xiong W, Jia Y, Wang J B, Liu D R, Chen H, Li X J. *Chin J Catal*

Scheme 2. Pathway of glyceraldehyde dehydration on the basic sites of ZnO.

Graphical Abstract

Chin. J. Catal., 2014, 35: 631–643 doi: 10.1016/S1872-2067(14)60094-2

Selective hydrogenolysis of glycerol to propylene glycol on hydroxycarbonate-derived Cu-ZnO-Al₂O₃ catalysts

Shuai Wang, Haichao Liu*
Peking University

The activity and stability of Cu-ZnO catalysts for glycerol hydrogenolysis to propylene glycol were enhanced by the introduction of aluminum in the Cu-Zn hydroxycarbonate precursor in the preparation of the catalyst.

- [1] 冯建, 熊伟, 贾云, 王金波, 刘德蓉, 陈华, 李贤均. 催化学报, 2011, 32: 1545
- [15] Ma L, Li Y M, He D H. *Chin J Catal* (马兰, 李宇明, 贺德华. 催化学报), 2011, 32: 872
- [16] Guan J, Chen X F, Peng G M, Wang X C, Cao Q, Lan Z G, Mu X D. *Chin J Catal* (关静, 陈秀芳, 彭功名, 王喜成, 曹泉, 兰峥岗, 牟新东. 催化学报), 2013, 34: 1656
- [17] Tan H, Hedhill M N, Wang Y, Zhang J, Li K, Sioud S, Al-Talla Z A, Amad M H, Zhan T, Talla O E, Han Y. *Catal Sci Technol*, 2013, 3: 3360
- [18] Durán-Martín D, Ojeda M, Granados M L, Fierro J L G, Mariscal R. *Catal Today*, 2013, 210: 98
- [19] Vasiliadou E S, Eggenhuisen T M, Munnik P, de Jongh P E, de Jong K P, Lemonidou A A. *Appl Catal B*, 2014, 145: 108
- [20] Wang S, Li Y, Liu H C. *Acta Chim Sin* (王帅, 李洋, 刘海超. 化学学报), 2012, 70: 1897
- [21] Montassier C, Dumas J M, Granger P, Barbier J. *Appl Catal A*, 1995, 121: 231
- [22] Bienholz A, Blume R, Knop-Gericke A, Girgsdies F, Behrens M, Claus P. *J Phys Chem C*, 2011, 115: 999
- [23] Wang S, Liu H. *Catal Lett*, 2007, 117: 62
- [24] Behrens M, Zander S, Kurr P, Jacobsen N, Senker J, Koch G, Ressler T, Fischer R W, Schlögl R. *J Am Chem Soc*, 2013, 135: 6061
- [25] Shishido T, Yamamoto M, Li D, Tian Y, Morioka H, Honda M, Sano T, Takehira K. *Appl Catal A*, 2006, 303: 62
- [26] Behrens M, Kasatkin I, Kühl S, Weinberg G. *Chem Mater*, 2010, 22: 386
- [27] Millar G J, Holm I H, Uwins P J R, Drennan J. *J Chem Soc, Faraday Trans*, 1998, 94: 593
- [28] Baltes C, Vukojević S, Schüth F. *J Catal*, 2008, 258: 334
- [29] Behrens M, Schlögl R. *Z Anorg Allg Chem*, 2013, 639: 2683
- [30] Behrens M, Girgsdies F, Trunschke A, Schlögl R. *Eur J Inorg Chem*, 2009: 1347
- [31] Behrens M. *J Catal*, 2009, 267: 24
- [32] Miao S, d'Alnoncourt R N, Reinecke T, Kasatkin I, Behrens M, Schlögl R, Muhle M. *Eur J Inorg Chem*, 2009: 910
- [33] Bond G C, Namijo S N. *J Catal*, 1989, 118: 507
- [34] Wang J, Zeng C. *J Nat Gas Chem*, 2005, 14: 156

Cu-ZnO-Al₂O₃复合催化剂上甘油选择氢解合成丙二醇

王 帅, 刘海超*

北京大学化学与分子工程学院, 北京分子科学国家实验室, 分子动态与稳态结构国家重点实验室, 北京100871

摘要: 分别采用均匀共沉淀法、沉积-沉淀法和传统的共沉淀法制备了3种具有相似组成的Cu-ZnO-Al₂O₃催化剂(CZA-HP, CAZ-DP和CZA-CP); 同时还采用均匀共沉淀法制备了Cu-ZnO催化剂(CZ-HP)以用于比较. X射线衍射表征结果表明, 以上方法制备的Cu-Zn-Al碱式碳酸盐前体中Cu²⁺, Zn²⁺和Al³⁺的混合均匀程度的顺序为CZA-DP < CZA-HP < CZA-CP. Al³⁺分散程度的提高和Al₂O₃与ZnO的紧密接触使得Cu-ZnO-Al₂O₃催化剂中金属Cu和ZnO具有更小的粒径. 但ZnO-Al₂O₃间紧密接触也阻隔了Cu-ZnO-Al₂O₃催化剂中金属Cu与ZnO之间的相互作用. 因此Al₂O₃的添加使得CZA-HP样品上的Cu粒子表现出最强的氧化还原能力. 在473 K和6.0 MPa H₂的反应条件下, 以上三种Cu-ZnO-Al₂O₃催化剂均高选择性地催化甘油氢解为丙二醇(30%甘油转化率下的选择性 > 90%). Cu-ZnO-Al₂O₃催化剂表面单位Cu原子的本征活性顺序为CZA-DP < CZA-CP < CZ-HP < CZA-HP, 与它们的氧化还原能力相一致. 此外, Al₂O₃的添加还显著地抑制了Cu粒子在反应过程中的聚集, 提高了催化剂的稳定性. 经6次循环使用后, CZ-HP中Cu粒子的粒径从13.2增至45.2 nm, 活性相应下降了45%; 而CZA-HP中Cu粒子的粒径从8.3增至19.0 nm, 活性仅下降了10%.

关键词: 甘油; 选择性氢解; 丙二醇; 铜; 氧化锌; 氧化铝; 碱式碳酸盐前体; 构效关系; 催化剂稳定性

收稿日期: 2014-03-20. 接受日期: 2014-03-27. 出版日期: 2014-05-20.

*通讯联系人. 电话/传真: (010)62754031; 电子信箱: hcliu@pku.edu.cn

基金来源: 国家重点基础研究发展计划(973计划, 2011CB201400, 2011CB808700); 国家自然科学基金(21173008, 21373019, 51121091).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

甘油选择性氢解制取丙二醇是利用生物柴油生产过程中大量联产甘油的有效途径之一,并在近十年中得到了广泛的研究^[1–5]. Cu基催化剂,例如, Cu-ZnO^[6], Cu-SiO₂^[7,8], Cu/Al₂O₃^[9], Cu-ZnO-Al₂O₃^[10,11]和 Cu/MgO-Al₂O₃^[12]等,均在高的甘油转化率下(> 75%)表现出高于90%的丙二醇选择性. 与之相反, VIII族金属催化剂,如 Ru, Rh, Pt和Ni等,倾向于断裂甘油的C-C键而生成乙二醇,甚至甲烷等深度氢解产物^[13–16]. 相对于Cu基催化剂突出的丙二醇选择性,其本征催化活性以及水热稳定性却低于VIII族金属催化剂^[1,2]. 因此,如何提高Cu粒子的活性和在甘油氢解反应水热条件下的稳定性是进一步设计合成高效铜基催化剂的关键. 相关研究表明^[6,17],小尺寸的Cu粒子以及金属Cu与载体之间的强相互作用均可以提高Cu粒子的氧化还原活性,从而提高其催化甘油氢解活性. 这缘于甘油在金属表面脱氢为甘油醛是甘油氢解反应的决速步^[6]. 此外,使用高水热稳定性载体可以抑制Cu粒子在水相氢解反应中的聚集^[21]. Bienholz等^[22]发现,在Cu-ZnO催化剂中引入Ga₂O₃显著地提高了Cu粒子的稳定性,循环使用四次后(473 K, 5.0 MPa H₂, 累积反应时间20 h),催化剂活性没有明显下降(< 10%).

我们此前的研究表明,以尿素为沉淀剂的均匀共沉淀方法可以制备Cu²⁺和Zn²⁺离子均匀混合的Cu-Zn碱式碳酸盐前体,从而得到具有小尺寸Cu粒子和强金属-载体相互作用的Cu-ZnO催化剂^[6,23]. 该催化剂在甘油选择氢解反应中表现出良好的活性和丙二醇选择性. 考虑到Al₂O₃具有比ZnO更大的比表面积和更高的水热稳定性^[24],因此,本文进一步引入Al₂O₃到Cu-ZnO催化剂中来提高Cu粒子的分散程度和稳定性,通过比较三种制备方法得到的Cu-ZnO-Al₂O₃催化剂来考察Al₂O₃的促进作用,同时揭示Cu-ZnO-Al₂O₃催化剂的结构与对应Cu-Zn-Al碱式碳酸盐前体晶相组成之间的关联.

2. 实验部分

2.1. 催化剂制备

三种具有相似组成的Cu-Zn-Al碱式碳酸盐前体(Cu:Zn:Al摩尔比为40:40:20)分别采用均匀共沉淀法^[25]、沉积-沉淀法^[8]和传统的共沉淀法^[26]制备. 其中, Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·3H₂O和Al(NO₃)₃·9H₂O为金属盐前体. 在均匀共沉淀方法中,三种金属硝酸盐和尿素按照所需比例溶解于100 mL水溶液中;三种金属离子

的总浓度为0.30 mol/L,而尿素浓度为3.0 mol/L. 将溶液加热至373 K,并保持3 h,从而得到Cu-Zn-Al碱式碳酸盐沉淀. 作为对比,同法制得Cu-Zn碱式碳酸盐(Cu:Zn摩尔比50:50). 沉积-沉淀法具有与均匀共沉淀方法相似的过程,除了Al(NO₃)₃·9H₂O被替换为Al(OH)₃凝胶. 其中, Al(OH)₃凝胶使用相同的均匀共沉淀法制得. 在传统的共沉淀方法中,将含有三种金属离子的水溶液同含有NaOH (0.34 mol/L)和Na₂CO₃ (0.060 mol/L)的水溶液在室温下并流滴入到50 mL去离子水中,之后过夜陈化. 在沉淀和陈化过程中,溶液pH控制在9–10. 通过以上三种方法得到的沉淀通过过滤分离,并使用去离子水充分洗涤至过滤液为中性,在383 K下干燥过夜. 之后,催化剂前体先后在空气气氛中于673 K下焙烧4 h,在20% H₂/N₂中于623 K下处理4 h,从而得到Cu-ZnO以及Cu-ZnO-Al₂O₃等催化剂. 元素分析(Vario EL)的结果表明,所制备的Cu-ZnO催化剂中的平均Cu:Zn摩尔比例为51:49;而通过均匀共沉淀、沉降-沉积和传统的共沉淀方法所制备的Cu-ZnO-Al₂O₃催化剂中的Cu:Zn:Al摩尔比例分别为39:39:22, 39:42:19和40:39:21. 以上元素含量组成均与实际加入值相近.

2.2. 催化剂表征

X射线粉末衍射谱($2\theta = 10^\circ - 80^\circ$)在Rigaku D/MAX-2400衍射仪上采集. 采用Cu K α_1 ($\lambda = 0.15406$ nm)射线,工作电压40 kV,工作电流100 mA. 样品中ZnO, CuO和Cu的晶体粒径通过Scherrer公式计算得到. N₂物理吸附在ASAP 2010吸附仪(Micromeritics)上测量. 测试前,样品于393 K下真空脱气4 h (真空度低于0.67 Pa). 催化剂比表面积通过BET吸附模型计算得到. N₂O 吸附-H₂程序升温还原(TPR)实验在TP5000多用吸附仪(天津先权)上完成^[6]. 使用5% N₂O/He混合气体(40 mL/min)在323 K下处理预还原过铜基催化剂0.5 h,使样品表面的Cu原子计量地氧化为Cu₂O. 之后,样品降至室温,并使用40 mL/min He吹扫掉弱吸附的N₂O. 进一步通过H₂-TPR实验(40 mL/min, 5% H₂/N₂, 室温至573 K, 0.17 K/h)将Cu₂O还原为金属Cu. 所消耗的H₂通过热导检测器(TCD)定量测量,并据此计算Cu粒子的分散度.

2.3. 甘油氢解反应

在反应釜(100 mL)中加入50 g甘油水溶液(10 wt%)和一定量的Cu基催化剂,并通入6.0 MPa H₂. 在800 r/min下将反应釜升温至473 K,进行甘油氢解反应. 反应后的催化剂和液体产物通过常压过滤分离. 液相产物通过气相色谱(Agilent 7890A GC)的氢离子火焰检测器

进行分析, 色谱柱为AT-Aquawax (30 m × 0.25 mm × 0.25 μm). 其中, 使用正丁醇为内标来定量甲醇和正丙醇等低沸点化合物; 使用1,4-丁二醇为内标来定量甘油、丙二醇和乙二醇等高沸点化合物. 气相产物, 主要包括甲烷和CO₂, 通过Porapak-Q色谱柱进行分离, 并使用TCD定量分析. 反应产物的碳平衡为100±5%. 与我们此前的报道一致^[6,13,20], 铜基催化剂的活性以催化剂表面暴露的单位Cu原子上的甘油转化速率来表示, 而甘油氢解产物的选择性以碳原子的选择性来表示.

3. 结果与讨论

3.1. Cu-Zn-Al碱式碳酸盐前体的合成

通过共沉淀法制备的Cu-ZnO催化剂的活性与其碱式碳酸盐前体有密切的关系^[27–29]. 例如, 绿铜锌矿相((Cu_xZn_{1-x})₅(OH)₆(CO₃)₂, 0 < x < 1) 和 偏绿铜锌矿相((Cu_xZn_{1-x})₂(OH)₂CO₃, 0 < x < 1)均由MO₆八面体单元(M = Cu和Zn)连接而成, 然而在绿铜锌矿相中CuO₆和ZnO₆的分布和结合要比在偏绿铜锌矿相更为均匀和紧密^[30]. 与它们的结构差别相一致, 由绿铜锌矿相获得的Cu-ZnO催化剂具有较小的Cu粒子粒径以及较强的Cu-ZnO相互作用^[27], 并在甘油氢解反应中表现出更好的活性^[6]. 根据这一规律, Al₂O₃引入对Cu-ZnO催化剂的影响应该可以追溯回Al₂O₃对CuO₆和ZnO₆等八面体结构单元在对应的Cu-Zn-Al碱式碳酸盐前体中连接情况的影响^[28,31].

以尿素为沉淀剂, 采用均匀共沉淀方法来制备Cu-ZnO-Al₂O₃催化剂(Cu:Zn:Al摩尔比为40:40:20); 作为对比, 同法制备了Cu-ZnO催化剂(Cu:Zn摩尔比为50:50), 分别标记为CZA-HP和CZ-HP. 图1为两种催化剂的碱式碳酸盐前体的XRD谱. CZ-HP的碱式碳酸盐前体在13.0°, 24.2°和34.3°处具有特征衍射峰, 为纯绿铜锌矿相(JCPDS 17-074); 而CZA-HP的碱式碳酸盐前体的衍射峰更为宽化, 并在14.6°, 17.5°和19.4°等处出现新的衍射峰. 其中, 14.6°和17.5°处的衍射峰归属于偏绿铜锌矿相(JCPDS 36-1475), 而19.4°处的衍射峰可能源自一种Zn-Al碱式碳酸盐^[32]. 由此可见, Al源的引入降低了Cu-Zn碱式碳酸盐的晶化程度, 并诱导了新的晶相结构的生成.

由于Jahn-Teller效应所带来的Cu²⁺离子配位环境的畸变, Al³⁺离子并不容易与Cu²⁺离子发生共沉淀^[26]. 因此, 在三种离子的共沉淀过程中, 部分Al³⁺离子与绿铜锌矿中的Zn²⁺离子进行交换, 从而使绿铜锌矿相的晶化程

度降低, 衍射峰相应宽化; 另一部分Al³⁺离子则与Zn²⁺离子共沉淀生成一种独立的Zn-Al碱式碳酸盐晶相. 以上两种影响带来了Cu-Zn碱式碳酸盐中Zn²⁺含量的偏离. 前期的研究表明^[6], 当Cu/Zn摩尔比 ≤ 1 时, 绿铜锌矿相的生成在热力学上更为有利; 当Cu/Zn摩尔比 > 1 时, 偏绿铜锌矿相的生成则更为有利. 因此, 在Cu-Zn碱式碳酸盐中Zn²⁺含量的下降导致了绿铜锌矿相向偏绿铜锌矿相的转变, 与XRD结果一致(图1). 由此可见, 使用尿素水解来均匀沉淀Cu²⁺, Zn²⁺和Al³⁺离子, 实际上得到的是不同Cu-Zn-Al碱式碳酸盐的混合物.

我们进一步通过沉降-沉积和传统的共沉淀方法来制备具有相同Cu/Zn/Al摩尔比例的Cu-ZnO-Al₂O₃催化剂(分别标记为CZA-DP和CZA-CP), 以期调变Cu-Zn-Al碱式碳酸盐前体的晶相组成. 在沉降-沉积方法中, 我们利用尿素水解将Cu²⁺和Zn²⁺离子共沉淀到均匀分散的Al(OH)₃凝胶上^[8]. 由于在Cu²⁺和Zn²⁺离子共沉淀时没有Al³⁺离子的干扰, 从而很大程度地降低了Al源引入所带来的对Cu-Zn碱式碳酸盐晶相结构的影响. 与我们的假设一致, CZA-DP的碱式碳酸盐前体具有与CZ-HP相似的XRD谱. 另外, 在14.6°和17.5°处表现出很微弱的偏绿铜锌矿相的衍射峰(图1), 这可能源自Al(OH)₃凝胶与Cu-Zn碱式碳酸盐在母液中的Ostwald熟化. 因此, CZA-DP碱式碳酸盐前体在组成上可以看做是无定型的Al(OH)₃与绿铜锌矿的混合物. 与此相反, 使用NaOH和Na₂CO₃为沉淀剂的传统共沉淀法可以制备出具有类水滑石晶相结构((Cu,Zn)_{1-x}Al_x(OH)₂(CO₃)_{x/2}, 0 < x < 1)的Cu-Zn-Al碱式碳酸盐^[26]. 如图1所示, CZA-CP的碱式碳酸盐前体的特征衍射峰为11.7°, 23.4°, 34.6°和38.9°, 是典型的类水滑石晶相结构(JCPDS 37-629). 单一的Cu-Zn-Al碱式碳酸盐结构暗示Cu²⁺, Zn²⁺和Al³⁺离子均匀地分布在CZA-CP的碱式碳酸盐前体中.

综上所述, 采用不同的制备方法实现了对Cu-Zn-Al碱式碳酸盐前体晶相组成的调控. Cu²⁺, Zn²⁺和Al³⁺离子在相应碱式碳酸盐前体中的混合均匀程度的顺序为CZA-DP < CZA-HP < CZA-CP. 可以预见, 三种离子在碱式碳酸盐前体中分布均匀程度的差别将会带来Cu-ZnO-Al₂O₃催化剂在甘油氢解反应中催化活性的不同.

3.2. Cu-ZnO-Al₂O₃催化剂的结构表征

Cu-Zn-Al碱式碳酸盐前体在673 K下焙烧后转变为CuO-ZnO-Al₂O₃复合氧化物. 它们的XRD谱与CuO-ZnO二元复合氧化物相似(图2). CuO-ZnO-Al₂O₃复合氧化物

上只出现单斜晶相CuO ($2\theta = 32.5^\circ, 35.7^\circ, 38.9^\circ$ 和 49.0°)以及六方晶相ZnO ($2\theta = 31.8^\circ, 34.4^\circ, 36.3^\circ$ 和 47.5°)对应的特征衍射峰。Al₂O₃呈无定型态。同时, CuO-ZnO-Al₂O₃复合氧化物中没有氧化物之间的共生晶相出现。与CuO-ZnO二元复合氧化物相比, Al₂O₃的引入带来的各晶相衍射峰的宽化, 并且其宽化随Cu²⁺, Zn²⁺和Al³⁺离子在相应碱式碳酸盐前体中的混合均匀程度的增加而更为明显(CZA-DP < CZA-HP < CZA-CP)。衍射峰的宽化意味着晶体粒径的减小。与此相符, 在CZ-HP, CZA-DP, CZA-HP和CZA-CP等复合氧化物中, CuO的晶相粒径分别为10.4, 9.3, 4.5 和3.0 nm; 而对应的ZnO的晶相粒径则分别11.8, 8.4, 6.0和4.1 nm (表1)。以上结果暗示, 在Cu-Zn-Al碱式碳酸盐前体中, CuO₆和ZnO₆八面体结构单元均被无定型的Al₂O₃所分散, 导致复合氧化物中CuO和ZnO晶体粒径的减小。该显著影响缘于无定型Al₂O₃的高比表面积和热稳定性。如表1所示, CZ-HP对应氧化物前体的比表面积仅为29 m²/g, 而CZA-DP, CZA-HP和CZA-CP对应氧化物前体的比表面积则分别为65, 101和97 m²/g。

CuO-ZnO-Al₂O₃ 复合氧化物在623 K用H₂处理4 h后得到Cu-ZnO-Al₂O₃催化剂。图3为各催化剂的XRD谱。经过H₂处理后, ZnO的晶相没有显著变化, 而单斜晶相CuO 对应的衍射峰完全消失。与之相应, 在 43.4° 和 50.6° 处出现新的属于立方相金属Cu的特征峰。结果表明, 在H₂处理过程中CuO被完全还原为金属Cu。相比于在复合氧化物中CuO和ZnO的晶体粒径, Cu-ZnO-Al₂O₃催化剂中金属Cu和ZnO具有更大的尺寸(表1)。其中, CZ-HP, CZA-DP, CZA-HP和CZA-CP的金属Cu的晶体粒径分别为13.2, 10.9, 8.3和7.4 nm; 而对应的ZnO的晶体粒径分别为17.0, 9.1, 6.9和4.9 nm。另外, Cu²⁺, Zn²⁺和Al³⁺离子分散得更为均匀的Cu-Zn-Al碱式碳酸盐前体使Cu-ZnO-Al₂O₃催化剂中的金属Cu和ZnO具有更好的分散程度和热稳定性。特别地, Al₂O₃的引入显著地提高了ZnO的稳定性。三种Cu-ZnO-Al₂O₃催化剂中ZnO的晶体粒径在H₂处理过程中仅略有增长(< 1.0 nm); 而CZ-HP中ZnO的粒径则在此过程中从11.8增长到17.0 nm。不过, 相应催化剂中Cu粒子的稳定性则没有如此明显的区别。这表明在Cu-ZnO-Al₂O₃催化剂中Al₂O₃与ZnO的接触要比与金属Cu的接触更为紧密。这与Cu-Zn-Al碱式碳酸盐前体的制备过程相符。由于Cu²⁺的Jahn-Teller效应, Al³⁺离子更倾向于与Zn²⁺离子共沉淀, 而非Cu²⁺离子。

Cu-ZnO-Al₂O₃催化剂的活性与Cu粒子的分散度和

本征的氧化还原能力相关。Cu粒子的分散度通过在323 K下N₂O的滴定实验来测定, 并假设N₂O与表面Cu原子的化学计量比为0.5^[33]。如表1所示, CZ-HP, CZA-DP, CZA-HP和CZA-CP等催化剂所测得金属Cu的分散度分别为9.8%, 13.8%, 15.1%和20.7%。Cu粒子分散度与其晶体粒径良好的对应关系表明在Cu-ZnO-Al₂O₃催化剂中所有的Cu粒子均暴露在催化剂的表面。此外, 催化剂表面Cu粒子本征的氧化还原能力可以通过N₂O滴定后所形成的表面Cu₂O物种的H₂-TPR过程来考察。研究发现^[6], 金属Cu粒子的氧化还原能力越强, 则其对应表面Cu₂O物种的还原温度越低。如图4所示, CZ-HP上的Cu₂O物种仅在436 K处出现单一的还原峰。这与CZ-HP碱式碳酸盐前体中单一的绿铜锌矿晶相组成相一致。与此相反, 在CZA-HP和CZA-DP上的Cu₂O物种均有两个还原峰, 其还原温度分别为431和444 K, 以及443和 454 K。这表明这两种催化剂表面均至少含有两类金属Cu粒子。这些不同的Cu粒子可能源于不同的分散度或者不同的金属-载体相互作用。如前所述, 在均匀共沉淀和沉降-沉积法中, Al的引入均造成了Cu-Zn碱式碳酸盐前体由绿铜锌矿相向偏绿铜锌矿相的转变。同时, 由偏绿铜锌矿相所得到的Cu粒子的活性要低于由绿铜锌矿相所得到的。因此, 我们推测在所得到的两个还原峰中, 低温的还原峰对应于由绿铜锌矿相所得到的Cu粒子; 而高温的还原峰则对应于由偏绿铜锌矿相所得到的Cu粒子。CZA-HP样品上高温还原峰与低温还原峰的面积比例要高于CZA-DP样品(1.4 vs 0.67), 即CZA-HP的碱式碳酸盐前体中的偏绿铜锌矿的含量要高于CZA-DP的碱式碳酸盐前体, 与XRD结果一致(图1)。与以上两种Cu-ZnO-Al₂O₃催化剂不同, CZA-CP上的Cu₂O物种仅在447 K处出现单一的H₂还原峰。同样, 这与CZA-CP的碱式碳酸盐前体中单一的类水滑石晶相结构相对应。

Cu-ZnO-Al₂O₃催化剂中Cu粒子的氧化还原能力主要取决于Cu粒子的粒径以及金属Cu与ZnO之间的相互作用。例如, 由绿铜锌矿相所得到的Cu粒子的氧化还原能力的关系为CZA-DP < CZ-HP < CZA-HP。一方面, CZA-DP相比于CZ-HP具有更小的Cu粒子粒径(10.9 vs 13.2 nm), 但是Al₂O₃的引入削弱了Cu与ZnO间相互作用, 使得CZA-DP中Cu粒子的氧化还原能力低于CZ-HP; 另一方面, 在CZA-HP中高的Al₂O₃分散程度使Cu粒子的粒径保持在8.3 nm, 明显低于CZA-DP和CZ-HP, 从而表现出更好的氧化还原能力。类似地, 尽管CZA-CP中均匀分散的Al₂O₃使得其中Cu粒子粒径更小(7.4 nm), 但其氧化

还原活性要低于CZA-HP上由绿铜锌矿相所得到的Cu粒子(447 vs 431 K). 这暗示在由类水滑石Cu-Zn-Al碱式碳酸盐前体所制备的Cu-ZnO-Al₂O₃催化剂中金属Cu与ZnO之间没有强的相互作用^[26].

上述结构表征结果表明, Cu-ZnO-Al₂O₃催化剂中Cu粒子的结构和性质与其对应的Cu-Zn-Al碱式碳酸盐前体有着非常密切的关联. 这种关联为进一步调控Cu-ZnO-Al₂O₃催化剂的活性提供了一条有效的途径. 例如, 我们可以有目的地控制Cu-Zn-Al碱式碳酸盐前体中Al³⁺的分散均匀程度.

3.3. Cu-ZnO-Al₂O₃催化剂在甘油氢解反应中的活性、选择性和稳定性

Cu-ZnO-Al₂O₃催化剂在甘油氢解反应中的活性和选择性均在动力学控制的区间内以及~30%的甘油转化率下进行比较(473 K和6.0 MPa H₂). 其中, Cu-ZnO-Al₂O₃催化剂的活性以表面金属Cu原子上的甘油转化速率来表示, 即TOF. 如表2所示, 在三种Cu-ZnO-Al₂O₃催化剂上甘油都高选择性地氢解为丙二醇(选择性 > 90%), 而与它们的制备方法无关. 乙二醇为主要的副产物, 其选择性为6%–10%. 此外, 还检测到微量的正丙醇、CH₄以及CO₂的生成. 与选择性的变化不同, 三种Cu-ZnO-Al₂O₃催化剂表现出明显不同的活性. 它们的活性关系为CZA-HP (5.7 mmol glycerol/(mol Cu_{surf}s)) > CZ-HP (4.6 mmol glycerol/(mol Cu_{surf}s)) > CZA-CP (4.4 mmol glycerol/(mol Cu_{surf}s)) > CZA-DP (2.8 mmol glycerol/(mol Cu_{surf}s)). 可以看到, 通过均匀共沉淀法制备的Cu-ZnO以及Cu-ZnO-Al₂O₃催化剂比其它两种方法制备的催化剂具有更高的本征活性.

根据我们此前对甘油氢解反应路径的研究^[6,20], 甘油首先在金属Cu表面脱氢为甘油醛. 甘油醛通过脱水为丙酮醛来断裂端位的C-O键, 并继续加氢得到羟基丙酮和丙二醇(图示1). 此外, 甘油醛还可以进一步在Cu表面上脱氢为2-羟基丙二醛. 2-羟基丙二醛通过retro-Claisen机理断裂端位的C-C键以得到甲酸和2-羟基乙醛. 一方面, 甲酸在反应条件下分解为CO₂和H₂, 或者加氢为甲醇. 另一方面, 2-羟基乙醛加氢得到乙二醇. 在以上反应路径中, 甘油脱氢为甘油醛很可能是反应的速率控制步骤. 与这一推测相一致, 我们在研究Cu-ZnO催化剂时发现铜基催化剂的活性与Cu粒子的氧化还原能力有着很好的对应关系^[6]. 不过结合表2发现, Cu-ZnO和Cu-ZnO-Al₂O₃催化剂的TOF与根据N₂O吸附-H₂-TPR实验所揭示的表面Cu粒子的氧化还原能力并没

有严格的对应关系. 例如, CZA-HP和CZ-HP上的Cu₂O物种具有相似的平均还原温度(~438 K), 但是CZA-HP催化剂的活性却高于CZ-HP催化剂(5.7 vs 4.6 mmol glycerol/(mol Cu_{surf}s)). 类似的, CZA-CP和CZA-DP上的Cu₂O物种具有相似的平均还原温度(~447 K), 然而CZA-CP的TOF是CZA-DP的1.6倍(4.4 vs 2.8 mmol glycerol/(mol Cu_{surf}s)), 与CZ-HP的TOF相近. 我们发现这种对应关系的偏离缘于Cu粒子粒径在催化甘油氢解反应时的增长, 因为小粒径Cu粒子的活性要明显高于大粒径的^[6,23]. 对于CZ-HP催化剂, Cu粒子在反应后增长至17.0 nm, 而Al₂O₃的存在使CZA-HP中的Cu粒子粒径在反应后仍稳定在13.4 nm. 同样地, CZA-CP和CZA-DP中Cu粒子在反应后的粒径分别增长为12.1和17.1 nm. 可以明显看到, 当Cu-Zn-Al碱式碳酸盐前体中的Cu²⁺, Zn²⁺和Al³⁺离子在原子尺度上混合时, 其所对应的Cu-ZnO-Al₂O₃催化剂, 如CZA-HP和CZA-CP, 具有更好的Cu粒子稳定性, 从而在甘油氢解反应中表现出更高的活性. 此外, 尽管CZA-HP和CZA-CP具有相似的Cu粒子尺寸和稳定性, CZA-CP催化剂的活性却要低于CZA-HP. 这说明在CZA-CP催化剂中过高的Al₂O₃的分散程度在一定程度上抑制了金属Cu与ZnO间相互作用, 造成Cu粒子活性的降低. 由此可见, Al₂O₃对Cu粒子分散度和稳定性的促进作用以及Al₂O₃对Cu-ZnO相互作用的削弱在优化Cu-ZnO-Al₂O₃催化剂时需要同时考虑.

我们在473 K和6.0 MPa H₂的反应条件下比较了CZ-HP和CZA-HP催化剂在循环反应中的活性变化, 以进一步考察Al₂O₃对催化剂稳定性的促进作用. 在反应循环时, 使用的催化剂通过过滤与液相产物分离, 在经过充分洗涤和真空干燥后直接用于下一次反应. 如图5所示, 两种催化剂的活性均随反应循环数的增加而逐渐下降, 并在四次循环后趋于稳定. 对于CZ-HP催化剂, 其活性在六次循环后达损失45% (累积反应时间36 h). 相比之下, CZA-HP催化剂的活性在六次循环后仅损失10%. 元素分析的结果表明, 两种催化剂中的Cu粒子在循环反应时均没有明显流失. 因此, 催化剂活性的下降主要缘于Cu粒子粒径的增长. 根据XRD测定结果, CZ-HP催化剂中的Cu粒子粒径经六次循环反应后增长至45.2 nm, 明显高于CZA-HP催化剂的19.0 nm. 由此可见, Al₂O₃的引入不仅提高了Cu-ZnO催化剂的活性, 而且还有效地抑制了催化剂在氢解反应中的失活.

与催化剂活性的变化不同, CZ-HP和CZA-HP催化剂的选择性在循环反应中基本保持不变(图5). 这表明

在甘油氢解反应的选择性对Cu粒子的粒径并不敏感, 尽管我们对这一现象的本质尚需进一步探究. 不过, 我们注意到 Al_2O_3 的引入使得Cu-ZnO催化剂对丙二醇的选择性从93.9% (CZ-HP)略降至91.6% (CZA-HP); 与之对应, 乙二醇的选择性从6.0%增长至8.2%. 在CZA-CP和CZA-DP等催化剂上也观察到类似现象. 根据图示1中的反应途径, 我们推测丙二醇与乙二醇的相对选择性主要决定于甘油醛脱水为丙酮醛来断裂甘油端位C-O键的速率. 在中性的水溶液中, 甘油醛脱水主要借助氧化物载体表面的碱性位的催化作用来完成^[13]. 如图示2所示, 甘油醛上具有酸性的 α -H首先被ZnO表面上具有碱性的晶格氧所活化, 然后该 α -H与甘油醛的 β -OH通过亲核反应而生成水分子, 从而断裂甘油的端位C-O键并生成丙酮醛. 由于 Al_2O_3 的酸性要高于 ZnO ^[34], 因此 Al_2O_3 与ZnO的混合会降低催化剂载体表面的碱性强度, 使得甘油醛的脱水速率以及相应丙二醇的选择性发生下降. 与这一推测相符, 在三种Cu-ZnO- Al_2O_3 催化剂中具有最高 Al_2O_3 分散度的CZA-CP催化剂表现出的丙二醇选择性相对最低(表2).

4. 结论

通过合成 Cu^{2+} , Zn^{2+} 和 Al^{3+} 离子均匀混合的Cu-Zn-Al碱式碳酸盐前体, 如Al取代的绿铜锌矿, 可以有效地将 Al_2O_3 引入到Cu-ZnO催化剂中而提高它在甘油氢解反应中的催化活性和稳定性. 在Cu-ZnO- Al_2O_3 催化剂中无定形态的 Al_2O_3 提高了金属Cu和ZnO的分散度, 并通过 Al_2O_3 与ZnO之间的紧密接触提高了催化剂的热稳定性, 从而使得Cu-ZnO- Al_2O_3 催化剂具有较小的Cu粒子粒径, 相应地表现出高的氧化还原能力和催化甘油氢解活性. 不过, Al_2O_3 与ZnO之间的紧密接触也抑制了金属Cu与ZnO之间的强相互作用, 在一定程度上抑制了Cu粒子的活性. 此外, Al_2O_3 的添加降低了Cu-ZnO催化剂的碱性, 使得丙二醇选择性略有下降. 这缘于甘油端位C-O键的断裂是通过碱催化的甘油醛脱水反应来实现. 以上结果表明, 通过调变催化剂中的 Al_2O_3 含量以及 Al_2O_3 与金属Cu和ZnO之间的相互作用等途径可进一步提高Cu-ZnO- Al_2O_3 催化剂在甘油氢解反应中的活性、选择性和稳定性.