

Contents lists available at ScienceDirect

Catalysis Communications



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

Short Communication

Highly active and selective Cu/SiO₂ catalysts prepared by the urea hydrolysis method in dimethyl oxalate hydrogenation

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ARTICLE INFO

Article history: Received 19 February 2011 Received in revised form 13 April 2011 Accepted 17 April 2011 Available online 22 April 2011

Keywords: Cu/SiO₂ Urea Ethylene glycol Dimethyl oxalate Hydrogenation Nanoparticle

ABSTRACT

Cu/SiO₂ catalysts have been successfully prepared via urea hydrolysis method. The catalysts have been systematically characterized by X-ray diffraction, high-resolution transmission electron microscopy, N₂-physisorption and H₂ temperature-programmed reduction. The results demonstrated the presence of copper nanoparticles and their high dispersion on the SiO₂ support. Catalysts with different copper loadings were prepared, and their performances in the hydrogenation of dimethyl oxalate to ethylene glycol were studied. A 100% conversion of dimethyl oxalate and maximum 98% selectivity of ethylene glycol were reached with 15.6 wt.% copper loading at 200 °C and 2 MPa. Furthermore, under the same reaction conditions, the catalyst can maintain the selectivity of 90% when the reduction temperature reduced from 350 °C to 200 °C. The high activity and selectivity over the catalyst may be ascribed to the homogenously distribution of copper nanoparticles on the large surface.

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1. Introduction

Ethylene glycol (EG) is an important chemical material, which is widely used in polyester and dynamite manufacture and in antifreeze production. Currently, EG is mainly synthesized by petroleum-based ethylene oxide hydrolysis, which is sharply influenced by the price of crude oil and strongly limited by the huge energy and water consumptions of the production process [1]. Hence, considerable global research effort has been directed towards the development of an alternative and sustainable approach for EG synthesis, and the process of indirect synthesis from syngas, which is produced by the gasification of coal and biomass, is becoming ever more attractive [2,3].

The process involves two steps: initial coupling of CO with methyl nitrite ester to form dimethyl oxalate (DMO), and then hydrogenation of the DMO to form EG [4,5]. Industrial-scale production of DMO has been realized, and so increasing attention has been paid to the development of highly active and stable catalysts for use in the hydrogenation of DMO to EG. A great deal of work has been carried out in this area. In early work, ruthenium-based homogeneous catalysts were used for the hydrogenation of oxalates [6,7]. The yield of EG reached 95% under an H₂ pressure of 7 MPa at 100 °C over a Ru-based homogeneous catalyst. However, the utility of this kind of catalyst proved to be limited due to problems of corrosion and separation. On the other hand, copper shows good performance in the hydrogenation of esters to alcohols, displaying high hydrogenation activity and a low tendency for C – C bond cleavage.

Therefore, it is an ideal alternative catalyst material for the hydrogenation of DMO. A considerable body of work has been devoted to comparing the performances of Cu-based catalysts supported on different carriers (SiO₂, Al₂O₃, ZnO, La₂O₃, and mesoporous materials such as HMS and SBA-15) [8–12]. Due to the weak acidic and basic properties of SiO₂, Cu/SiO₂ shows the highest yield of EG in the hydrogenation of DMO. Moreover, catalyst prepared by the homogeneous deposition–precipitation method has been shown to have a higher activity than that prepared by an impregnation method [13].

However, to the best of our knowledge, the preparations of Cu/SiO₂ catalysts by the aforementioned precipitation method have employed ammonia as a precipitant, whereas the influence of urea, which is also commonly used as a precipitant, has yet to be studied. Catalysts prepared by the urea hydrolysis method have a slow precipitation rate due to the slow decomposition of urea at temperatures of 90–100 °C, and this results in greater dispersion of the catalytically active component. In the present work, Cu/SiO₂ catalyst prepared by the urea hydrolysis method has been investigated. The purpose of this study has been to reveal the effect of the urea hydrolysis method on the texture and structure of Cu/SiO₂ catalysts, and to evaluate the performance of the prepared catalysts in the hydrogenation of DMO to EG.

2. Experimental

2.1. Catalyst preparation

 Cu/SiO_2 catalysts were prepared by the urea hydrolysis method described below. The requisite quantity of Cu(NO_3)_2 \cdot 3H_2O (depending

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^{1566-7367/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2011.04.019

on the desired copper content of the catalyst) was dissolved in deionized water (300 mL). The solution was then mixed with an appropriate quantity of urea (the mole ratio of urea to copper was 3:1), and the mixture was stirred until the urea had dissolved. Subsequently, silica sol was added to the solution, and the mixture was stirred for a further 4 h. It was then heated and kept at 90 °C to decompose the urea. When the pH of the suspension reached 6.5, the heating process was terminated. The mixture was filtered and the collected solid was washed with deionized water (500 mL), dried at 120 °C overnight, and calcined in air at 350 °C for 4 h. The calcined samples were crushed and sieved to 40–60 mesh. Catalysts with three different copper loadings were prepared, which we denote as 5 U, 20 U, and 40 U, respectively, where the numbers 5, 20, and 40 represent the copper loadings (see Table 1).

2.2. Catalyst characterization

The BET surface areas, pore volumes, and pore size distributions of the prepared catalysts were determined by measuring nitrogen adsorption–desorption isotherms using a Quantachrom-Autosorb-1-C apparatus. The real content of copper in the catalyst was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), using a Thermo iCAP 6000 device.

Powder X-ray diffraction (XRD) analysis of the prepared catalysts was carried out on a D/max-Ra X-ray diffractometer with a Cu- K_{α} radiation source operated at 40 kV and 30 mA. HRTEM images were obtained using a Philips Tecnai G²F30 transmission electron microscope.

Temperature-programmed reduction (TPR) was conducted using an AutoChem II 2920 instrument. A calcined catalyst sample (30 mg) was purged with Ar at 100 °C for 30 min and then cooled to room temperature. The reduction was carried out with 10% H₂/Ar (40 mL/min), and the sample was heated at a rate of 2 °C/min up to 600 °C. The amount of H₂ consumed was monitored by a thermal conductivity detector.

2.3. Catalytic activity test

The reactions were carried out in a continuous fixed-bed reactor. 1 g catalyst (about 3 mL) was sandwiched with quartz sand and packed in a steel tube reactor with an inner diameter of 8 mm. A thermocouple was inserted into the center of the catalytic bed to monitor the reaction temperature. Before the reaction, the catalyst was activated with pure hydrogen at 350 °C for 4 h at a ramping rate of 4 °C/min. After cooling to the reaction temperature, a solution of 12.5 wt.% DMO in methanol was fed into the preheater by means of a syringe pump, vaporized, and mixed with the required amount of H₂ at 200 °C. The liquid products were condensed and analyzed on an Agilent 7890 GC equipped with a flame-ionization detector (FID).

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the as-prepared and reduced Cu/SiO_2 catalysts are shown in Fig. 1. The peak of SiO_2 in the 40 U catalyst was shifted and broadened, suggesting that amorphous SiO_2 and silicate were

 Table 1

 Physical properties and Cu loadings of the prepared Cu/SiO₂ catalysts.

Catalyst	Cu loading ^a (wt.%)	$S_{BET} \over (m^2 g^{-1})$	V_{pore} (cm ³ g ⁻¹)	D _{pore} (nm)	d _{Cu} (nm)	
					TEM	XRD ^b
5 U	4.3	229	0.75	10.4	4	< 3
20 U	15.6	319	0.68	6.9	7.6	5.1
40 U	36.7	336	0.86	9.3	17.5	12.2

^a Measured by ICP-AES.

^b Calculated according to Scherrer-Warren equation, Cu(111).

formed due to the high copper content in the catalyst. In contrast to that of the 40 U catalyst, the patterns of 5 U and 20 U do not exhibit an obvious CuO diffraction peak, indicating that the crystalline CuO was highly dispersed on the SiO₂ and was too small to be detected. The 40 U catalyst reduced at 350 °C exhibited four main peaks that can be assigned to Cu₂O at $2\theta = 36.8^{\circ}$, Cu (111) at $2\theta = 43.3^{\circ}$, Cu (200) at $2\theta = 50.4^{\circ}$ and Cu (220) at $2\theta = 74.1^{\circ}$ [13]. The peaks of Cu and Cu₂O detected in the reduced 20 U were much weaker and broader than the peaks in the 40 U. However, there were no visible Cu and Cu₂O peaks in the reduced 5 U, suggesting that the particles were well dispersed and their sizes were quite small in the 5 U catalyst. The Cu crystallite size calculated by Scherrer–Warren equation increased from <3 nm to 12.2 nm with the increase of the copper loading (summarized in Table 1).

Fig. 2 shows the typical HRTEM images of the calcined and reduced Cu/SiO₂ catalysts. The particle sizes in the calcined samples were in the range of 3–5 nm in the 5 U and 20 U catalysts. However, a wire-like structure was observed in the 40 U catalyst, suggesting that a silicate phase was produced, which is in good agreement with the results of XRD measurement. The histograms of the particle size distribution for the reduced catalysts were inserted in the top-right corner of the HRTEM images. The average particle size of Cu (summarized in Table 1) was calculated as

$$d_{\text{TEM}} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where n_i is the number of particles having a characteristic diameter d_i (within a given diameter range) [14]. Highly dispersed and nano-size Cu particles were detected in all the catalysts prepared by urea hydrolysis method. The average sizes of Cu nanoparticles were 4 and 7.6 nm for 5 U and 20 U, respectively. These sizes of Cu nanoparticles were in good accordance with the unsupported copper nanoparticles (diameter = 3 ± 1.5 nm) and the supported copper nanoparticles on activated carbon (diameter = 6 ± 2 nm) prepared by Francisco et al. [15,16]. The average particle size of 40 U (17.5 nm) was larger than the former two.

The physical properties and copper loadings of the prepared Cu/SiO₂ catalysts are provided in Table 1. The BET surface area increased from 229 to 336 m²/g when the copper loading was increased from 4.3 to 36.7 wt.%. This might be induced by the formation of copper phyllosilicate [17]. The N₂ adsorption–desorption isotherms of the 5 U, 20 U and 40 U catalysts are shown in Fig. 3A. All of them revealed a type IV Langmuir adsorption isotherm according to the IUPAC classification, while the hysteresis loop changed from H1-type to H3-type with copper



Fig. 1. XRD patterns of the as-prepared and reduced Cu/SiO_2 catalysts. (a) 5 U, (b) 20 U, (c) 40 U, (d) 5 U after reduction, (e) 20 U after reduction, and (f) 40 U after reduction.



Fig. 2. HRTEM images of the as-prepared and reduced catalysts. (A) 5 U, (B) 20 U, (C) 40 U, (D) 5 U after reduction, (E) 20 U after reduction, and (F) 40 U after reduction.

loading increasing. These results inferred that there were a large amount of mesopores in three catalysts and the pores shape changed from cylindrical channels to slit-like channels. Furthermore, the pore size distributions curves obtained from the BJH desorption branch are shown in Fig. 3B. It showed that a bimodal pore structure was formed in the 20 U catalyst.

Fig. 4 illustrates the H_2 -TPR profiles of the calcined Cu/SiO₂ catalysts with different copper loading. The observation of a narrow reduction peak indicated that the copper particles were uniformly

dispersed on the SiO₂ support. Meantime, the low reduction temperature (centered at 170 °C) suggested the weak interaction between copper oxide and SiO₂. The slight shift of different copper loading catalysts may be caused by different copper particle sizes and different copper oxide dispersions. Besides the main reduction peak, there was a shoulder peak at 185 °C for the catalysts of 40 U, which should be ascribed to a double reduction step: $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^{0}$ [12]. It was in good agreement with the result of XRD. Furthermore, the stability of the catalyst can be significantly improved due to the



Fig. 3. Nitrogen adsorption–desorption isotherms (A) and pore size distributions (B) of the prepared catalysts. (a) 5 U, (b) 20 U, and (c) 40 U.

relatively low temperature at which the reduction is conducted, which reduces the aggregation and growth of the copper particles. We suggest that the Cu/SiO₂ catalyst prepared by urea hydrolysis represents an effective material for overcoming the bottleneck of Cu/SiO₂ catalyst stability in the industrial production of EG by DMO hydrogenation.



Fig. 4. H₂-TPR of the prepared Cu/SiO₂ catalysts (a) 5 U, (b) 20 U, and (c) 40 U.

3.2. Catalytic performance

The DMO hydrogenation proceeds according to the following reactions:

$$CH_{3}OOCCOOCH_{3} + 2H_{2} \rightarrow HOCH_{2}COOCH_{3} + CH_{3}OH$$
(1)

$$HOCH_2COOCH_3 + 2H_2 \rightarrow HOCH_2CH_2OH + CH_3OH$$
 (2)

$$HOCH_2CH_2OH + H_2 \rightarrow CH_3CH_2OH + H_2O$$
(3)

The catalytic performances of the prepared Cu/SiO₂ catalysts in the gas-phase hydrogenation of DMO to EG are shown in Fig. 5A and B. The DMO conversion was increased with increasing copper loading, climbing from 50% to 100% when the copper content reached 15.6 wt.%. The selectivity for EG on the 20 U and 40 U catalysts also shows a dramatic improvement compared with that produced by the low copper loading of the 5 U catalyst. This can be mainly attributed to the dramatic increase of catalyst surface area and the increase of copper content in the catalyst, which may increase the number of active sites. The 20 U catalyst showed the highest selectivity for EG (90%) under the same reaction conditions: a reaction temperature of 200 °C, an H₂/DMO molar ratio of 200, LHSV maintained at 0.8 h^{-1} , and system pressure maintained at 2 MPa. However, the selectivity for EG was only 80% when the copper loading was 36.7 wt.%. Differences in the pore structures, particle sizes, particle dispersions, and the phases of copper and SiO₂ resulted in different catalytic performances for the 20 U and 40 U catalysts.

Meantime, as shown in Fig. 5B, at an increased H₂/DMO molar ratio (260), the conversion of DMO on the 20 U catalyst was maintained at 100% as the temperature was varied from 195 to 215 °C. The selectivity for EG first increased and reached 98% when the reaction temperature was raised to 200 °C, but then decreased to 84% at 215 °C, indicating that the hydrogenation of DMO over Cu/SiO₂ for EG production is a temperature-sensitive reaction. The selectivity of EG obtained here was higher than that the results obtained by using deposition-precipitation method (94%) or incipient wet impregnation (92%) [12,13], and no less than that obtained by using ammonia-evaporation method (the selectivity reached 95% and 98% respectively) [11,17].

Furthermore, since the low reduction temperature disclosed in the TPR measurement, it is suggested that the process of reduction for the prepared Cu/SiO₂ catalysts can be operated under a temperature of 200 °C. The reduction temperature is very important for the copperbased catalyst, which has a significant effect on catalyst stability in the industrial application. Aggregation and growth of the copper particles in Cu/SiO₂ catalyst can be effectively inhibited by operating at low reduction temperature. So the performances of the 20 U catalyst reduced at low temperature of 200 °C were tested, and the results are shown in Fig. 5C. It demonstrated that the conversion of DMO reached 100% and the selectivity of EG can reached 90%, suggesting that the Cu/SiO₂ catalyst prepared via urea hydrolysis method may extend the catalyst life-time. The changes of the catalytic performance with temperature variation were in good accordance with the 20 U catalyst which was reduced at 350 °C. What's more, it was also confirmed that the hydrogenation of DMO to EG over Cu/SiO₂ catalyst was a temperaturesensitive reaction.

4. Conclusions

The presented work has demonstrated that the Cu/SiO₂ catalysts prepared by urea hydrolysis method have nano-size and highly dispersed copper particles. Coupled with an efficient copper loading, high surface area and bimodal pore structure, the prepared catalysts showed high catalytic performance in the gas-phase hydrogenation of



Fig. 5. (A) Catalytic performances of the prepared Cu/SiO₂ catalysts with different copper mass concentration in the hydrogenation of DMO. Reaction conditions: p = 2 MPa, T = 200 °C, $H_2/DMO = 200$ mol/mol, and LHSV = 0.8 h⁻¹. (B) Variations in catalytic activity of the 20 U catalyst reduced at 350 °C with reaction temperature. Reaction conditions: p = 2 MPa, $H_2/DMO = 260$ mol/mol, and LHSV = 0.8 h⁻¹. (C) Variations in catalytic activity of the 20 U catalyst reduced at 200 °C with reaction temperature. Reaction conditions are the same with (B).

DMO for EG production. The catalyst with a 15.6 wt.% copper loading showed the highest DMO conversion (100%) and selectivity for EG (98%) under the optimized reaction conditions. Besides, it was found that the hydrogenation of DMO for EG production over Cu/SiO₂ catalyst was a temperature-sensitive reaction.

Furthermore, the influences of the reduction temperature at 350 °C and 200 °C on the catalyst performance were also discussed. It was found that the catalyst also exhibited a high DMO conversion (100%) and EG selectivity (90%) when the reduction temperature was reduced to 200 °C. The relatively low reduction temperature of the copper-based catalyst would suggest that the method of Cu/SiO₂ catalyst preparation via urea hydrolysis is an effective way to overcome the bottleneck of Cu/SiO₂ catalyst stability in the industrial production of EG by DMO hydrogenation.

Acknowledgement

The authors are grateful for financial support from the Doctoral Program of Higher Education of China (20090101110034), the Zhejiang Provincial Natural Science Foundation of China (R1110089), the International Science and Technology Cooperation Program (2009DFA61050), the National High Technology Research and Development Program of China (2009AA05Z407), and the National Basic Research Program of China (2007CB210200).

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