

Nano CuO/ZSM-5 zeolite as a green and efficient catalyst for dehydration of 1,4-butanediol to tetrahydrofuran

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Received November 25, 2016; accepted January 12, 2017; published online April 26, 2017

Nano CuO/ZSM-5 zeolite was prepared and used as a catalyst for dehydration of 1,4-butanediol (BDO) to tetrahydrofuran (THF) in liquid-phase. It was found that the 4.6 wt% CuO/ZSM-5 displayed good catalytic performance, and nearly 100% of BDO conversion and more than 99% of THF selectivity could be achieved by a rotary evaporator reactor at 170 °C under the atmospheric pressure. With such mild reaction conditions, 2400 g BDO could be converted to THF over 1 g catalyst under semi-continuous operation. Characterizations with X-ray diffraction (XRD), temperature-programmed reduction (TPR), NH₃-temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and Brunauer-Emmett-Teller (BET) over fresh and used 4.6 wt% CuO/ZSM-5 were conducted. Based on the results of the characterization and catalytic performance of 4.6 wt% CuO/ZSM-5, it can be conjectured that the formed 1–3 nm CuO nanoparticles, suitable acidity of the catalyst due to the synergic interaction of CuO and ZSM-5 support promoted the dehydration of BDO to THF.

copper, ZSM-5 zeolite, tetrahydrofuran, 1,4-butanediol, green catalysis

Citation: Long Y, Liu S, Fei Y, Li Q, Deng Y. Nano CuO/ZSM-5 zeolite as a green and efficient catalyst for dehydration of 1,4-butanediol to tetrahydrofuran. *Sci China Chem*, 2017, 60: 964–969, doi: 10.1007/s11426-016-9002-x

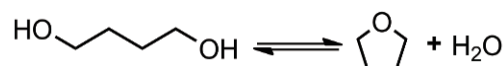
1 Introduction

Tetrahydrofuran (THF) has been widely used in many fields, especially as a solvent for various high polymers, such as polyvinyl chloride (PVC), rubber and buna. Besides, it was also known as the monomer for polytetramethylene ether glycol, which is one of the important materials for production of spandex and thermoplastic polyurethanes elastomer.

At present, there are several routes to produce THF in industrial manufacture. Thereinto, dehydration of 1,4-butanediol (BDO) and hydrogenation of furan were the most com-

monly used methods to afford THF. However, the hydrogenation of furan often suffers from dangerous operation as well as high reaction temperature. Consequently, dehydration of BDO to THF has attracted extensive interest in point of view BDO of economic and environmental benignancy, because only H₂O as by-product was formed in this process (Scheme 1).

As is well known, dehydration of BDO usually proceeds with acid catalysts. Although the traditional acid catalysts, such as sulfuric acid and phosphoric acid, show high activity



Scheme 1 Synthesis of THF from BDO.

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for the BDO dehydration, however, the used acids were corrosive, hazardous and polluttional. Therefore, the development of new catalysts with highly performance and environmentally friendly character is highly desired. Up to now, various catalytic systems have been reported for the dehydration of BDO to THF. According to the previous literatures [1–4], THF could be obtained from BDO in the presence of cation exchange resins at relatively low temperature (<120 °C), but the disadvantages are also obvious, including low reaction rate, low yield of THF (less than 83%), the massive catalyst dosage (throughput: 1.42 t BDO per m³ catalyst in 1 h [5]), and the difficulty regeneration of catalyst. Besides, the metal salts of sulfate, phosphate or halide [6–10] displayed high activity for the BDO dehydration, but these catalysts still have strong corrosion and toxicity. Oxides-based catalysts could be also employed for dehydration of BDO to THF, including ZrO₂ [11], lanthanide oxides [12], sol-gel alumina [13], and supported rare earth oxides [14]. However, all of the above mentioned oxide catalysts exhibited relatively low THF selectivity in this reaction, for example, 3-buten-1-ol could be produced competitively during the dehydration of BDO over by ZrO₂. Heteropolyacids [15–18] could also improve such reaction, but the high cost of catalysts would limit their practical application. In addition, Aghaziarati *et al.* [19] described the dehydration of BDO over NH₄-ZSM-5 zeolite, which performed highly activity with nearly 100% THF selectivity, but the reaction was carried out under more than 1.5 MPa pressure. In view of green chemistry and catalyst, to save energy, reduce waste and enhance the catalytic performance, further study should be implemented for this reaction.

In this work, nano CuO/ZSM-5 zeolite was prepared and used as a catalyst for dehydration of BDO to THF in liquid-phase. It was found that the 4.6 wt% CuO/ZSM-5 displayed the best catalytic performance, nearly 100% of BDO conversion and more than 99% of THF selectivity could be achieved with a rotary evaporator at 170 °C under the atmospheric pressure, and 2400 g BDO could be converted over 1 g 4.6 wt% CuO/ZSM-5 catalyst under semi-continuous operation. At the same time, Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), H₂-temperature-programmed reduction (TPR) and NH₃-temperature programmed desorption (TPD) studies were conducted to explore the relationship between structure and performance. Moreover, the influences of catalyst type, Cu loadings, reaction temperatures, were also investigated in detail.

2 Experimental

2.1 Catalysts preparation and characterization

The zeolite HZSM-5 materials having a Si/Al ratio of 80 obtained from the catalyst plant of NanKai University,

China, and other materials (A. P.) all supplied by Sinopharm Chemical Reagent Co., Ltd. (China), the metal-exchanged ZSM-5 zeolite were obtained by impregnation method using H-ZSM-5 zeolite and Cu(CH₃COO)₂·H₂O as starting materials. The calculated materials were added to 1000 mL deionized water and stirred for 24 h. After impregnation, the precursor was dried at 110 °C for 8 h, and then the samples were calcined at 500 °C for 3 h. ZSM-5 supported copper oxide with 2.5 wt%, 5 wt%, 10 wt% and 20 wt%, denoted as CuO/ZSM-5, were prepared respectively. For the comparison, FeO_x/ZSM-5, CuO/SiO₂ and CuO/Al₂O₃ were also prepared with similar method.

XRD was measured on a Siemens D/max-RB powder X-ray diffract meter (China). Diffraction patterns were recorded with Cu K α radiation (40 mA, 40 kV) over a 2 θ range of 5°–90° and a position-sensitive detector using a step size of 0.01° and a step time of 0.15 s.

Surface analysis of the catalysts was performed by X-ray photoelectron spectroscopy (XPS) on VG ESCALAB210 (UK) using an Mg K α radiation at a pass energy of 20 eV. The energy scale was calibrated and corrected for charging using the C 1s (285.0 eV) line as the binding energy (BE) reference.

TEM analysis was carried out using a TF20 (FEI, USA) field emission transmission electron microscope apparatus operating at 300 kV. Single-particle energy dispersive X-ray (EDX) mapping analysis was performed using a TF20 field emission TEM in the STEM mode.

TPR of H₂ was carried out on TPR/TPD flow system equipped with a thermal conductivity detector (TCD). TPR analysis was conducted with 10% H₂/Ar (30 mL/min). In a typical experiment the solid sample (100 mg with particle size 160–200 μ m) was pretreated at 500 °C for 1 h under air flow (30 mL/min). The profile was recorded at a heating rate of 10 °C/min from room temperature to 800 °C and maintained at this temperature until the TCD signal of H₂ returned to the baseline. Quantitative hydrogen consumptions were obtained by use of TPR calibration runs using a standard copper oxide sample (Micromeritics) in place of the catalyst.

The surface acid properties of the catalysts were measured by TPD of NH₃ and carried out on TPD flow system equipped with a TCD detector. In a typical experiment, the solid sample (100 mg with particle size 160–200 μ m) was pretreated at 500 °C for 1 h under argon gas flow (30 mL/min) and then cooled to room temperature. The sample was subsequently exposed to NH₃ stream (30 mL/min) at room temperature for 1 h and flushed again with argon gas for 1 h to remove any physico-adsorbed NH₃. The desorption profile was recorded at a heating rate of 10 °C/min from room temperature to 600 °C and maintained until the TCD signal of NH₃ returned to the baseline. The quantitative analysis for NH₃ desorption is calculated based on the integration of the corresponding TPD trace, preliminarily calibrated by the injection of pure NH₃

pulses.

The BET surface areas, pore volumes and average pore radius of catalysts were obtained with physisorption of N₂ using a Micromeritics ASAP 2010 (USA).

Thermal analysis (TGA) was carried out using a METTLER TG1 model (Switzerland). Samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.

2.2 THF synthesis from BDO

The catalytic reactions were tested with a 500 mL rotary evaporator reactor under the atmospheric pressure with temperatures ranging from 140 to 180 °C and 3–4 h for each reaction. In such reactor system, the resulted THF and water could be continuously removed from the reaction to increase BDO conversion due to greater boiling points differences between THF, water and BDO. The qualitative and quantitative analysis of the resulted liquid mixture was conducted with gas chromatograph-mass spectrometer (GC-MS, Agilent 6890/5973, USA) and GC (Agilent 7890, USA) equipped with a SE-54 capillary column (Agilent Technologies Shanghai Co. Ltd., China) and a flame ionization detector (FID).

3 Results and discussion

3.1 Catalytic performance of CuO/ZSM-5 for BDO dehydration to THF

A series of catalysts including H-ZSM-5, CuO, physical mixture of CuO and ZSM-5, Fe/ZSM-5, CuO/ZSM-5, CuO/SiO₂ and CuO/Al₂O₃ were prepared and their catalytic performances for BDO dehydration to THF were investigated. It is found that CuO/ZSM-5 catalyst exhibited the best catalytic performance. In order to optimize reaction conditions, the influence of various reaction parameters was investigated.

Firstly, to evaluate the effect of Cu loadings on the conversion of BDO, the catalysts with different Cu loadings from 2.5% to 20 wt% were tested. As shown in Table 1, with the increase of Cu loadings, the conversion of BDO increased obviously, and conversion of BDO could be up to 89% as the Cu loading was 4.6 wt%. But the conversion of BDO declined when the Cu loading on ZSM-5 was further increased. The reason may be due to more Cu loadings may lead to the agglomeration of copper oxide to block support pores. These results indicated that CuO/ZSM-5 with 4.6 wt% loading has better catalytic performance for dehydration of BDO to THF in liquid-phase.

The influence of temperature on the catalyst performance was studied and the results were listed in Table 2. It can be seen that the conversion of BDO increased gradually as the reaction temperature raised, and complete BDO conversion could be obtained at 170 °C. Meanwhile, the selectivity of THF could maintain more than 99% at various temperatures.

Although the 100% conversion of BDO was achieved within 2 h at 180 °C, the selectivity of THF reduced slightly, because a small amount of BDO was brought in the product at such high reaction temperature. Therefore, most suitable reaction temperature is 170 °C for BDO dehydration over 4.6 wt% CuO/ZSM-5 catalyst.

The conversion rate of BDO in different periods of reaction time at 170 °C was also tested. As the result shown in Figure 1, in the course of fore 3 h, the conversion rate of BDO followed by 37%, 62%, 89% and the conversion rate of BDO ascend to 100% at 3.8 h.

The thermal stability of 4.6 wt% CuO/ZSM-5 and H-ZSM-5 was checked by TGA (Figure 2). As the result shows, the thermal weight loss of CuO/ZSM-5 was less than 1.5% in the whole heating process, and the pyrolysis process occurred lower than 200 °C, which should be corresponding to the water loss. The result indicated that the catalyst has high thermal stability.

Table 1 Catalytic performance of different Cu loadings^{a)}

Catalyst	Conversion of BDO (%)	Selectivity of THF (%)
2.5 wt% CuO/ZSM-5	38	>99
4.6 wt% CuO/ZSM-5 ^{b)}	89	>99
10 wt% CuO/ZSM-5	57	>99
20 wt% CuO/ZSM-5	43	>99

a) Reaction conditions: 50 g BDO, 2.5 g catalyst, 170 °C, 3 h; b) the actual content of Cu was analyzed by ICP.

Table 2 The influence of temperature on the reaction^{a)}

Reaction temperature	Conversion of BDO (%)	Selectivity of THF (%)
140	13	>99
150	21	>99
160	55	>99
170	100	>99
180 ^{b)}	100	96

a) Reaction conditions: 50 g BDO, 2.5 g catalyst, 4 h; b) the 100% conversion of BDO was achieved within 2 h.

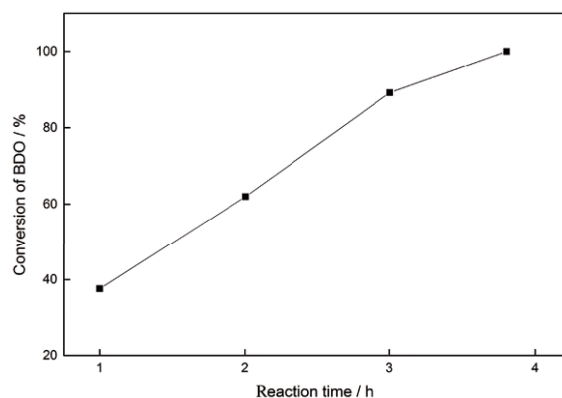


Figure 1 Conversion rate of BDO in different periods.

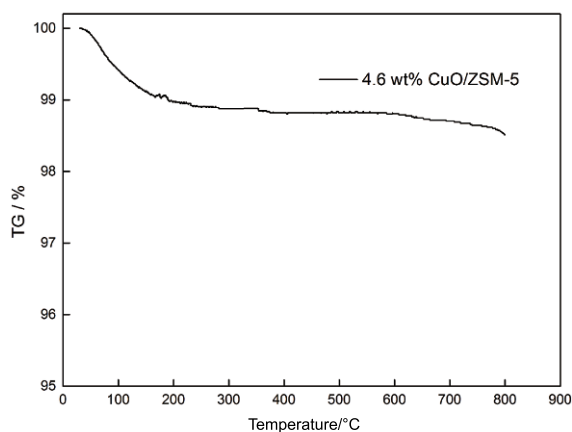


Figure 2 TGA curve of the 4.6 wt% CuO/ZSM-5.

The reusability of catalysts is a key parameter in determining their suitability in practical applications. Therefore, the repeatability of 4.6 wt% CuO/ZSM-5 catalyst for BDO dehydration was also studied. In a typical reaction, BDO and catalysts were added in the reactor and then the reaction was operated at 170 °C for 4 h. After each test, the reactor was weighed to evaluate the surplus stock and then fresh BDO was charged in maintaining the BDO was 50 g. For the first time, the BDO could convert completely with more than 99% THF selectivity and the catalyst was present as dry powders after reaction. In the subsequent recycles, the conversion of BDO declined to about 64%, and the possible reason of the deactivation for CuO/ZSM-5 was due to the adsorption of a very little amount of heavy components on the surface of catalysts. Moreover, the regeneration of catalyst was also attempted in this study. The catalytic activity for 4.6 wt% CuO/ZSM-5 after using 5 times could be recovered after calcination for 3 h at 500 °C (entry 5*, Table 3). The treatment capacities of catalyst evaluated by semi-continuous operation (add BDO every 3 h) was also carried out, and 2400 g BDO could be converted to THF over 1 g catalyst over 1 g 4.6 wt% CuO/ZSM-5 catalyst.

3.2 Results of the catalysts characterizations

In order to explore the relationship between structure and performance of catalyst, a series of characterizations were conducted.

The TEM image of 4.6 wt% CuO/ZSM-5 is shown in Figure 3. As can be seen in the TEM image, the nano-size of metal particles with high dispersion could be observed on the support, and the average size of CuO nanoparticles was 1–3 nm, which may be one of the reasons for the highly catalytic performance of 4.6 wt% CuO/ZSM-5 catalyst.

The BET and XPS results of CuO/ZSM-5 were summarized in Table 4. It was found that with the increase of Cu loadings, the surface area and average pore radius decreased gradually. As the 4.6 wt% CuO/ZSM-5 catalyst, the BET

of surface area was 311 m²/g and 1.6 nm radius. If the Cu loading were further increased, the oxide would be agglomerated on surface of the ZSM-5 support, thus resulted in the decline of catalytic activity. The XPS analyses of 4.6 wt% CuO/ZSM-5 sample were also performed. The binding energies of these peaks were observed with Cu 2p_{3/2} (934.8 eV), and Cu 2p_{1/2} (955.2 eV), suggesting that the chemical states of Cu species on the catalyst surface was mainly Cu²⁺. A slight increase in binding energies of these peaks was observed in comparison with standard binding energy of CuO (Cu 2p_{3/2} 933.6 eV and Cu 2p_{1/2} 953.6 eV), which implied that the surface Cu species in this sample displayed more deviation of electron cloud owing to the interaction between Cu species and the ZSM-5. Moreover, XPS analyses manifested that the surface atom ratio of Cu²⁺ to Si⁴⁺ was 0.046, which slightly lower than the theoretical value 0.048, meaning that slightly more CuO species enters the bulk of the ZSM-5 support.

The XRD of the fresh and after 5 times used 4.6 wt% CuO/ZSM-5 catalysts are shown in Figure 4. The characteristic peaks of ZSM-5 could be observed in both samples XRD patterns. For the fresh catalyst, the diffraction peaks at 36° and 38.9° indicated the generation of CuO (JCPDS No.48-1548). However, the intensity of CuO and ZSM-5 peaks of catalyst became weak after using 5 times, which might be due to the reduction of CuO during the dehydration of BDO, which might be one of the reasons for the decline of

Table 3 The reusability of the 4.6 wt% CuO/ZSM-5^{a)}

Reused times	Conversion of BDO (%)	Selectivity of THF (%)
1	100	>99
2	67	>99
3	64	>99
4	63	>99
5	65	>99
5* ^{b)}	100	>99

a) Reaction conditions: 50 g BDO, 2.5 g catalyst, 170 °C, 4 h; b) the catalyst was calcination for 3 h at 500 °C after using 5 times.

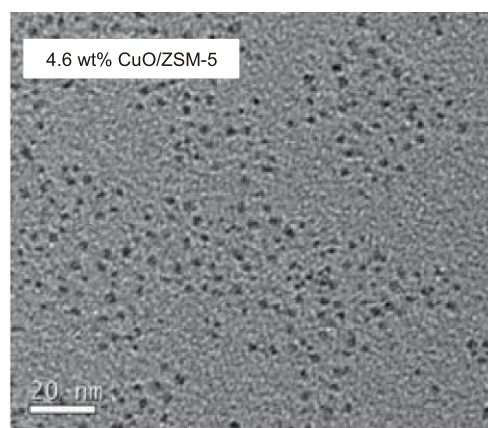


Figure 3 TEM image of 4.6 wt% CuO/ZSM-5.

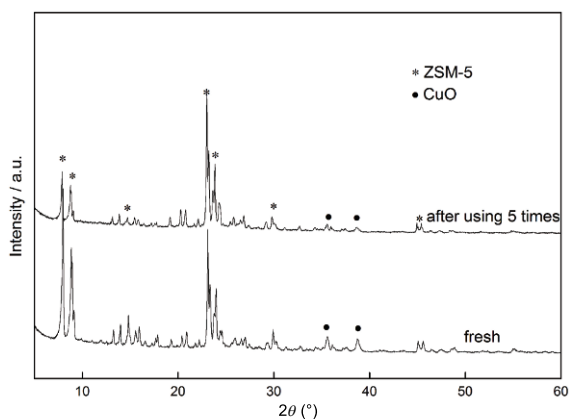
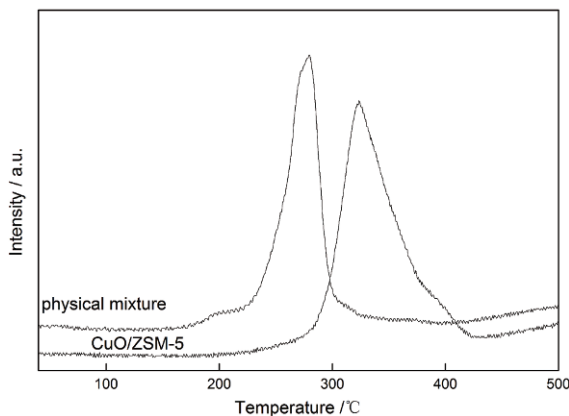
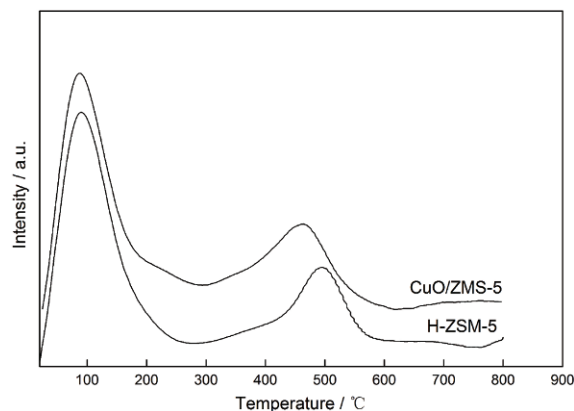
Table 4 BET and XPS of different CuO/ZSM-5 samples

Sample	BE (eV)	Specific surface area (m ² /g)	Pore volume (mL/g)	Average pore radius (nm)
H-ZSM-5		326	0.270	1.66
2.5 wt% CuO/ZSM-5		314	0.236	1.61
4.6 wt% CuO/ZSM-5	Cu 2p _{3/2} 934.8/Cu 2p _{1/2} 955.2	311	0.229	1.59
10 wt% CuO/ZSM-5		296	0.227	1.47
20 wt% CuO/ZSM-5		258	0.208	1.45

catalytic activity.

TPR patterns were measured for the 4.6 wt% CuO/ZSM-5 catalyst and compared with the physical mixture (4.6 wt% CuO and 95.4 wt% H-ZSM-5) and the results were described in Figure 5. As shown in Figure 5, for the physical mixture, the reduction temperature was at 280 °C, while the peak of CuO/ZSM-5 occurred at 323 °C respectively, which was higher than that of the physical mixture one. The TPR results revealed that there is interaction between CuO species and the ZSM-5 support, which was one of reasons for the highly catalytic performance for CuO/ZSM-5. This result is in well accordance with the XPS patterns.

The acid properties of 4.6 wt% CuO/ZSM-5 and H-ZSM-5 samples were studied with NH₃-TPD (Figure 6). A low

**Figure 4** XRD patterns of 4.6 wt% CuO/ZSM-5.**Figure 5** H₂-TPR patterns of 4.6 wt% CuO/ZSM-5.**Figure 6** NH₃-TPD patterns of 4.6 wt% CuO/ZSM-5.

temperature desorption peak at about 86 °C could be detected in the two samples, and for the 4.6 wt% CuO/ZSM-5, a desorption peak appears at around 463 °C, which lower than that of H-ZSM-5 (497 °C), indicating that the acid strength on the support surface decreased appropriately after the introduction of CuO.

Based on the results of the characterization and catalytic performance of 4.6 wt% CuO/ZSM-5 catalyst, it can be conjectured that the formed 1–3 nm CuO nanoparticles, and suitable acidity of the catalyst due to the synergic interaction of CuO and ZSM-5 support promoted the dehydration of BDO to THF.

4 Conclusions

In conclusion, a green and relatively cheaper CuO/ZSM-5 catalyst was prepared via impregnation method, which exhibited highly catalytic performance for THF production from BDO. With the mild reaction conditions at 170 °C under atmospheric pressure, complete conversion of BDO could be obtained with more than 99% selectivity of THF, and the 2400 g BDO could be converted to THF over 1 g 4.6 wt% CuO/ZSM-5 catalyst. The characterization results of the catalyst suggested that the formed CuO nanoparticles, and suitable acidity of the catalyst due to the synergic interact of CuO and ZSM-5 support promoted the dehydration of BDO to THF, which resulted in the highly catalytic activity of 4.6 wt% CuO/ZSM-5. This process as the alternative clean synthesis of THF has great developmental potential in industrial application.

Acknowledgments This work was supported by the National Natural Science Foundation of China (21173240).

Conflict of interest The authors declare that they have no conflict of interest.

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