

Synthesis and applications of mesoporous Cu-Zn-Al₂O₃ catalyst for dehydrogenation of 2-butanol

Deren Fang^{1,2}, Wanzhong Ren², Zhongmin Liu^{1*}, Xiufeng Xu², Lei Xu¹, Hongying Lü², Weiping Liao², Huimin Zhang²

1. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China;

2. Institute of Applied Catalysis of Yantai University, Yantai 264005, Shandong, China

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Abstract

A series of mesoporous Cu-Zn-Al₂O₃ materials have been synthesized at ambient temperature and their structure was characterized by XRD, N₂ physical adsorption and TPR techniques. Their catalytic applications for the dehydrogenation of 2-butanol to methyl ethyl ketone (MEK) were evaluated in a fixed-bed flow reactor at atmospheric pressure. It is demonstrated from the XRD patterns that both the as-synthesized samples and calcined samples have the typical XRD patterns of meso-structured materials and the results of N₂O chemical adsorption showed that Cu was embedded in the framework of the mesoporous materials and homogeneously dispersed in the mesoporous Cu-Zn-Al₂O₃ materials. The catalytic activity of 2-butanol dehydrogenation was varied in the order of CZA(10) < CZA(CP) < CZA(20) < CZA(30); while the selectivity of MEK was increased in the order of CZA(CP) < CZA(10) < CZA(20) < CZA(30).

Key words

Cu-Zn-Al₂O₃; mesoporous materials; dehydrogenation of 2-butanol; catalyst

1. Introduction

The dehydrogenation of higher alcohol to produce the corresponding ketone or aldehyde is an important industrial process. The products are widely used as industrial solvent and chemical reaction intermediate compound. For example, the dehydrogenation of sec-butyl alcohol (2-butanol) to yield methyl ethyl ketone (MEK) is an important industrial process. The MEK is a widely used industrial solvent. In addition to the dehydrogenation of 2-butanol, the dehydrogenation of isopropanol to acetone, isoamyl alcohol to isovaleraldehyde and cyclohexanol to cyclohexanone and so on are all important industrial processes. The Cu-ZnO/Al₂O₃ catalysts are widely used in these processes [1–6]. At present, Cu-ZnO/Al₂O₃ catalysts are commonly prepared by the precipitation method, and the surface area of the catalysts and the dispersion of active center (CuO) are quite low, which result in a low catalytic activity. So how to increase the activity of the catalyst is an important matter to be considered.

Mesoporous material is a kind of material with a regular channel structure and high surface area. Since it was dis-

covered by research group at Mobil corporation in 1992 [7], various synthesis methods have been developed and a large progress has been made. Its application in heterogeneous catalysis is a promising field, while the pure silica MCM-41 showed very limited catalytic activities. It is necessary to incorporate metals into the silicate framework to create active sites for catalytic reactions, such as Al, Ti, Cr, V, Sn, Co, Pd, Fe, Ga, Zr, Mn and Cu [8–15]. Valange *et al.* synthesized a mixed [Cu, Zn, Al] hexagonal and lamellar mesophase [16]. In the present study, a series of Cu-Zn-Al₂O₃ ternary mesoporous materials were synthesized at ambient temperature and their applications for the dehydrogenation of 2-butanol to methyl ethyl ketone (MEK) were studied.

2. Experimental

2.1. Catalyst preparation

The ternary mesoporous materials (Cu-Zn-Al₂O₃) were prepared by direct synthesis at ambient temperature. Lauric acid and Al₂(NO₃)₃ were dissolved in distilled water. A

* Corresponding author. Tel: +86-411-84685510; Fax: +86-411-84691570; E-mail: zml@dicp.ac.cn

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mixture of $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ solution (mole ratio of Cu to Zn = 2 : 1) was quickly added to the lauric acid- $\text{Al}(\text{NO}_3)_3$ solution with vigorous stirring at 20 °C, followed by the addition of NaOH (2 M) to adjust the pH value to 9, and continuous stirring was performed for another 30 min. The resultant slurry was transferred into a plastic bottle and aged at 20 °C for 100 h. Then the precipitate was separated by centrifuge and washed with distilled water. The powder product was recovered by filtration and dried at 298 K. The surfactant was removed by calcination at 500 °C in N_2 and then in air for 5 h. The products were designated as CZA(10), CZA(20), CZA(30), respectively, where 10, 20 and 30 indicate the nominal content (wt%) of Cu+Zn in the products.

For comparison, a sample of $\text{Cu-Zn-Al}_2\text{O}_3$ was prepared by coprecipitation method. NaOH aqueous solution (2N) was added to a $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2\text{-Al}(\text{NO}_3)_3$ mixed solution (its components were the same as those in $\text{CuZnAl}(30)$) with vigorous stirring at 20 °C to adjust the pH value to 9, and continuous stirring was performed for another 60 min. Then the precipitate was separated by centrifuge and washed with distilled water, dried at 393 K and calcination at 500 °C in air for 5 h. The sample was designated as CZA(CP).

2.2. Catalyst characterization

All the as-synthesized and calcined samples of mesoporous $\text{Cu-Zn-Al}_2\text{O}_3$ materials were characterized by powder X-ray diffraction (shimadzu XRD6100 X-ray powder diffractometer, $\text{Cu } K_\alpha$ radiation). Nitrogen sorption isotherms were obtained on a Quantachrome NOVA 3000 Instrument. Temperature-programmed reduction (TPR) was performed using a TP5000 multifunction absorber. 50 mg catalyst of a particle size of 40–60 mesh was reduced by a mixture of H_2/N_2 (1 : 9) in the temperature range of 100–500 °C at a heating rate of 10 °C/min. The Cu surface area and particle sizes of the catalysts were measured by the N_2O passivation method [17,18] using the same equipment as TPR test.

2.3. Catalytic testing

The catalytic activity for the dehydrogenation of 2-butanol to methyl ethyl ketone (MEK) was evaluated in a fixed-bed flow reactor at atmospheric pressure with a liquid space velocity of 4 h^{-1} . The catalyst particle size was 40–60 mesh. Before the reactants was introduced, the catalyst was reduced in a diluted hydrogen gas (10%) under atmospheric pressure. The temperature was increased from room temperature to 200 °C with a temperature ramp of 5 °C/min, and then was raised to 350 °C with a temperature ramp of 2 °C/min. The final temperature was kept for 2 h. After the catalyst reduction, the temperature of reactor was lowered to the reaction temperature, and the feed liquid was pumped with a plunger pump into the system to test the catalytic activity. The products were collected with a cold tank and analyzed by gas chromatography using capillary tube of PEG-20M and FID detector, and the column temperature was 80 °C.

3. Results and discussion

3.1. Ternary meso-structured materials

X-ray diffraction (XRD) patterns of the as-synthesized samples and calcined samples are illustrated in Figure 1. It is demonstrated from the XRD patterns that both the as-synthesized samples and calcined samples have the typical XRD patterns of meso-structured materials.

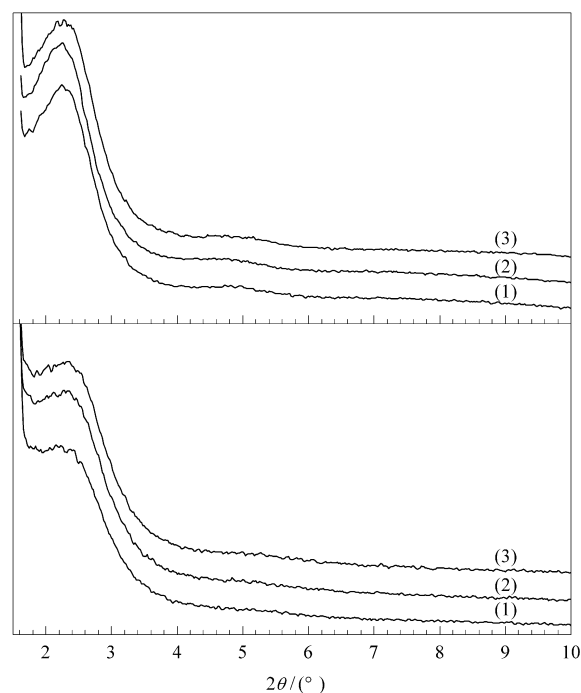


Figure 1. X-ray diffraction patterns of as-synthesized and calcined mesoporous $\text{Cu-Zn-Al}_2\text{O}_3$ materials. (1) CZA(10), (2) CZA(20), (3) CZA(30)

The N_2 adsorption-desorption isotherms of these samples (Figure 2) showed that all the curves of CZA(10), CZA(20) and CZA(30) were the type IV isotherms, *i.e.* the sample of CZA(10), CZA(20) and CZA(30) has mesoporous structure. While the curves of CZA(CP) were the type III isotherms, that is to say, the sample possesses macroporous structure. The pore distribution of CZA(30) and CZA(CP) is illustrated in Figure 3. The pore distribution curve of CZA(30) has a single peak around 20 nm, while the sample of CZA(CP) has two very dispersive peaks, of which maximum value shifts to the bigger pore. The surface areas of calcined samples are summarized in Table 1. It is evident that the meso-structured material has a bigger surface area than the sample prepared by the coprecipitated method.

Table 1. Structural properties of mesoporous $\text{Cu-Zn-Al}_2\text{O}_3$ materials

Sample	S (m^2/g)	V (cm^3/g)	Pore size (BJH, nm)	d_{100} (nm)	a_0 (nm)	Wall thickness (nm)
CZA(10)	512.5	0.4687	1.91	4.28	4.94	3.03
CZA(20)	520.8	0.4673	1.90	4.37	5.05	3.15
CZA(30)	503.5	0.4548	1.92	4.38	5.06	3.14
CZA(CP)	117.6	0.2515	1.35	—	—	—

S —surface area, V —pore volume

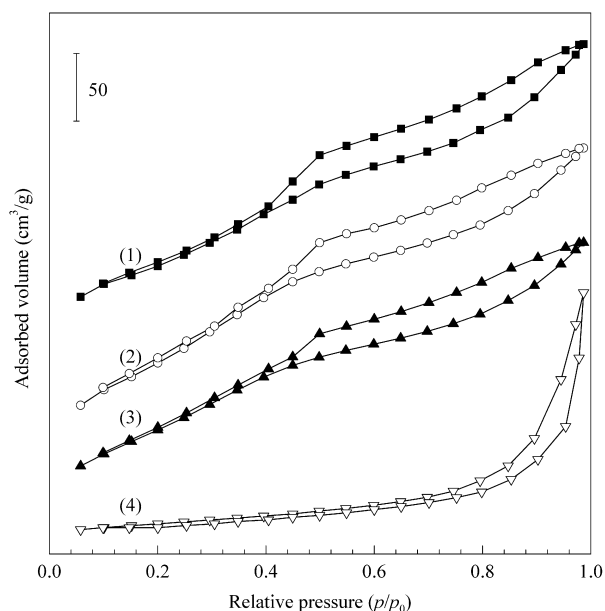


Figure 2. Nitrogen adsorption and desorption isotherm curves at 77.3 K. (1) CZA(10), (2) CZA(20), (3) CZA(30), (4) CZA(CP)

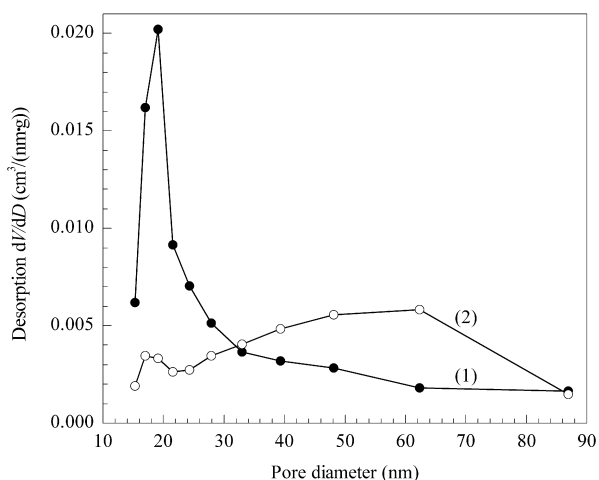


Figure 3. Pore size distribution curves. (1) CZA(30), (2) CZA(CP)

3.2. Catalyst reducibility

The TPR profiles (Figure 4) showed that the meso-structured materials CZA(30) have single reduction peaks, indicating that CuO and ZnO were homogeneously dispersed in the mesoporous materials. On the other hand, the sample CZA(CP) has two reduction peaks, implying there exist two forms of CuO in CZA(CP).

3.3. Catalytic performance

The dehydrogenation of 2-butanol was carried out on the four calcined samples and the results are illustrated in Figure 5.

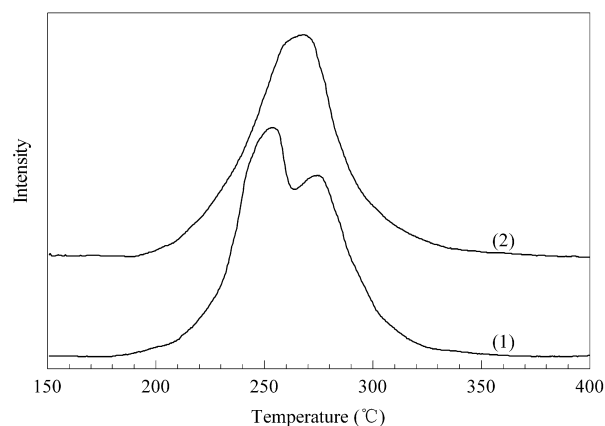


Figure 4. The TPR profiles of calcined mesoporous Cu-Zn-Al₂O₃ materials. (1) CZA(CP), (2) CZA(30)

The 2-butanol conversion varied with reaction temperature, and high temperature favored the reaction. In the case of meso-structured Cu-Zn-Al₂O₃ materials, increasing the metal content enhanced the conversion of 2-butanol. The conversion of 2-butanol on CZA(CP) is lower than that on CZA(20), and slightly higher than that on CZA(10). This difference may be explained as follows: in the case of meso-structured Cu-Zn-Al₂O₃ material, since it has a bigger surface area, more Cu species on the surface resulted in better performances with higher 2-butanol conversion. The result of N₂O passivation method showed that the Cu surface area increased as the content of Cu increased in the meso-structured Cu-Zn-Al₂O₃ materials, while the Cu particle size and Cu dispersion remained constant (Table 2). This result may indicate that the Cu was embedded in the framework of the mesoporous materials to retard the growth of Cu particle as the Cu content increased.

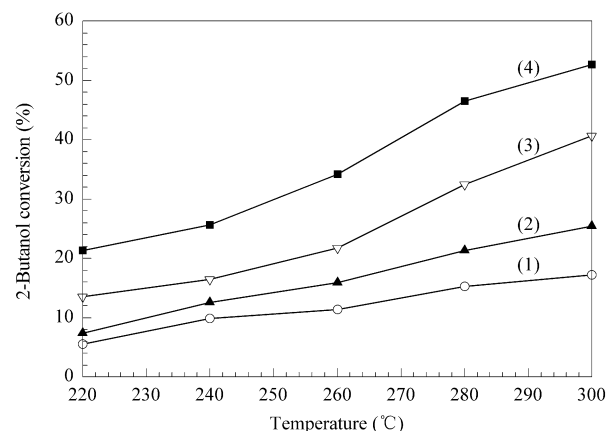


Figure 5. Evolution of 2-butanol conversion with reaction temperatures. (1) CZA(10), (2) CZA(CP), (3) CZA(20), (4) CZA(30)

Table 2. Cu surface area and Cu dispersion of the different catalysts

Catalyst	Cu surface area (m ² /g)	Cu particle size (nm)	Cu dispersion (%)
CZA(10)	8.2	3.52	28.4
CZA(20)	13.8	3.61	27.7
CZA(30)	21.6	3.68	27.2
CZA(CP)	10.5	7.89	12.7

The XRD patterns of CZA(30) and CZA(CP) at $2\theta = 10^\circ - 80^\circ$ (Figure 6) further verified the supposition. There was no CuO or ZnO diffraction peak in CZA(30), while in the sample of CZA(CP) there were two diffraction peaks of CuO at $2\theta = 35.8^\circ$ and 39.4° , respectively. The selectivity of MEK was increased in the order of CZA(CP) < CZA(10) < CZA(20) < CZA(30) (Figure 7). The impurity of 2-butanol dehydrogenation was mainly various isomers of octanone, and small amount of isomers of octanol (Table 3). They are the products of 2-butanol dimerization, and produced by dehydrogenation or dehydration. The dimerization activity was proportional to the acidity of the catalysts and the limitation of internal diffusion. This test results may be explained from two aspects as follows: On one hand, the coprecipitated sample CZA(CP) was in an amorphous state and hence more B acid and L acid site were present; while the mesoporous Cu-Zn-Al₂O₃ material possessed a regular structure in the pore wall, and thus little B acid or L acid site was present. On the other hand, the octanone and octanol were the products of series reaction of 2-butanol dehydrogenation and their amounts were limited and proportional to the internal diffusion of methyl ethyl ketone in the pore of the catalysts. The meso-structured Cu-Zn-Al₂O₃ materials displayed little internal diffusion compared to the coprecipitated sample CZA(CP) because the former possessed regular pore structure, and favored the diffusion of reactants and products of bigger molecules and thus restrained the formation of by-products.

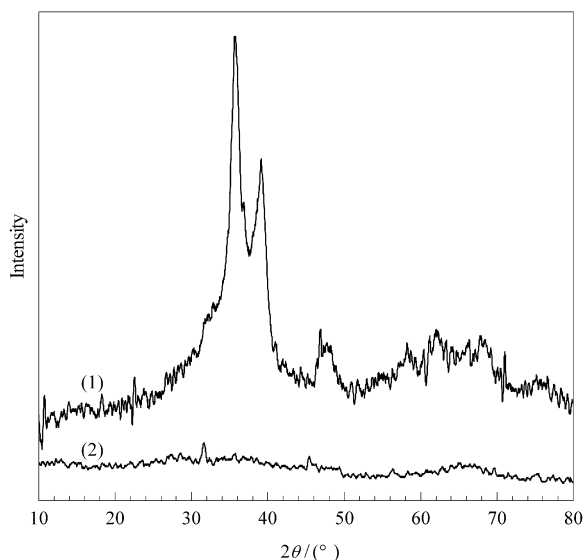


Figure 6. Wide angle XRD patterns of samples. (1) CZA(CP), (2) CZA(30)

Table 3. The impurities of 2-butanol dehydrogenation at 260 °C

Sample	Impurity (%)		
	MEK	Octanone	Octanol
CZA(10)	83.3	14.3	2.4
CZA(20)	84.2	13.6	2.2
CZA(30)	87.5	11.2	1.3
CZA(CP)	76.7	21.2	2.1

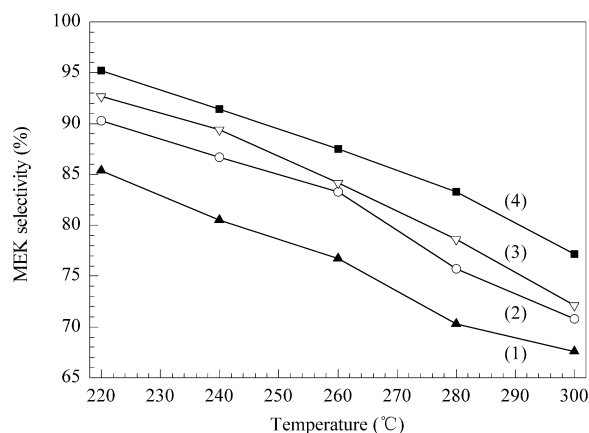


Figure 7. Evolution of MEK selectivity with reaction temperatures. (1) CZA(CP), (2) CZA(10), (3) CZA(20), (4) CZA(30)

4. Conclusions

In this work, a series of meso-structured Cu-Zn-Al₂O₃ materials were synthesized and their catalytic activity for the dehydrogenation of 2-butanol was studied. Up to 30% of Cu+Zn content, the Cu-Zn-Al₂O₃ materials displayed a regular mesoporous structure, the CuO and ZnO was embedded in the framework of the mesoporous materials; the mesoporous Cu-Zn-Al₂O₃ catalysts were more favorable in the formation of MEK and unfavorable for the formation of by-products than the catalysts made by coprecipitation method.

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