Electronic Supplementary Material (ESI) for Green Chemistry

One-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol catalyzed by Ru@ZIF-8+CuO/basic ionic liquid system

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1. **Preparation of catalysts**
2. **Synthesis of the basic ionic liquid**
3. **Characterization of catalysts**

1. Preparation of the catalysts

1.1 Preparation of the CuO nanoparticles

CuO nanoparticles were prepared as follows: 1.2 g $Cu(NO_3)_2$•$3H_2O$ and 5 mg PEG200 were added into 300 mL water, and then 2.0 g NaOH was added into the above solution. Blue-black precipitate was obtained after 6 h, which was washed by water (3×10 mL) and ethanol (3×10 mL) separately. Copper oxide was obtained when the precipitate was dried at 40 ^{o}C for 24 h.

1.2 Synthesis of ZIF-8

The procedures were similar to that reported in the literature.[S1] In a typical preparation, a solid mixture of zinc nitrate hexahydrate ($Zn(NO_3)_2$•$6H_2O$, 0.48 g) and 2-methylimidazole (0.12 g) was dissolved in 36 mL of N,N'-dimethylformamide (DMF) and then loaded into a 20 mL vial. The vial was tightly capped and heated to 140 ^{o}C in an oven at a rate of 5 ^{o}C/min and held at this temperature for 48 h, then cooled to room temperature. After removal of the mother liquor from the mixture, chloroform (20 mL) was added to the vial. The residual was removed by vacuum at 130 ^{o}C for 10 h, and ZIF-8 was obtained.

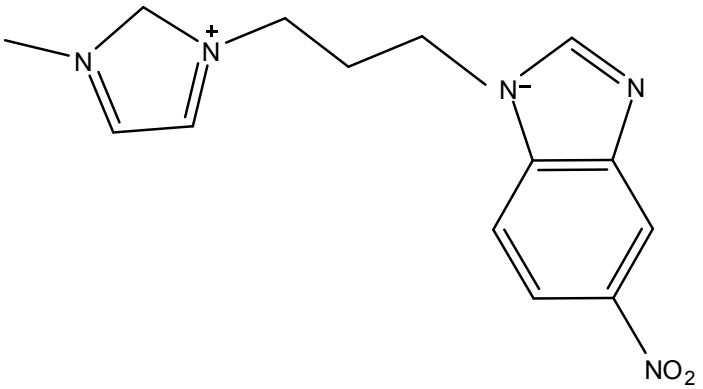
1.3 Preparation of Ru@ZIF-8

The method to prepare the Ru@ZIF-8 catalyst was reported previously.[S2] In the experiment, ZIF-8 powder (0.18 g) was dispersed in 5 mL of 0.8 mg/mL ruthenium chloride hydrate methanol solution. The mixture was placed into a Teflon-lined stainless-steel reactor of 8 mL. After the air in reactor was replaced by CO_2, the reactor was held at 35 °C for 1 h, and then CO_2 was charged into the reactor to 5.0 MPa. The reactor was then heated at 185 °C for 5 h. After cooling to room temperature, the CO_2 in the reactor was slowly released. The resulting grey solid was washed twice with 20 mL of ethanol and dried under vacuum at 60 °C for 24 h, and

dried Ru@ZIF-8 was obtained.

2. Synthesis of basic ionic liquid

The basic ionic liquid was prepared by the method similar to that reported by other authors.[S3] In the experiment, 1.0 g NaOH was added to 40 mL of methanol. Then 4.0 g of 5-nitrobenzimidazole was added into the above solution, and the mixture was stirred for 40 min. Then, 4.6 g of 1-butyl-3-methyl imidazole chloride was loaded into the solution above and stirred for 3 hours at room temperature. Then, the 30 mL of anhydrous ether was introduced into the reaction mixture, which was stirred for 20 h at room temperature and filtered to remove the salt and obtain filtrate. The solvents in the filtrate were removed by the rotary evaporation. The mixture left was washed using ether (3×10 mL) and the basic ionic liquids (1-butyl-3-methylimidazolium 5-nitrobenzimidazolide) were obtained after drying under vacuum at 50 ^{o}C overnight. The chemical structure of the IL is showed in Scheme S1:



Scheme S1 Chemical structure of 1-butyl-3-methylimidazolium 5-nitrobenzimidazolide

3. Characterization of catalysts

3.1 XRD patterns of the catalysts The XRD patterns of CuO nanoparticles and ZIF-8 are presented in Figure S1. The XRD patterns of CuO nanoparticles are consistent with that in the JCPDS database. The XRD patterns of ZIF-8 are consistent with the data reported in reference S1.

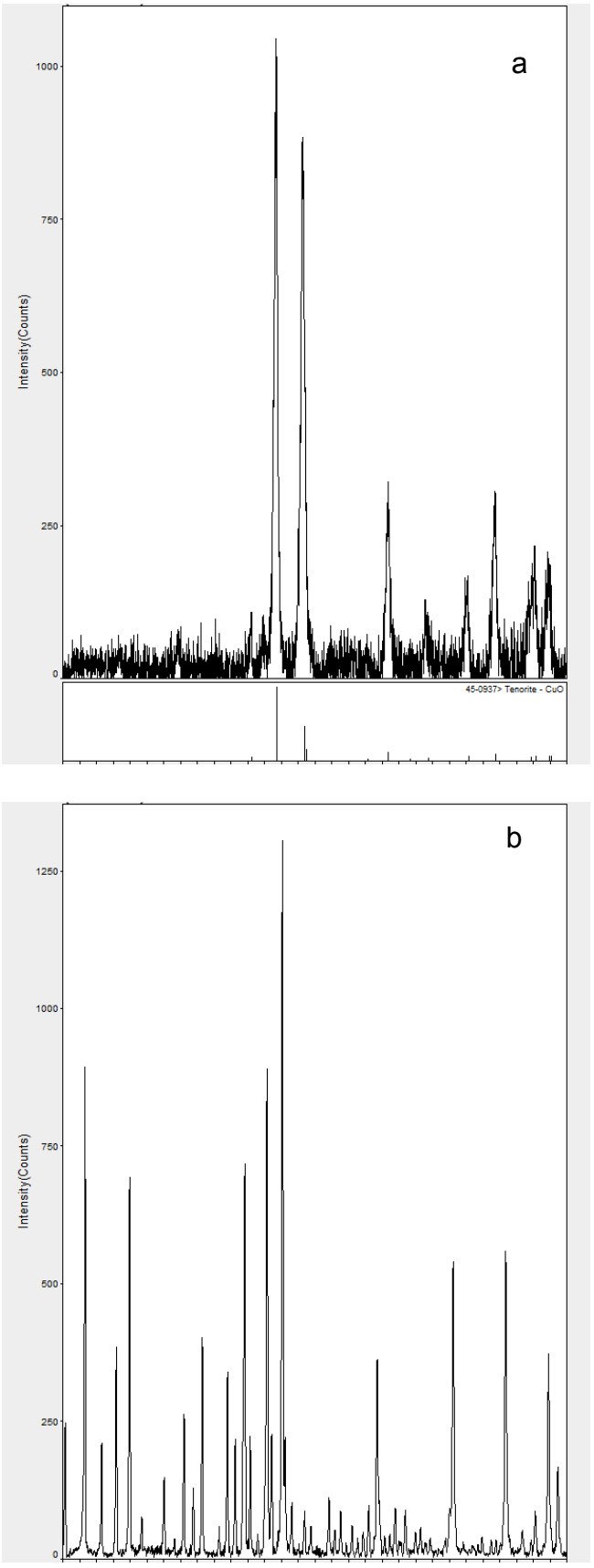


Figure S1. XRD patterns of CuO nanoparticles and ZIF-8

3.2 TEM images of the catalysts TEM images of Ru@ZIF-8 and CuO nanoparticles are given in Figure S2. The size of the Ru particles in the catalyst Ru@ZIF-8 was in the range of 3 to 5 nm. The horizontal axis of CuO nanoparticles was about 100 nm and the vertical axis was about 600 nm.

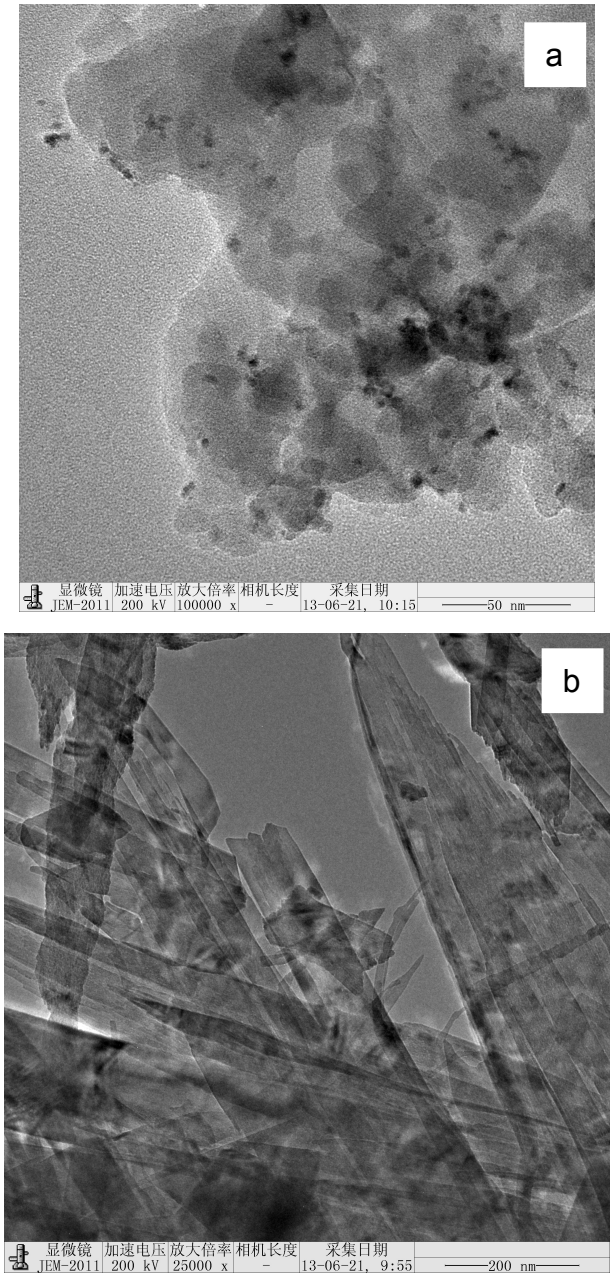


Figure S2. TEM images of Ru@ZIF-8(a) and CuO nanoparticles(b).

References

[S1] L. T. L. Nguyen, K. K. A. Le, N. T. S. Phan, *Chin. J. Catal.*, 2012, **33**, 688-696.

[S2] T. Wu, P. Zhang, J. Ma, H. Fan, W. Wang, T. Jiang and B. Han, *Chin. J. Catal.*, 2013, **34**, 167-175.

[S3] X. chen, X. Li, H. Song, Y. Lu, F. Wang and A. Hu，*Chin. J. Catal.*, 2008, **29**, 957-959.