

Selective Conversion of Furfural to Cyclopentanone with CuZnAl Catalysts

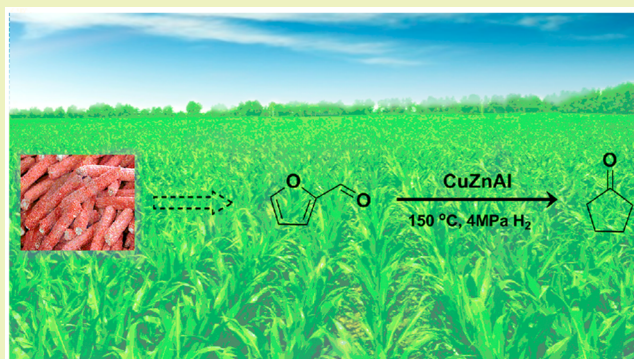
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Supporting Information

ABSTRACT: A new catalytic system was developed for the selective conversion of biomass-derived furfural to cyclopentanone in aqueous solution. CuZnAl catalysts with different Cu/Zn molar ratios (0.5, 1, 2, and 3) and calcination temperatures (350, 500, and 700 °C) were investigated, and the CuZnAl-500-0.5 catalyst (Cu/Zn = 0.5, calcined at 500 °C) showed a remarkable catalytic performance in the reaction. A 62% yield of cyclopentanone was obtained at the optimized conditions (150 °C, 4 MPa H₂, 6 h), and the TOF was 9.4 h⁻¹. The catalysts were characterized by nitrogen adsorption, XRD, TEM, N₂O titration, ICP, XPS, and a carbon-sulfur analyzer. The factors that influenced the activity of catalysts were also investigated. Additionally, the CuZnAl-500-0.5 was recycled five times and maintained good activity and stability. Hence, the current work presents a new and efficient catalytic system for the conversion of furfural to cyclopentanone. The low-cost nature of the CuZnAl makes it a potential catalyst for the production of cyclopentanone in industry.

KEYWORDS: Furfural, CuZnAl catalyst, Cyclopentanone, Cyclopentanol, Hydrogenation



INTRODUCTION

Recently, the utilization of biomass has attracted more and more attention for the urgent demand of sustainable and clean fuels and chemicals.^{1–4} Furan derivatives are easily obtained from biomass-derived carbohydrates and sustainable feedstocks. Specifically, furfural as a platform molecule is an appropriate substitute to produce a wide range of important nonpetroleum-derived chemicals,^{5–8} such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (2-MeF), tetrahydrofuran (THF), pentylenediol, and so on.^{9–11}

Cyclopentanone (CPO) is an important fine chemical intermediate. It can be used in the synthesis of medicines, pesticides, herbicides, and perfume. Additionally, high-purity CPO behaves consistently well in the electronics industry as a widely applied solvent for its good dissolving property of resins. In addition, it can also be used to synthesize long-chain alkanes through condensation followed by hydrogenation.¹²

The traditional methods for CPO synthesis were the pyrolysis of adipic acid and its derivatives and the oxidation of cyclopentene.^{13–15} However, the feedstocks come from unsustainable fossil fuel, and the reactions require high temperature and even high pressure. Recently, furfural was found to be a good feedstock to synthesize CPO.^{12,16–19} Hronec et al. described a new route for the synthesis of CPO from furfural in aqueous solution under mild conditions.¹⁶ They found that metal catalysts, such as Pt/C, Ru/C, and Raney Ni, had good performances in the selective synthesis of CPO and cyclopentanol (CPL) from furfural in aqueous

solution. The best yield (76.5 mol % of CPO) was obtained when Pt/C was employed as the catalyst. In their following study, a reaction mechanism was proposed where the carbocation of the carbon in the aldehyde group was first bonded to the metal surface, and then, it interacted with the coadsorbed water and rearranged to a possible intermediate, 3-hydroxy-4-cyclopentenone. Subsequently, it was hydrogenated to CPO.¹⁷ Their recent study on the selective conversion of furfural to CPO proved that the furanic polymers created on the catalyst surface will competitively prevent CPO consecutive hydrogenation to CPL.¹⁹ In other literature, Yang et al. reported the same conversion of furfural over Ni–Cu/SBA-15 catalysts.¹² They developed the mechanism that the rearrangement of the furan ring was independent of hydrogenation, while the key step was the attack of the H₂O molecule to the 5-position of furfuryl alcohol, thus leading to both opening and closure of the furan ring.

Although some work has been done on the synthesis of CPO from biomass-derived furfural, the study is still in its infancy. So far, only some precious metal catalysts (Pt/C, Pd/C, and Ru/C) and Ni-based catalysts demonstrated good activities. It will be significant to develop new catalytic systems, especially catalysts with low cost and high activity and stability, to enrich the synthetic routes of CPO.

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Table 1. Characteristics of Cu-Based Catalysts

entry	code	Cu (wt %)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)		d_{Cu} (nm)		D_{Cu} (%) ^c	S_{Cu} ($\text{m}^2 \text{g}_{\text{cat}}^{-1}$) ^d
					XRD ^a	N_2O^b	XRD ^a	N_2O^b		
1	CuZnAl-350-0.5	27.9	43.1	0.176	15.6	7.6	6.6	15.2	29.5	
2	CuZnAl-500-0.5	28.5	25.0	0.089	14.0	12.8	11.5	8.7	17.0	
3	CuZnAl-700-0.5	28.7	4.9	0.018	17.3	33.8	51.9	1.9	3.6	
4	CuZnAl-500-1	40.2	23.6	0.087	10.9	35.3	38.5	2.6	8.1	
5	CuZnAl-500-2	52.9	14.0	0.057	15.1	46.2	49.4	2.0	8.8	
6	CuZnAl-500-3	63.8	10.9	0.038	15.8	53.5	76.4	1.3	6.4	
7	CuZn-500-0.5	27.9	18.7	0.082	22.4	13.9	17.2	5.8	11.8	
8	Cu/C	25.3	558.3	0.526	30.6	32.5	34.0	2.9	6.0	
9	Cu/ γ - Al_2O_3	24.8	96.2	0.217	86.8	45.3	46.7	2.1	4.9	
10	Cu/ SiO_2	25.4	9.7	0.049	19.1	42.6	42.7	2.3	5.1	
11	Cu/SBA-15	25.7	260.9	0.4066	62.3	9.5	12.3	8.1	16.2	

^aCrystal size was calculated by the Scherrer equation through the Cu(111) diffraction peak. ^bAverage volume–surface diameter was calculated from the N_2O titration method; $d \approx 0.5 \times A_1/A_2$ (nm). ^cDispersion (D) of Cu was determined by the N_2O titration method; $D = 2A_2/A_1 \times 100\%$. ^dThe Cu metal surface area was determined by the N_2O titration method.

In the research of furfural hydrogenation, Cu-based catalysts exhibited excellent activity. Compared to the precious metals, earth-abundant copper is more economical and environmentally friendly. It has the potential to be applied in the transformation of furfural into CPO. Among the Cu-based catalysts, CuZnAl is an important industrial catalyst and has been widely used in methanol synthesis and water gas shift with excellent activity and stability.^{20,21} In addition to the catalytic activities mentioned above, it has displayed good performance in hydrogenation reactions. In a catalyst, copper is the active component for hydrogenation, while zinc oxide is proved to effectively improve Cu dispersion and thus provide a larger number of active sites toward the reaction.^{22–24} Small amounts of alumina could stabilize the Cu–Zn structure and increase the surface area, while higher concentrations could oppositely decrease the activity of the catalysts.^{25,26}

In this work, a series of CuZnAl catalysts were prepared and tested for the production of CPO from furfural. The effects of the Cu/Zn molar ratios and calcination temperatures on the physicochemical properties and activities of CuZnAl catalysts were investigated in detail. The influence of reaction conditions, including reaction temperature, reaction time, and H_2 pressure, on the catalytic performance was studied. Moreover, the experiments of catalyst recycling were also performed.

EXPERIMENTAL SECTION

Materials. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>99.0%, AR), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.0%, AR), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>99.0%, AR), Na_2CO_3 ($\geq 99.8\%$, AR), furfural (>99.0%, AR), furfuryl alcohol (>99.0%, AR), and tetrahydrofurfuryl alcohol (>99.0%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Catalyst Preparation. CuZnAl catalysts were prepared by coprecipitation. A certain proportion of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (molar ratios were Cu:Zn:Al = 3:6:1, 4.5:4.5:1, 6:3:1, and 6.75:2.25:1, respectively) were dissolved in 150 mL of deionized water with mechanical stirring at 80 °C. Then, a Na_2CO_3 aqueous solution was added until the pH was 8. The mixture was stirred for 1 h and then aged for 15 h at 80 °C. The obtained solid was washed by deionized water and dried at 105 °C for 30 h, followed by calcination at different temperatures (350, 500, or 700 °C) for 6 h with a steady heating rate of 3.0 °C/min. Then, the calcined catalyst was reduced in a H_2 atmosphere at 280 °C for 3 h with a heating rate of 1.0 °C/min before reaction. The flow rate of H_2 was 60 mL/min. The catalysts prepared above were labeled as CuZnAl-xxx (calcined

temperature: 350, 500, or 700 °C)-xx (Cu/Zn molar ratio: 0.5, 1, 2, or 3).

Cu/C, Cu/ γ - Al_2O_3 , Cu/ SiO_2 , and Cu/SBA-15 with Cu loading as 25 wt % were synthesized by the impregnation method.

Characterization of Catalysts. Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer that reports the adsorption isotherm, specific surface area, and pore volume automatically. The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area in the range of relative pressures between 0.05 and 0.20. The pore sizes were calculated from the adsorption branch of the isotherms using the thermodynamic-based Barrett–Joyner–Halenda (BJH) method.

XRD analysis was conducted on a X-ray diffractometer (TTR-III, Rigaku Corp., Japan) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The data were recorded over 2θ ranges of 20–80°.

Transmission electron microscopy (TEM) images were taken by a JEM 2011 electron microscope.

The specific surface areas of metallic copper and copper dispersion of the Cu catalysts were measured by N_2O titration. The process consisted of three sequential steps:



First, 50 mg of calcined catalyst was purged with He (30 mL/min) at 200 °C for 1 h. After being cooled to 60 °C, the calcined catalyst was reduced in a 5 vol % H_2/Ar mixture (40 mL/min) to a final temperature of 500 °C with a heating rate of 10 °C/min. The amount of H_2 consumption was denoted as A_1 . Second, N_2O (30 mL/min) was used to oxidize the surface Cu to Cu_2O at 30 °C for 0.5 h. Subsequently, the catalyst was purged with He (30 mL/min) at 30 °C for 0.5 h to remove residual N_2O . Finally, the oxidized catalyst was reduced in a 5 vol % H_2/Ar mixture (40 mL/min) to a final temperature of 500 °C with a heating rate of 10 °C/min. The amount of H_2 consumption was denoted as A_2 . The dispersion (D) of Cu was calculated as follows: $D = 2A_2/A_1 \times 100\%$. The specific area of Cu was calculated from the amount of H_2 consumption (A_2) with 1.46×10^{19} copper atoms per m^2 .²⁷ The average volume–surface diameter can be calculated as follows: $d = 6/(S \times \rho_{\text{Cu}}) \approx 0.5 \times A_1/A_2$ (nm). ρ_{Cu} in this equation is the density of copper (8.92 g/cm^3).²⁸

The Cu content of catalysts was analyzed by an Optima 7300 DV ICP-OES.

The carbon on the catalyst was analyzed by a high frequency infrared carbon–sulfur analyzer (CS-600 series, LECO, U.S.A.). The catalysts were washed with acetone after being separated from the

reaction and dried at 100 °C to remove the adsorbed solvent before the test.

XPS was obtained with an X-ray photoelectron spectroscopy (ESCALAB250, Thermo-VG Scientific, U.S.A.) using monochromatized Al K α radiation (1486.92 eV).

Experimental Procedure. The hydrogenation of furfural was explored with different Cu-based catalysts. In a typical test, 5 mmol of furfural, 0.2 g of CuZnAl, and 15 mL of water were added to a 50 mL Parr reactor with a quartz lining. After purging the reactor with H₂, the reaction was conducted with 4 MPa H₂ (room temperature) at a series of temperature (130–170 °C) for 6 h with a stirring speed of 1000 rpm. Subsequently, the reactor was cooled to room temperature. The liquid and solid were taken out for further analysis. The organic products were extracted by ethyl acetate from the liquid and then analyzed by a gas chromatograph (GC, Kexiao 1690) with an OV1701 capillary column (30 m \times 0.25 mm \times 0.25 μ m). The products were identified by a GC (Agilent 7890A) mass spectrometer detector (Agilent 5975C with Triple-Axis Detector).

The separated catalyst was dried at 40 °C after filtration and acetone sequential washing. During the catalyst stability test, the catalyst was then reused without any further treatments.

RESULTS AND DISCUSSION

Catalyst Characterization. A series of CuZnAl catalysts with different calcination temperatures and Cu/Zn molar ratios were prepared (Al content was fixed as 10 mol %). The main characteristics of the CuZnAl catalysts are shown in Table 1. Among the CuZnAl catalysts calcined at different temperatures (Table 1, entries 1–3), CuZnAl-350–0.5 had the highest surface area (43.1 m² g⁻¹) and the largest pore volume (0.176 cm³ g⁻¹) (Table 1, entry 1), while the catalyst calcined at a high temperature (700 °C) had the smallest surface area (4.9 m² g⁻¹) and pore volume (0.018 cm³ g⁻¹) (Table 1, entry 3). According to the data of the catalysts with various Cu/Zn molar ratios (entries 2, 4–6), the surface areas and pore volumes of catalysts decreased with a rise in Cu content, while the pore diameters of CuZnAl catalysts rarely changed with different Cu contents and calcination temperatures. Comparing entry 2 with entry 7, the surface area of CuZn-500–0.5 (18.7 m² g⁻¹), which was prepared without adding Al, was lower than that of CuZnAl-500–0.5 (25.0 m² g⁻¹). While the pore diameter of CuZn-500–0.5 (22.4 nm) was larger than that of CuZnAl-500–0.5 (14.0 nm).

Figure 1 shows the powder XRD patterns of Cu catalysts with different calcination temperatures and Cu/Zn molar ratios. The peaks at 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.9°, and 67.9° corresponded to the diffraction peaks of (100), (002), (101), (102), (110), (103), and (112) planes, respectively, of ZnO (JCPDS Card No. 36-1451). The peaks at 43.3°, 50.4°, and 74.1° corresponded to the diffraction peaks of (111), (200), and (220) planes, respectively, of Cu⁰ (JCPDS Card No. 65-9026). No peaks of Al₂O₃ were observed in the XRD patterns, which indicated that Al₂O₃ existed in an amorphous state.²⁹ The crystal sizes of Cu⁰ were calculated by the Scherrer equation (Table 1). Basically, the crystal sizes of Cu increased with increasing Cu content and calcination temperature. The crystal sizes of Cu in CuZnAl-500–0.5 and CuZn-500–0.5 were almost the same, which showed that the addition of Al₂O₃ did not have much influence on the Cu-0.5-catalysts calcined at 500 °C.

The TEM images of CuZnAl-350–0.5, CuZnAl-500–0.5, CuZnAl-700–0.5, CuZnAl-500–1, CuZnAl-500–2, CuZnAl-500–3, and CuZn-500–0.5 are shown in Figure 2a–g. As revealed in Figure 2a–c, the calcination temperature had a great effect on the morphology of catalysts. High temperature

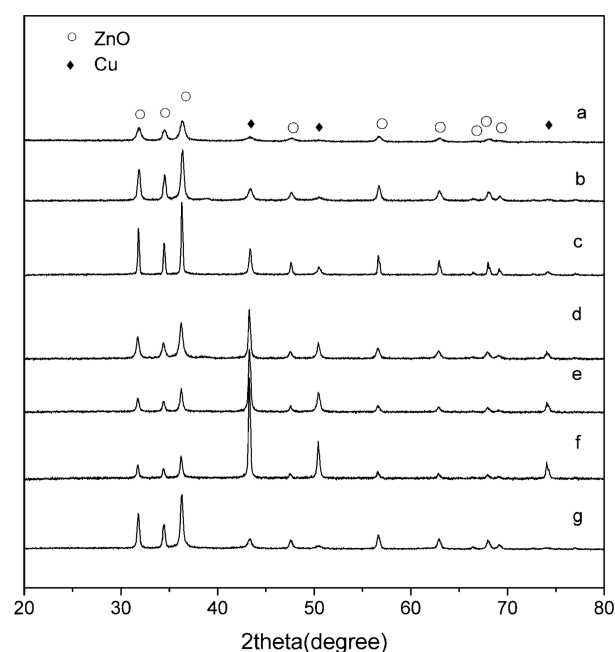


Figure 1. XRD patterns of the Cu-catalysts: (a) CuZnAl-350–0.5, (b) CuZnAl-500–0.5, (c) CuZnAl-700–0.5, (d) CuZnAl-500–1, (e) CuZnAl-500–2, (f) CuZnAl-500–3, and (g) CuZn-500–0.5.

promoted the agglomeration of the catalyst. For the catalysts calcined at the same temperature, a high Cu/Zn ratio contributed to the agglomeration of the catalyst (Figure 2b and d–f). CuZnAl-500–0.5 and CuZn-500–0.5 had a similar morphology.

Copper dispersion, specific area, and average particle size determined by the N₂O titration method are summarized in Table 1. The Cu particle sizes increased with an increase in the calcined temperature and Cu content, which was similar to the trend of the crystal sizes calculated by XRD. The CuZnAl-350–0.5 catalyst had the highest Cu dispersion (15.2%) and specific area (29.5 m² g_{cat}⁻¹) and smallest average particle size (6.6 nm). The calcination temperature had a great influence on these characters (entries 1–3). The Cu specific area and dispersion decreased sharply, and the average particle size grew quickly with an increase in calcination temperature. The CuZnAl-500 catalysts with a Cu/Zn molar ratio of 1, 2, and 3 had a similar Cu specific area (6.4–8.8 m² g_{cat}⁻¹) and dispersion (1.3–2.6%). The average diameter increased with the Cu/Zn molar ratio, obviously. The Cu specific area (11.8 m² g_{cat}⁻¹) and dispersion (5.8%) of the CuZn-500–0.5 catalyst was lower than that of CuZnAl-500–0.5, which indicated that the addition of Al₂O₃ could improve the specific area and dispersion of Cu and meanwhile decrease the average diameter of Cu.

CONVERSION OF FURFURAL TO CPO

Hydrogenation of Furfural with Different Cu Catalysts. In organic solvents, furfural was mainly converted into hydrogenated products. In contrast, in aqueous solution, furfural could be converted to CPO or CPL through furan ring rearrangement.^{12,16–19} Thus, water was employed as the solvent in our following reactions. Table 2 shows the hydrogenation of furfural in aqueous solution at 150 °C and 4 MPa H₂ with different Cu-based catalysts. The Cu-based catalysts include CuZnAl-0.5 catalysts with different calcination temperatures (350, 500, and 700 °C), CuZnAl-500 catalysts

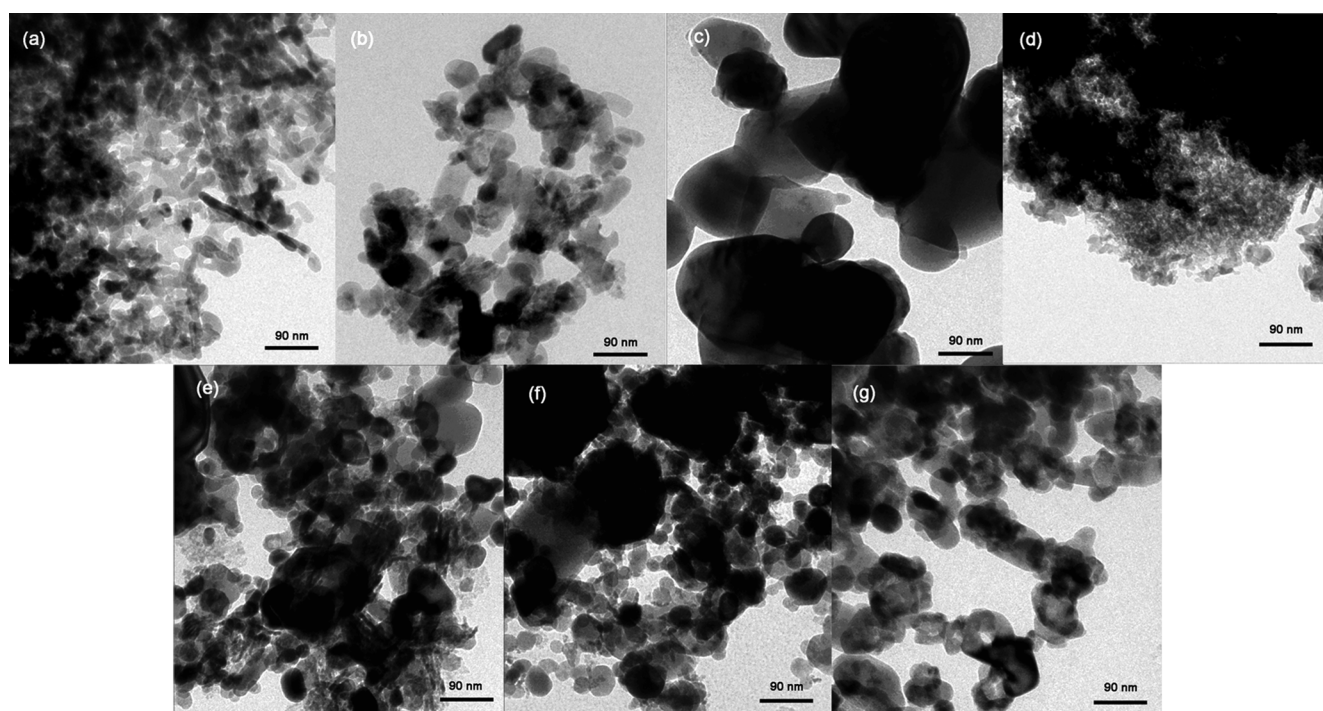


Figure 2. TEM micrographs of the Cu-catalysts: (a) CuZnAl-350-0.5, (b) CuZnAl-500-0.5, (c) CuZnAl-700-0.5, (d) CuZnAl-500-1, (e) CuZnAl-500-2, (f) CuZnAl-500-3, and (g) CuZn-500-0.5.

Table 2. Hydrogenation of Furfural in the Presence of Various Catalysts.^a

entry	catalyst	conv. (%)	yield (%)				others (%) ^b	TOF/h ^{-1c}	total carbon (%)
			CPO	CPL	FA	THFA			
1	CuZnAl-350-0.5	99.2	55.5	8	0	0	35.7	9.8	64.3
2	CuZnAl-500-0.5	97.9	60.3	2.5	0	0	35.1	9.4	64.9
3	CuZnAl-700-0.5	74.7	8.8	0.1	2.2	0	63.6	1.5	36.4
4	CuZnAl-500-1	77.0	5.2	0	3.2	0	68.6	4.6	31.4
5	CuZnAl-500-2	77.2	6.2	0.1	2.5	0	68.4	2.3	31.6
6	CuZnAl-500-3	73.4	4.7	0	3.0	0	65.7	1.7	34.3
7	CuZn-500-0.5	85.9	36.1	0.8	0.8	0.1	48.1	8.3	51.9
8	Cu/C	33.5	0	0	8.8	0	24.7	0	75.3
9	Cu/ γ -Al ₂ O ₃	21.4	0	0	0.8	0	20.6	0	79.4
10	Cu/SiO ₂	71.9	7.3	0	0	0.3	64.3	0	35.7
11	Cu/SBA-15	89.6	10.5	13.7	0.2	0	65.2	7.5	34.8

^aReaction conditions: 5 mmol of furfural, 0.2 g of catalyst, 15 mL of H₂O, reaction temperature 150 °C, hydrogen pressure 4 MPa, and 6 h reaction time. ^bOthers: undetermined compounds. ^cTOF = ((mol of CPO)/(mol of surface Cu atom))/(reaction time).

with different Cu/Zn molar ratios (0.5, 1, 2, and 3), CuZn-500-0.5, and supported Cu-catalysts (Cu/C, Cu/ γ -Al₂O₃, Cu/SiO₂, and Cu/SBA-15).

In the aqueous system, the main products detected from the reaction were CPO, CPL, FA, and THFA. The undetermined chemicals could be attributed to the polymerization reaction. As shown in Table 2, the CuZnAl-500-0.5 catalyst displayed good performance in the selective conversion of furfural to CPO in an aqueous solution (Table 2, entry 2). A total 60.3% yield of CPO and 2.5% yield of CPL were obtained with a furfural conversion of 97.9%. Among the CuZnAl-0.5 catalysts prepared at different calcination temperatures (entries 1–3), the catalysts calcined at 350 and 500 °C showed better activity (TOF was 9.8 and 9.4 h⁻¹, respectively). The total yield of rearrangement products (CPO and CPL) were both about 63% (entries 1 and 2), and more CPL (8% yield) was obtained with CuZnAl-350-0.5 catalyst. However, the CuZnAl-350-0.5 was unstable in the

reaction conditions. The inner wall of the quartz lining was covered with a layer of red copper after the reaction, while this phenomenon did not occur when CuZnAl-500-0.5 or CuZnAl-700-0.5 was used as the catalyst. This indicates that the CuZnAl calcined at low temperature is unstable.

When CuZnAl-500-1, CuZnAl-500-2, and CuZnAl-500-3 were used as catalysts (Table 2, entries 4–6), the conversion of furfural was above 70%. However, the total yield of CPO, CPL, and FA was very low (<9%). The TOF was between 1.7 and 4.6 h⁻¹, much lower than that of CuZnAl-500-0.5. CuZnAl-500-0.5 had a higher Cu specific surface area and smaller particle size than CuZnAl-500-1, CuZnAl-500-2, and CuZnAl-500-3 (Table 1), which indicated that the high activity might benefit from the high Cu dispersion, high Cu specific surface area, and small Cu particle size.

The catalyst without Al₂O₃ (CuZn-500-0.5) was also tested (Table 2, entry 7). The conversion of furfural (85.9%), yield of

CPO (36.1%) and CPL (0.8%), and TOF (8.3 h^{-1}) were lower than those using CuZnAl-500–0.5. It demonstrated that the addition of Al_2O_3 could improve the activity of the catalyst, which could also be attributed to the increase in Cu dispersion and Cu specific surface area and the decrease in Cu particle size.

The performance of other supported Cu catalysts was poor for the same reaction (Table 2, entries 8–11). No CPO or CPL was detected when Cu/C and Cu/ $\gamma\text{-Al}_2\text{O}_3$ were used as catalysts. Silica-supported Cu catalysts displayed better activity but only 7.3% yield of CPO for Cu/ SiO_2 , 10.5% yield of CPO, and 13.7% yield of CPL for Cu/SBA-15 were achieved, respectively. It is worth mentioning that compared with the CuZn500–0.5 catalyst, the TOF of the Cu/SBA-15 catalyst was slightly lower, and the particle size of Cu was smaller. However, overall conversion and target products were much lower after a 4 h reaction time. This indicated that ZnO could be favorable for this process.

Effect of Reaction Conditions. The influences of the reaction temperature, H_2 pressure, and reaction time on the furfural conversion were investigated over the CuZnAl-500–0.5 catalyst. Figure 3A demonstrates the yields of the main products at different reaction temperatures ranging from 130 to 170 °C. It is shown that the temperature had a great effect on the product distribution. At low temperature (130 °C), FA (46.1% yield), one of the intermediate compounds of furfural conversion, was the major product. With the rising temperature, more FA was converted to CPO and CPL. The yield of CPO reached its summit at 150 °C. However, the undesired coking and polymerization reaction at higher temperature (170 °C) would significantly lower the CPO yield (32.4%).

H_2 pressure is also an important factor that should be taken into account. The reactions were conducted at H_2 pressure ranging from 2 to 8 MPa. From Figure 3B, the yield of CPO and CPL were very low at 2 MPa. At 4 MPa, the yield of CPO reached the highest value. Under higher H_2 pressure (6 and 8 MPa), more CPL was obtained. It demonstrated that a desired H_2 pressure existed for the formation of CPO.

Figure 3C shows the effect of reaction time on the conversion of furfural over a CuZnAl-500–0.5 catalyst. At first, the yield of CPO increased with the extension of reaction time and reached the highest yield (60.3%) at 6 h, reducing to a 28.3% yield when the reaction time further extended to 8 h. The yield of FA reduced from 17.4% (at 2 h) to 0 (at 6 h), which also indicated that furfural was first converted to FA. The total yield of CPO and CPL was almost the same after 6 h, while CPO was converted into CPL by further hydrogenation.

Mechanism of the Reaction. To further study the mechanism, a series of reactions were tested (Scheme 1). First, the main products detected in furfural hydrogenation were used as substrates (Table 3). It is shown that FA can also be converted into CPO and CPL. According to Figure 3C, the yield of FA increased in the first 2 h and decreased later as time extended. The variation tendency revealed that the first step of the reaction was hydrogenation of furfural to FA. According to refs 30 and 31, 4-hydroxy-2-cyclopentenone can be prepared by heating FA in aqueous media. The FA aqueous solution (5 mmol of FA in 15 mL of H_2O) was heated in a N_2 atmosphere without any catalyst, and 4-hydroxy-2-cyclopentenone was detected (by GC/MS) as an intermediate formed from spontaneous hydrolysis of FA. THFA, the hydrogenated product of FA, cannot be further converted into CPO (Table 3, entry 2), which indicated that THFA cannot be the intermediate of the reaction. Then, the yield of CPO

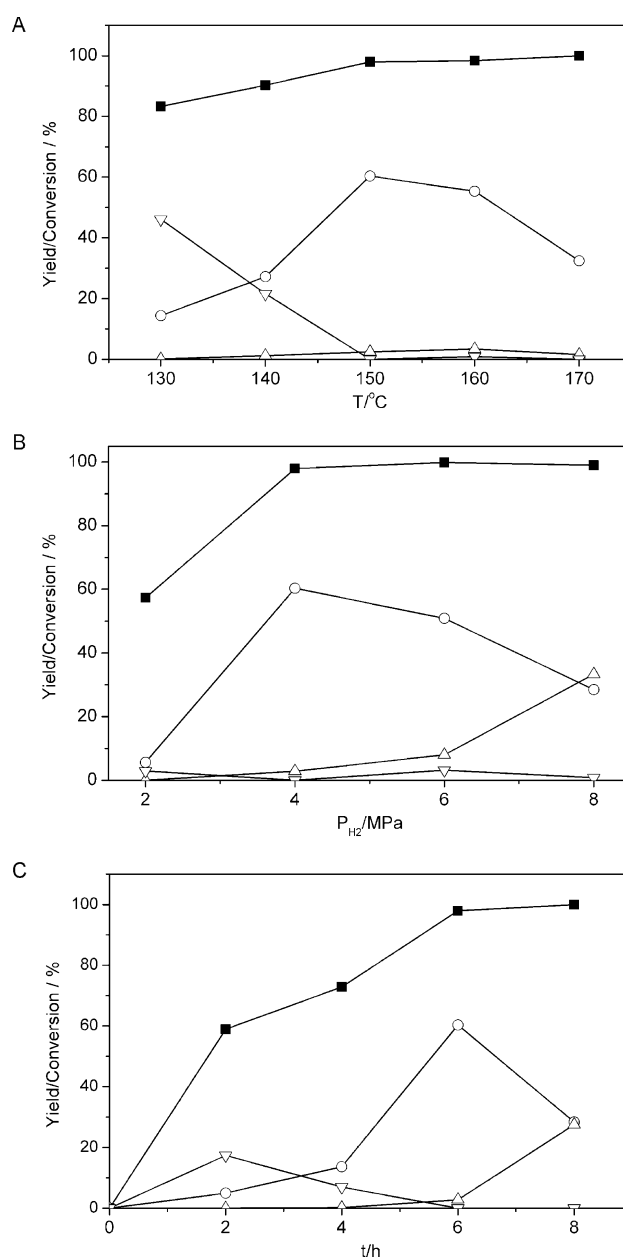


Figure 3. Catalytic performance of CuZnAl-500–0.5 at different reaction conditions. (A) Temperature effect. Reaction conditions: 5 mmol of furfural, 0.2 g of catalyst, 15 mL of H_2O , hydrogen pressure 4 MPa, and 6 h reaction time. (B) Hydrogen pressure effect. Reaction conditions: 5 mmol of furfural, 0.2 g of catalyst, 15 mL of H_2O , reaction temperature 150 °C, and 6 h reaction time. (C) Reaction time effect. Reaction conditions: 5 mmol of furfural, 0.2 g of catalyst, 15 mL of H_2O , reaction temperature 150 °C, and hydrogen pressure 4 MPa. Conversion of furfural (■), yield of CPO (○), CPL (Δ), and FA (▽).

increasing over time proved the next step was conversion of 4-hydroxy-2-cyclopentenone into 2-cyclopentenone followed by the hydrogenation to CPO. After a 6 h reaction, the hydrogenation trend of CPO to CPL became noticeable (Figure 3C). The data in Table 3, entries 3–4, also shows the process. In the meantime, traces of secondary reactions occurred to form 2-hydroxymethyl-tetrahydrofuran and cyclopentane-1,3-diol from FA and 4-hydroxy-2-cyclopentenone, respectively, which were detected by GC/MS.

Scheme 1. Proposed Reaction Pathway in Furfural Hydrogenation

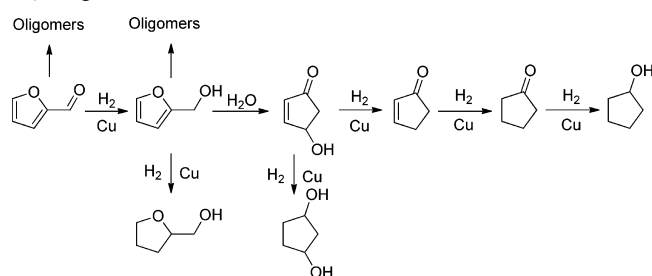


Table 3. Hydrogenation of Main Products Detected in Furfural Hydrogenation.^a

entry	substrate	conv. (%)	composition of mixture (%)				total carbon (%) ^b
			CPO	CPL	FA	THFA	
1	FA	100	37.3	22.7	0	0	70
2	THFA	0	0	0	0	100	100
3	CPO	97.6	3.4	90.2	0	0	93.6
4	CPL	6.4	0.5	93.6	0	0	94.1

^aReaction conditions: 5 mmol of substrate, 0.2 g of catalyst, 15 mL of H₂O, reaction temperature 150 °C, hydrogen pressure 4 MPa, and 6 h reaction time. ^bLoss of carbon could be contributed to coking of the substrate in the aqueous solution.

In summary, furfural was first hydrogenated to FA, which could be hydrolyzed to 4-hydroxy-2-cyclopentenone spontaneously in aqueous phase. After that, 4-hydroxy-2-cyclopentenone, CPO, and CPL were obtained through hydrogenation catalyzed by CuZnAl in a H₂ atmosphere, successively. The aforementioned process agreed with the previous study of Yang et al.¹²

Stability of the Catalyst. The stability of CuZnAl-500-0.5 was examined. A batch of CuZnAl-500-0.5 was recycled five times and tested on the conversion of furfural. As shown in Figure 4, the conversions of furfural were all above 90% in five cycles, with a maximum CPO yield of 62.1% in the second run. The yield of CPO decreased to 53.3% and the yield of FA increased to 5.6% in the fifth run. While the TOF was maintained stable in the first three runs (9.2–9.4 h⁻¹), it

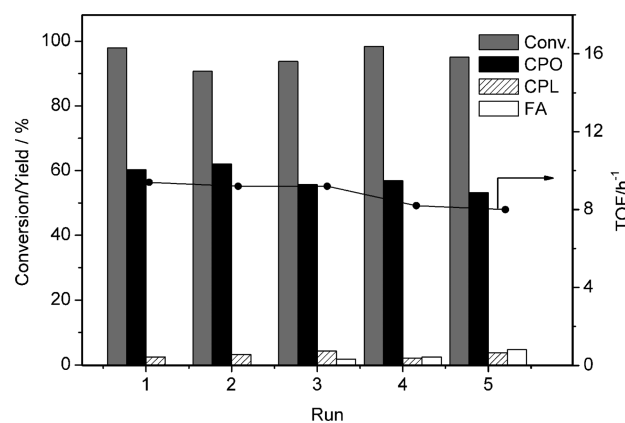


Figure 4. Performance of the CuZnAl-500-0.5 catalyst in the recycling experiment. Five mmol of furfural, 0.20 g of CuZnAl-500-0.5, 15 mL of H₂O, reaction temperature 150 °C, and 6 h reaction time.

decreased in the last two runs (8–8.2 h⁻¹). It is shown that the activity of catalyst decreased to some extent.

A series of tests were also carried out to determine the key factors leading to the slight activity loss of the catalyst.

There was no significant change in the XRD patterns between fresh and reused CuZnAl-500-0.5 catalyst (Figure 5). The morphology of CuZnAl-500-0.5 was also not changed after the reaction (Figure 6).

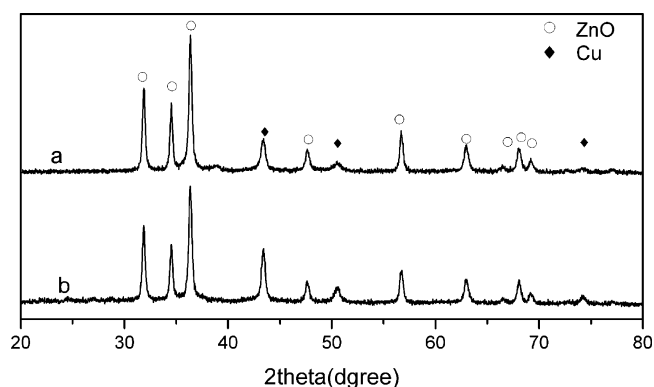


Figure 5. XRD patterns of the CuZnAl-500-0.5 catalyst: (a) before reaction and (b) after five reaction cycles.

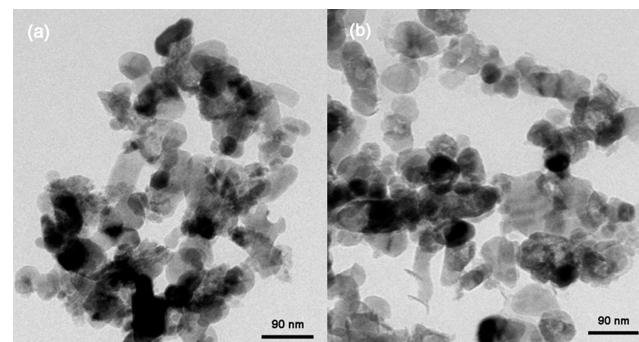


Figure 6. TEM micrographs of the CuZnAl-500-0.5 catalyst: (a) before reaction and (b) after five reaction cycles.

The characteristics of the CuZnAl-500-0.5 catalysts are given in Table 4. The Cu content decreased slightly from 28.5 to 27.7 wt % after being recycled five times, which indicated that the metal leaching existed in the reaction but was not serious. The solution was also collected after a batch of reaction with the CuZnAl-500-0.5 catalyst to explore the effect of the leached metal. The Cu content in the solution was 1.12×10^{-3} g/L. The conversion of furfural in the solution without the CuZnAl-500-0.5 catalyst was 67.4%, but no hydrogenated product was obtained. There was also serious coking in the reactor. Therefore, the Cu leached into solution could not catalyze the hydrogenation reaction. It was found that the Cu dispersion and Cu specific area decreased after being used five times, which might be the factors that caused the loss of activity.

The carbon on the catalyst was analyzed to explore whether the coke formed on the catalyst. After being used five times, the carbon on the catalyst increased from 0.22% to 2.33% (Table S1, Supporting Information). The increased carbon content could be attributed to the coke formed on the catalyst, which was also a factor that caused the loss activity.

Table 4. Characteristics of CuZnAl-500-0.5 Catalysts

catalyst	Cu (wt %)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)	d_{Cu} (nm)		D_{Cu} (%) ^c	S_{Cu} ($\text{m}^2 \text{g}_{\text{cat}}^{-1}$) ^d
					XRD ^a	N_2O ^b		
before reaction	28.5	25.0	0.089	14.0	12.8	11.5	8.7	17.0
after five reaction cycles	27.7	19.5	0.190	45.1	15.1	12.4	8.1	14.2

^aCrystal size was calculated by the Scherrer equation through the Cu(111) diffraction peak. ^bAverage volume–surface diameter was calculated from the N_2O titration method; $d \approx 0.5 \times A_1/A_2$ (nm). ^cDispersion (D) of Cu was determined by the N_2O titration method; $D = 2A_2/A_1 \times 100\%$. ^dThe Cu metal surface area was determined by the N_2O titration method.

Another factor that caused the loss of activity of the catalyst could be the oxidation of Cu^0 . XPS spectra of the fresh and spent CuZnAl-500–0.5 catalysts were employed to investigate the nature of Cu. The narrow scan spectra of Cu 2p and Zn 2p are shown in Figure 7A. The peaks appearing at 932.6 and

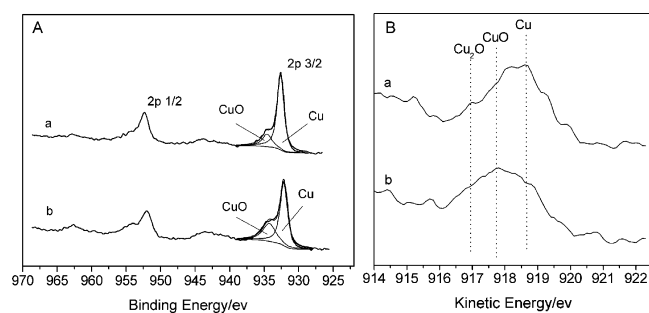


Figure 7. (A) XPS spectra of Cu 2p signals and (B) Auger electron spectra of Cu for the CuZnAl-500–0.5 catalyst: (a) before reaction and (b) after five reaction cycles.

952.4 eV correspond to the signals of $2p_{3/2}$ and $2p_{1/2}$, respectively. The core-level Cu $2p_{3/2}$ spectrum was deconvoluted, and the peaks at 932.5 and 934.4 eV corresponded to Cu^0 and Cu_2O , and CuO .^{32–35} The binding energy of Cu $2p_{3/2}$ and Cu_2O $2p_{3/2}$ were so close that they could not be distinguished, while they can be distinguished by the Auger electron spectra of Cu. The peaks at 916.9, 917.7, and 918.6 eV corresponded to Cu_2O , CuO , and Cu^0 , respectively (Figure 7B). The major valent state of Cu was Cu^0 , while more CuO was obtained after the reaction. The decrease in Cu^0 content might be a factor that influences the activity of the used catalysts. CuO might form in the reaction or partial oxidation of Cu exposed to the air, while the activity could also be easily recovered by reducing in hydrogen.

Then, the catalyst was calcined at 500 °C to remove the coke on the surface. After been calcined at 500 °C, the carbon on the catalyst was similar to that of the fresh catalyst. The calcined catalyst was reduced and then used in another run. The yield of CPO and CPL was 57.5% and 2.9%, respectively, which were better than those in the fifth run. It is shown that after removal of the coke and being further reduced by hydrogen, the catalyst can be recovered to a certain extent.

CONCLUSION

In conclusion, a CuZnAl catalyst was synthesized and used to selectively catalyze furfural into CPO. Among the catalysts prepared with different molar ratios of Cu/Zn at different conditions, CuZnAl-500–0.5 had the optimal activity and stability. Under the optimized conditions (150 °C, 4 MPa H_2 pressure, 6 h), the yields of CPO and total rearrangement products could reach up to 62% and 65%, respectively. Although the activity of the catalyst decreased slightly after

being used five times, it could be recovered to some extent by calcination and reduction. If the stability of the catalyst can be further optimized by some new techniques such as atomic layer deposition,³⁶ it has the potential to produce CPO from furfural on a large scale by using CuZnAl catalysts.

ASSOCIATED CONTENT

Supporting Information

XRD patterns of supported Cu-catalysts, H_2 -TPR of Cu catalysts, and carbon content of the catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

FA, furfuryl alcohol; THFA, tetrahydrofurfuryl alcohol; 2-MeF, 2-methylfuran; THF, tetrahydrofuran; CPO, cyclopentanone; CPL, cyclopentanol

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