

Electronic Supplementary Material

Benzenesulfonic acid-grafted UIO-66 with improved hydrophobicity as a stable Brønsted acid catalyst

Zongliang Kou¹, Guanlun Sun¹, Qiuyan Ding¹, Hong Li (✉)¹, Xin Gao^{1,2}, Xiaolei Fan (✉)^{3,4}, Xiaoxia Ou⁴, Qinhe Pan (✉)⁵

1 School of Chemical Engineering and Technology, National Engineering Research Center of Distillation Technology, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, China

2 Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

3 Department of Chemical Engineering, School of Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom

4 Nottingham Ningbo China Beacons of Excellence Research and Innovation Institute, University of Nottingham Ningbo China, Ningbo 315191, China

5 Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, School of Chemical Engineering and Technology, Hainan University, Haikou 570228, China

E-mails: lihongtju@tju.edu.cn (Li H); xiaolei.fan@manchester.ac.uk (Fan X); panqh@hainanu.edu.cn (Pan Q)

The cyclohexyl acetate conversion, the selectivity to cyclohexanol were defined as follows:

$$X = \frac{m_{ca0(g)} - m_{ca1(g)}}{m_{ca0(g)}} \times 100\% \quad (\text{S1})$$

$$S = \frac{m_{ca(g)} - m_{cp(g)}}{m_{ca(g)}} \times 100\% \quad (\text{S2})$$

where m_{ca0} is the initial mass of cyclohexyl acetate (ca) in the reaction system; m_{ca1} is the final mass of cyclohexyl acetate after the reaction in the system; m_{ca} is the converted cyclohexyl acetate ($m_{ca} = m_{ca0} - m_{ca1}$); m_c is the mass of cyclohexene (c) produced.

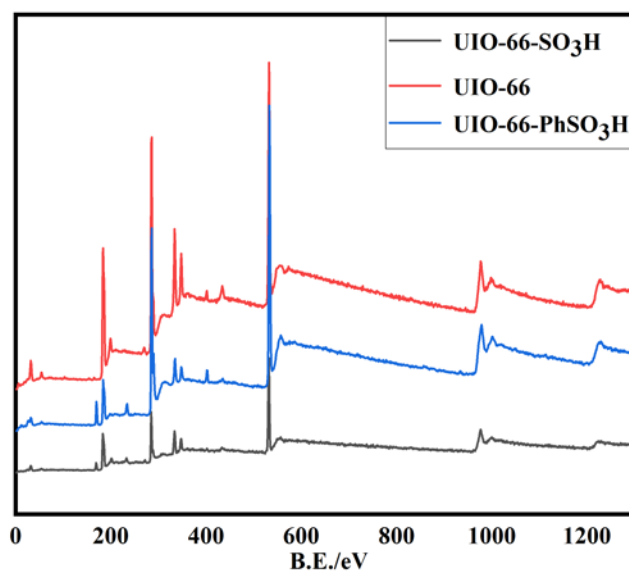


Fig. S1 XPS scan survey of relevant materials

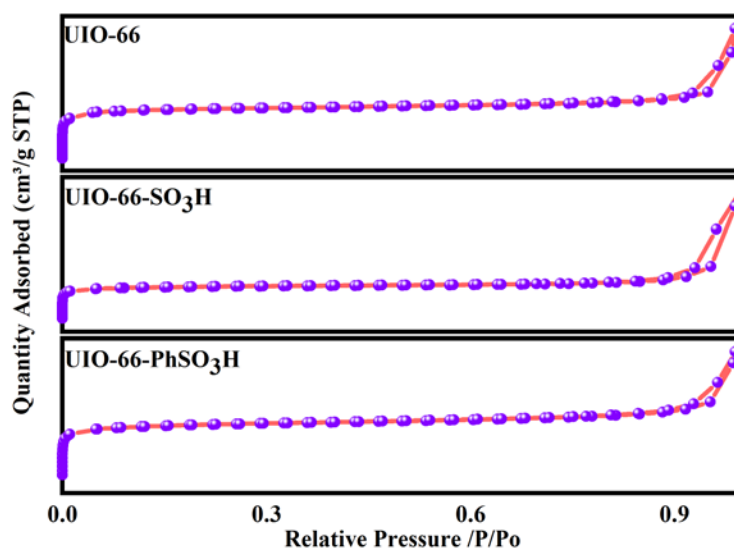


Fig. S2 N₂ adsorption/desorption isotherms of relevant materials

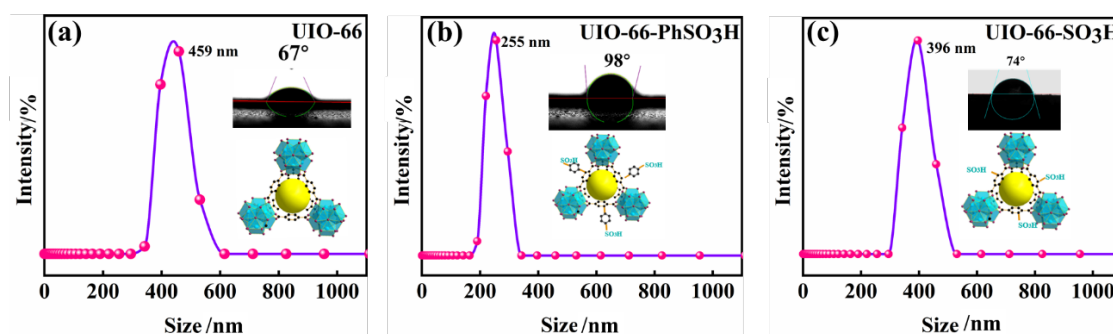


Fig. S3 Particle size analysis of catalysts: particle size distribution of (a) UIO-66, (b) UIO-66-PhSO₃H and (c) UIO-66-SO₃H (insets: the measured contact angles for the materials)

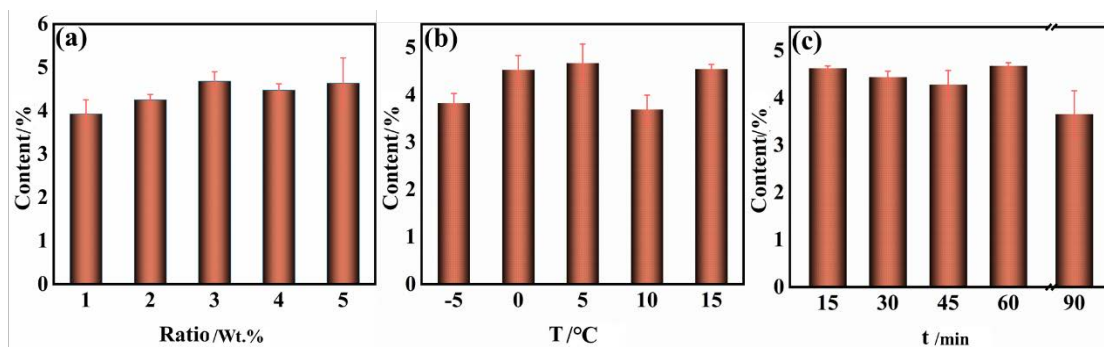


Fig. S4 Catalyst optimization: the effect of (a) the ratio of 4-chlorobenzenesulfonic acid to UIO-66, (b) synthesis temperature and (c) synthesis time on the S content of UIO-66-PhSO₃H

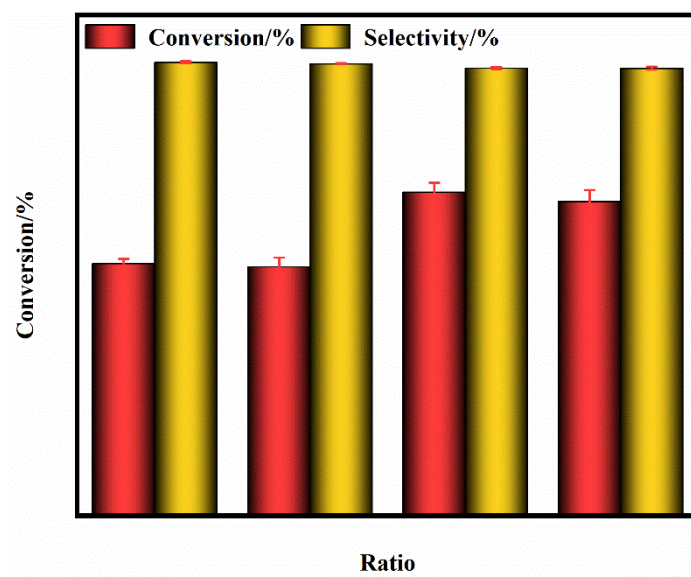


Fig. S5 Variation of cyclohexanol conversion as a function of the water-to-ester ratio

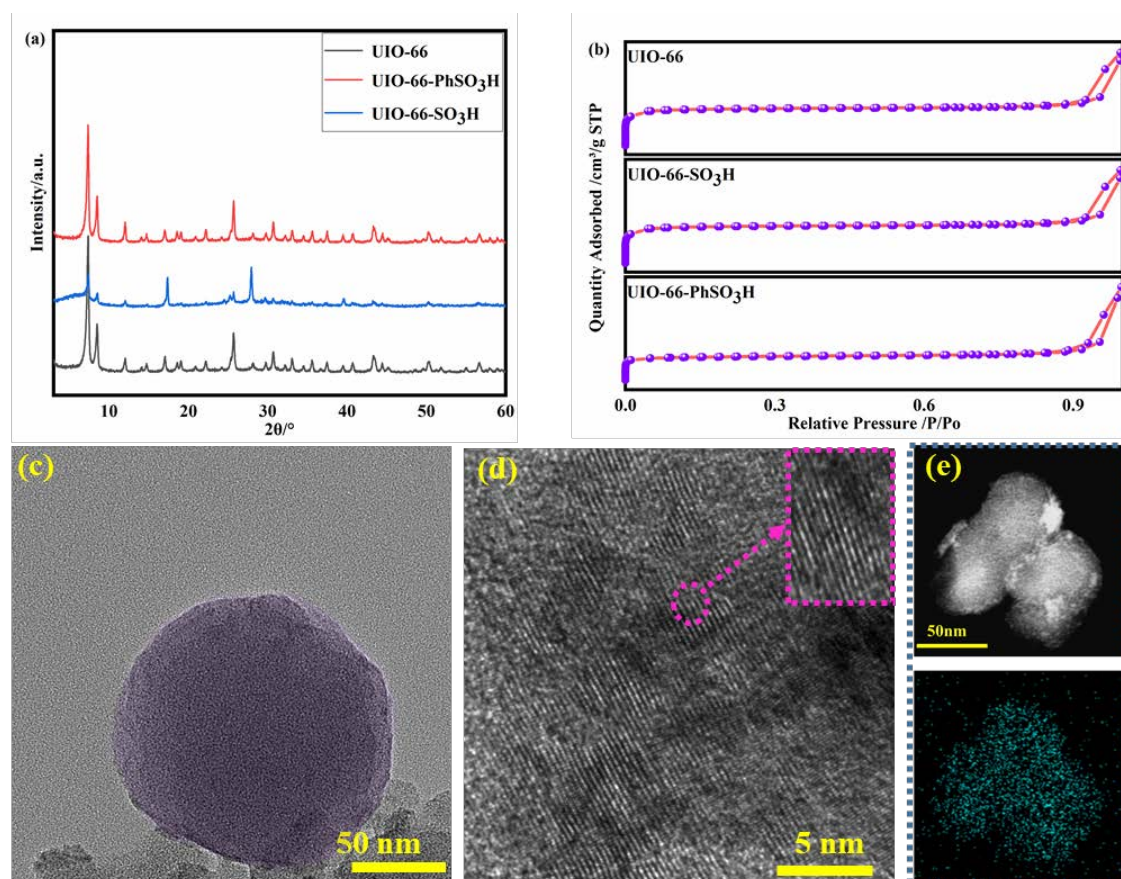


Fig. S6 Structural and morphological analysis of catalysts after regeneration: (a) XRD patterns; (b) N_2 physisorption isotherms of the used catalysts from the stability test; (c,d) morphology and lattice of UIO-66-PhSO₃H; (e) EDS mapping analysis

Table S1 Comparison of textural properties of the used materials from the stability tests

Samples	S_{BET} original /cm ² /g	S_{BET} /cm ² /g	D_{meso} original /nm	D_{meso} (nm)	V original /cm ³ /g	V /cm ³ /g
UIO-66	1,051	1,038	2.1	2.1	0.5	0.6
UIO-66-SO ₃ H	1,051	648	2.1	2.4	0.5	0.5
UIO-66-PhSO ₃ H	648	731	2.4	2.3	0.4	0.5