

Electronic Supplementary Information

Porous Cu-BTC silica monoliths as efficient heterogeneous catalysts for the selective oxidation of alkylbenzenes

Guo-Qiang Song^a, Ying-Xun Lu^a, Qi Zhang^b, Fan Wang^a, Xiao-Kun Ma^a, Xian-Feng Huang^{a,*}, Zhi-Hui Zhang^{b,*}

^a School of Pharmaceutical Engineering and Life Science, Changzhou University, Changzhou 213164, P. R. China. E-mail: xianfenghh@163.com

^b Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, P. R. China. E-mail: zhangzhjpu@gmail.com

Experimental Section

Synthesis of silica monolith-supported Cu-BTC catalysts

All chemicals were commercial available and used as received. In a typical synthesis of macro-/mesoporous silica monolith, HNO_3 (68%) and distilled H_2O were mixed for 15 min at 0 °C followed PEG (20,000, 99%) added and the mixture was stirred for 1 h. Then TEOS (99%) were added and the mixture was stirred for 1 h (HNO_3 : PEG: TEOS: H_2O = 31: 1: 76: 1074). The resulting solution was poured into PVC tubes of 8 cm length and 12 mm internal diameter and kept at 40 °C for 3 days. The monoliths were then washed in water and treated in an ammonia solution (0.1 M) at 40 °C for 20 h. The final monoliths were obtained after being dried at 40 °C for 24 h and being calcined at 550 °C for 8 h.

With molar ratio of H_3BTC : $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: DMSO = 5: 9: 115, a precursor solution of Cu-BTC was prepared under slow dissolution of cupric nitrate trihydrate in the DMSO solution of H_3BTC . The as-synthesized Cu-BTC powder (crystals of ca. 1 μm) was obtained by evaporating DMSO solution at 120°C for 72 h and refluxing powder with 30 mL ethanol for 1 h, featuring the characteristic XRD pattern of Cu-BTC (Fig. 3a). Then the Cu-BTC powder was activated at 150 °C for 4 h under vacuum to be ready for the catalysis.

For the synthesis of silica monolith-supported Cu-BTC, activated (150 °C under vacuum for 4h) silica monoliths were immersed in the CuBTC precursor solution by heating at 100 °C for 3 h. The impregnated monolith was dried at 80°C for 2 h and kept at 120 °C for 12 h to allow Cu-BTC crystallization by solvent evaporation. Unreacted $\text{Cu}(\text{NO}_3)_2$ salts were removed through refluxing of the monoliths in boiling ethanol. The monoliths were finally vacuum dried at 80 °C for 24 h.

Characterization

The as-synthesized products were characterized by X-ray diffraction (XRD) on a Rigaku D/Max 2,500 diffractometer using Cu $\text{K}\alpha$ radiation (40 kV, 100 mA) in the 2θ range between 3° and 80°. N_2 adsorption isotherms were obtained using a Micromeritics ASAP 2010C instrument. The samples were outgassed at 150 °C for 8 h before measurements. Microstructure and morphology of samples were characterized by field-emission Scanning Electron Microscopy (SEM) on a ZEISS Supra 55 microscope operated at 30 kV. The

Transmission Electron Microscopy (TEM) was carried on using JEOL-2100 transmission electron micro-scope with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) experiments were performed on a TG/DTA 6300 thermoanalyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

Typical Procedure for Oxidation of Alkylbenzenes.

Ethylbenzene (0.1 mmol), tert-butyl hydroperoxide (TBHP, 0.15 mmol), catalyst (0.005 mmol), acetonitrile (1.0 mL), acetic acid (0.2 mL), and water (0.2 mL) were stirred at 60 °C for 6 h. The identity of the product was determined by analyzing aliquots of the bulk solution using GC–MS and compared with standard samples analyzed under the same conditions, while the conversion and selectivity were obtained by GC analysis.

The recyclability of catalysts was examined on the oxidation of ethylbenzene under the same catalytic conditions with the exception that the amount of Cu-BTC catalyst was scaled up by four times (0.02 mmol instead of 0.005 mmol). After the oxidation reaction, the used Cu-BTC-SiO₂ monoliths catalyst was recovered by filtration, washed with acetonitrile several times, and subsequently used in the successive runs. In the case of Cu-BTC as the catalyst, the used one was recovered via centrifugation at the end of the reaction to remove the supernatant, washed with acetonitrile, activated at 150 K for 4 h under vacuum in order to remove the adsorbed species, and then reused for the reaction.

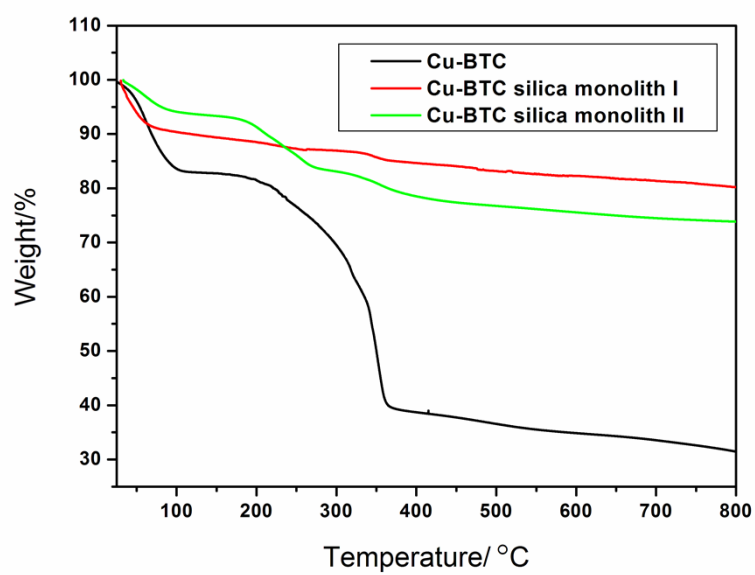


Fig. S1 TG curves.

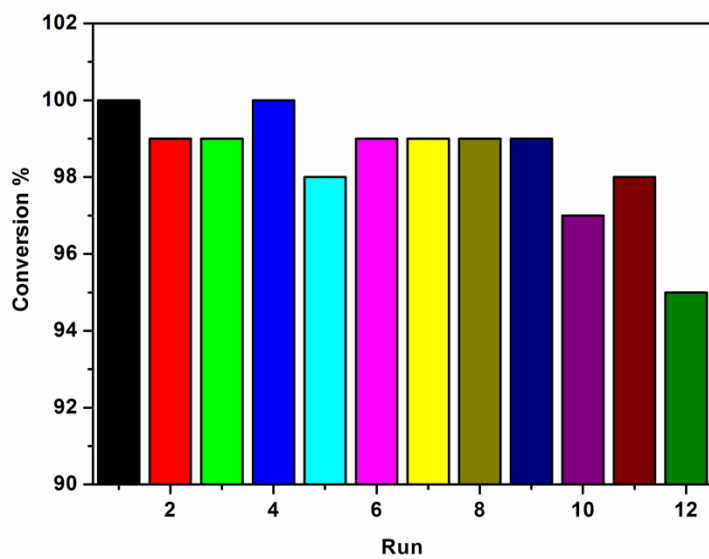


Fig. S2 Catalytic oxidation of ethylbenzene by Cu-BTC-SiO₂ monolith II at different runs.

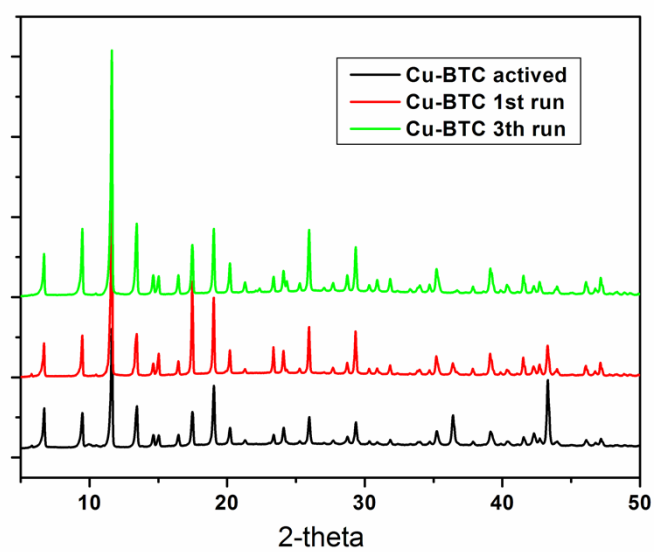


Fig. S3 XRD patterns of Cu-BTC catalysts.