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Highly Efficient Sulfonated-Polystyrene-Cu(II)@$Cu_3(BTC)_2$ Core-Shell Microsphere Catalysts for Base-Free Aerobic Oxidation of Alcohols

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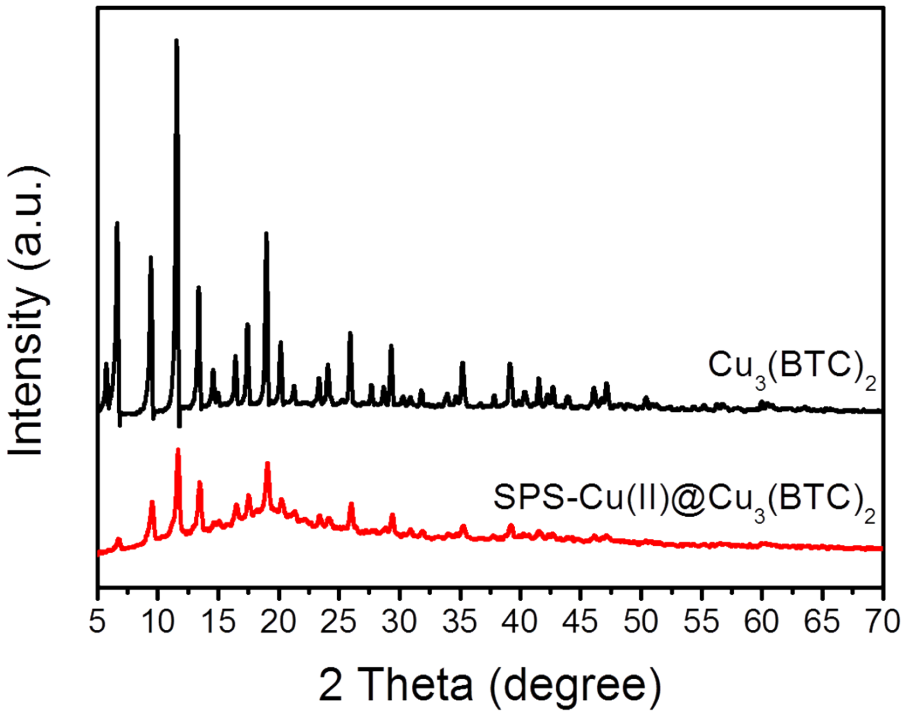

Fig. S1 Powder XRD patterns of the as prepared $Cu_3(BTC)_2$ and SPS-Cu(II)@$Cu_3(BTC)_2$ nanoparticles.

Powder XRD patterns of the as prepared $Cu_3(BTC)_2$ and SPS-Cu(II)@$Cu_3(BTC)_2$ nanoparticles are indexed on the basis of a face-centered cubic unit cell with refined cell = 26.31918 (0.004868) Å and 26.35236 (0.002407) Å, respectively. The unit cell parameters match well with the reported HKUST-1 crystal structure[1], which has a secondary building unit of paddle-wheel type metal corners connected with bytrimesic acid linkers. The 3D unit cell crystal framework of these two kinds of $Cu_3(BTC)_2$ is composed of large central cavities (diameter 0.9 nm) surrounded by small pockets (diameter 0.5 nm). The XRD peak intensity of the SPS-Cu(II)@$Cu_3(BTC)_2$ nanoparticles is weaker than that of the pure $Cu_3(BTC)_2$ sample, which is attributed to the presence of the SPS template.

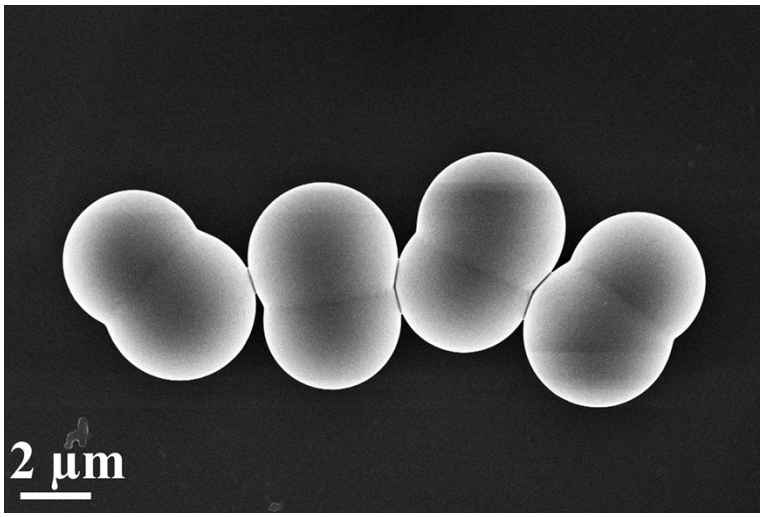

Fig. S2 FESEM image of the PS microspheres before sulfonation.

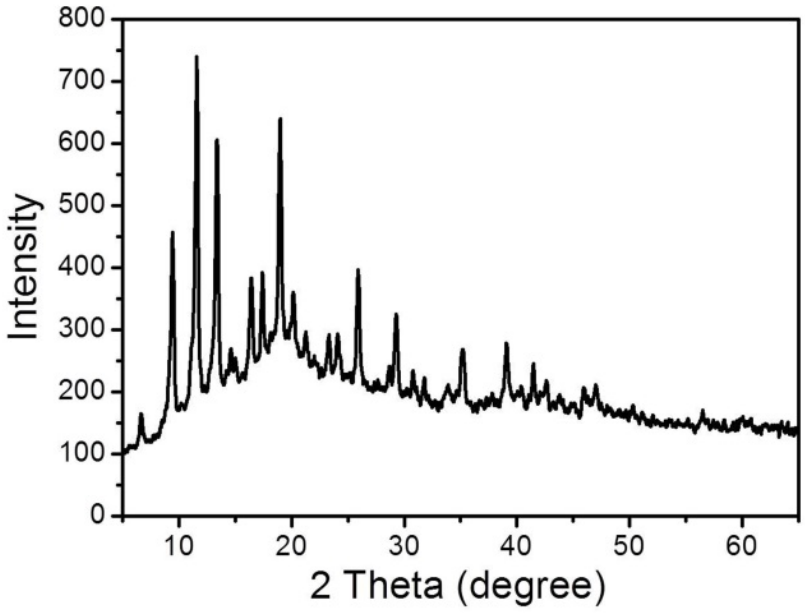

Fig. S3 Powder XRD patterns of the SPS-Cu(II)@$Cu_3(BTC)_2$ catalyst after 10 runs of aerobic oxidation of benzyl alcohol under base-free conditions.

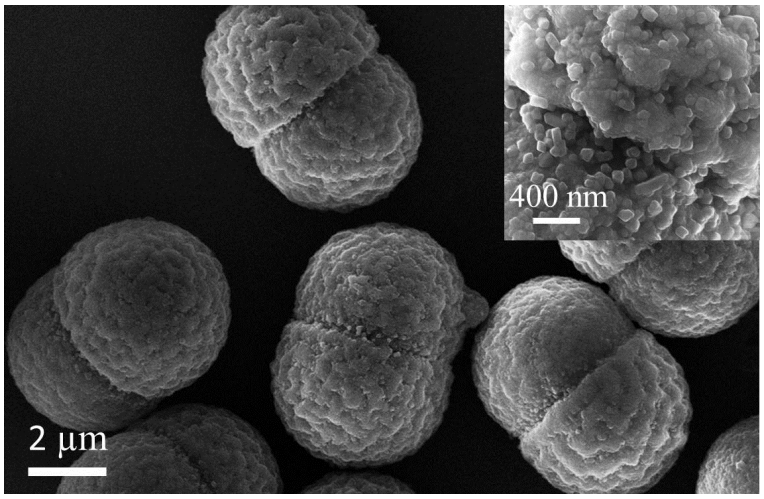

Fig. S4 FESEM photograph of the SPS-Cu(II)@$Cu_3(BTC)_2$ catalyst after 10 runs of aerobic oxidation of benzyl alcohol under base-free conditions.

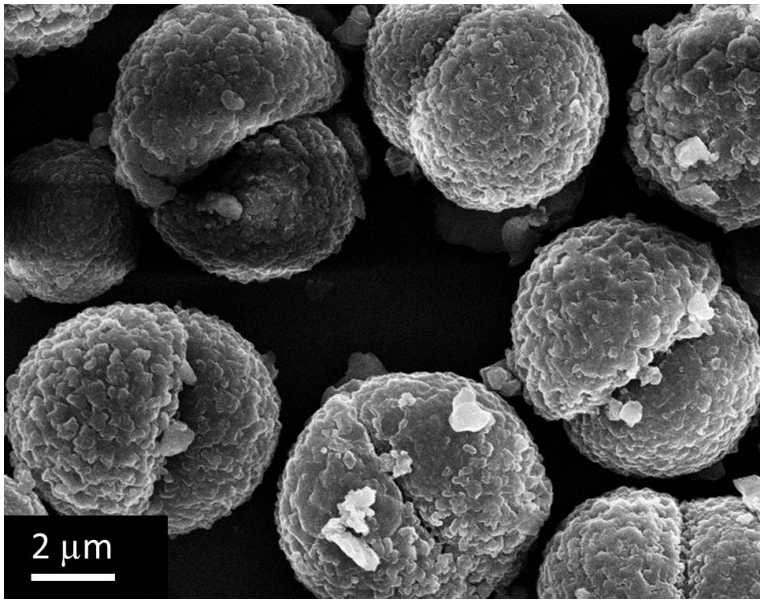

Fig. S5 FESEM image of SPS-Cu(II)@$Cu_3(BTC)_2$ composite after 18 catalytic reaction cycles of aerobic oxidation of benzyl alcohol under base-free conditions.

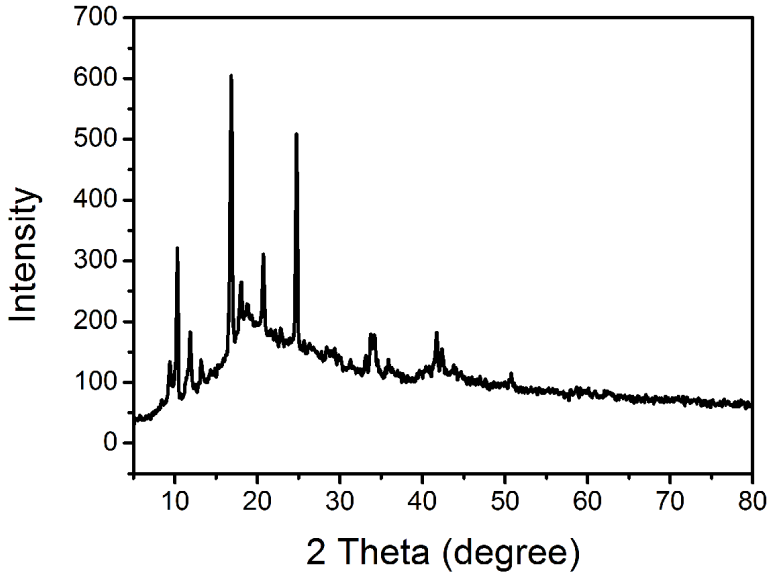

Fig. S6 Powder XRD patterns of the SPS-Cu(II)@CuBDC composite.

The crystalline nature and chemical composition of the as-prepared SPS-Cu(II)@CuBDC product were confirmed by powder XRD. As shown in Figure S6, a broad diffraction peak at around 2θ = 20.0° can be observed, which is attributable to the SPS template. Other relatively high peaks can be indexed as the crystallographic planes of the CuBDC with a layered crystalline structure.[2]

References

1. S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and L. D. A Williams, *Science*, 1999, **283**, 1148-1150.
2. R. Adams, C. Carson, J. Ward, R. Tannenbaum and W. Koros, *Micropor. Mesopor. Mater.* 2010, **131**, 13-20.