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Supporting information

Oxidation of Benzyl Alcohol over Metal Organic Frameworks M-BTC

(M = Co, Cu, Fe)

Ling Peng^a, Shujie Wu^a, Xiaoyuan Yang^a, Jing Hu^a, Xiaoran Fu^a, Min Li^a, Lu Bai^a, Qisheng Huo^b, Jingqi Guan^a*

 ^a Address, College of Chemistry, Jilin University, Changchun, 130023, P.R. China.
 ^b Address, State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China.

Experimental details

Materials

1,3,5-benzenetricarboxylic acid (H₃BTC, 98%), N,N-dimethylformamide (DMF, 99.8%), Ferric(III) chloride hexahydrate (FeCl₃·6H₂O, 99%), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.5%). All chemical reagents were obtained from commercial sources and used without further purification.

Synthesis of catalyst

M-BTC (M=Co, Cu, Fe) was synthesized via a facile encapsulation method¹².

For the synthesis of Co(Cu)-BTC, taking Co-BTC for an example, Co(NO₃)₂·6H₂O (1.65 mmol) was dissolved into deionized water (15 mL), and 1,3,5-benzenetricarboxylic acid (0.95 mmol) was added to ethanol (15 mL) in another flask. After they was completely dissolved, the two solutions were mixed and stirred at room temperature for 8 h, and then transferred to Teflonlined autoclave. The mixture was heated to 140 °C and held at the temperature for 24 h, then cooled to 120 °C and held for 5 h, followed by further cooling to 100 °C and held for another 5 h, finally cooling to room temperature. The resulting crystals (Co₃(BTC)₂·12H₂O) were filtered, washed three times with 10 mL deionized water and ethanol, respectively, and then dried in vacuum at 50 °C for one day. As a comparison, Cu-BTC MOF was synthesized with a similar method, except that Co(NO₃)₂·6H₂O was replaced with Cu(NO₃)₂·3H₂O.

Fe-BTC was synthesized according to the related literature². FeCl₃·6H₂O and 1, 3, 5benzenetricarboxylic acid (H₃BTC) were dissolved in 5 mL of N, N-dimethylformamide (DMF) according to the 1:1 molar ratio were. Then the mixture was transferred to Teflonlined autoclave (20 mL). The mixture was heated at 150 °C for 24 h. A red powder was isolated by filtering and washed three times with 10 mL of DMF and ethanol, and then dried at 50 °C in vacuum for one day. The dried Fe-BTC polymer powder was obtained.

Catalyst characterization

Wide angle powder X-ray diffraction (XRD) patterns was collected on a Rigaku X-ray diffractometer using Cu Kα radiation carried at 40 kV and 40 mA. The morphology of the samples were observed by an S-4800 (Hitachi) with a cold field emission gun. Thermogravimetric analysis (TG) were conducted using NETZSCH STA 449c thermal station in nitrogen stream with a heating rate of 10 °C min⁻¹. The infrared spectra of the materials were recorded on IFS-66V/S, and the range of 400-4000 cm⁻¹ using the KBr pellet technique. The Raman measurements were performed using a Nicolet Almega XR Dispersive Raman spectrometer from Thermofisher. N₂ adsorption-desorption isotherms were measured with a Micromeritics ASAP 2010 system at -196 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and pore size distributions were evaluated from adsorption branches of nitrogen isotherms using the Barret-Joyner-Halenda (BJH) model. The elemental analysis of samples were estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a PerkinElmer emission spectrometer.

The study of catalytic reaction

Typically, the aerobic oxidation of benzyl alcohol was tested in 50 mL two neck flask equipped with a magnetic stirrer and a reflux condenser at atmospheric pressure. A mixture of catalyst (10 mg), benzyl alcohol (1mmol) and DMF (10 mL) were added to vessel. The mixture of reactor temperature was kept at 90 °C, combined with bubbling air (80 ml/min) as oxidant at the reaction temperature. The reactants and products were analyzed online by gas chromatograph (GC-8A) equipped with an HP-5 capillary column and a FID detector. After the reaction was finished, the solid catalyst was filtered, washed with ethanol, and dried at 60 °C overnight and reused without further purification.

References

- 1 B. J. Zhu, X. Y. Yu, Y. Jia, F. M. Peng, B. Sun, M. Y. Zhang, T. Luo, J. H. Liu and X. J. Huang, *Journal Of Physical Chemistry C*, 2012, **116**, 8601-8607.
- 2 K. Schlichte, T. Kratzke and S. Kaskel, Microporous Mesoporous Mat., 2004, 73, 81-88.



Fig. S1. XRD pattern of Fe-BTC catalyst: (a) the reported data in the literature (RSC Adv., 2016, 6, 1136) and (b) this work.



Fig. S2. FT-IR spectra of (a) Fe-BTC, (b) Cu-BTC and (c) Co-BTC.







Fig. S4. The pore size distributions of M-BTC.



Fig.S5. TG curves of M-BTC.



Fig. S6. Recycling experiments of Co-BTC for oxidation of benzyl alcohol.



Fig. S7. XRD patterns of the fresh (a) and reused (b) Co-BTC catalyst.



Fig. S8. Leaching experiment of Co-BTC catalyst.

Entry	Sample	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
1	Cu-BTC	917	0.037
2	Fe-BTC	369	0.18
3	Co-BTC	18	0.02

 Table S1 The BET parameters of the samples.

TableS2 The elemental analysis for M-BTC

Entry	Sample	M(Co, Cu, Fe) (wt%)	H (wt%)	C (wt%)
1	Co-BTC	21.6	3.6	26.7
2	Cu-BTC	28.2	2.0	31.8
3	Fe-BTC	24.8	1.6	25.2

Table S3 Catalytic performance of Co-BTC in oxidation benzyl alcohol ^a

Entry	Catalyst	Temperature	Solvent	Time	Catalyst dosage	Conversion	Selectivity (%)	
		(°C)		(h)	(mg)	(%)	Benzaldehyde	Benzoic acid
1	No catalyst	95	DMF	10	0	3	>99	
2	Co-BTC	95	DMF	10	10	92.9	97.1	2.9
3	Co-BTC	95	DMF	10	50	88.9	97.6	2.4
4	Co-BTC	95	DMF	10	100	88.3	98.1	1.9
5	Co-BTC	95	DMF	2	10	58.1	>99	
6	Co-BTC	95	DMF	4	10	75.4	>99	
7	Co-BTC	95	DMF	6	10	84.7	98.2	1.8
8	Co-BTC	95	DMF	8	10	90.4	97.7	2.3
9	Co-BTC	85	DMF	10	10	86.7	>99	
10	Co-BTC	105	DMF	10	10	91.3	95.3	4.7
11	Co-BTC	95	CH₃CN	10	10	15.4	>99	
12	Co-BTC	95	Toluene	10	10	11.6	>99	

^a Reaction conditions: benzyl alcohol (1mmol), solvent (10 mL), and a flow air (80mL/min) as oxidant.