

Supporting Information

High-efficiency Catalyst CuSO<sub>4</sub>/SBA-15 Toward  
Butylated Hydroxytoluene Synthesis in Heterogeneous  
System

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## 1. Catalyst characterization

Low- and wide-angle powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8-Advance diffractometer using Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation. Analysis was performed in the  $2\theta$  range from  $0.1^\circ$  to  $4^\circ$  (low angle) and from  $10^\circ$  to  $80^\circ$  (wide angle) with a scan rate of  $0.02^\circ/\text{s}$ . The chemical states of catalysts were detected by X-ray photoelectron spectroscopy (XPS, PHI 550). The measured spectra were corrected for peak position with C1s (284.6 eV) using Al as the target ray source. The samples were degassed at 373 K for 6 h and the adsorption-desorption isotherms were recorded at 77 K using a MicrotracBEL BELSORP-MAX II specific surface area and pore size analyzer. The specific surface area was calculated using the BET method, and the pore volumes were calculated from the corresponding desorption isotherms. The pore size distributions were estimated using the Barrett, Joyner, and Halenda (BJH) algorithm. The Fourier infrared spectra (FT-IR) of the catalysts were measured with a Thermo Fisher NICOLEIS10 infrared spectrometer, using anhydrous KBr as a standard. The mass ratio of catalyst to KBr was 100:1, the scanning wavenumber range was  $500\text{-}4000\text{ cm}^{-1}$ , and the number of scans was 64. Thermogravimetric analysis (TG) of the catalysts was performed on a NETZSCH STA-499F3 thermal analyzer. From room temperature to  $900^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , air with a flow rate of  $20\text{ mL}/\text{min}$  was taken as a carrier gas and  $\text{N}_2$  as a protective gas. The ultrastructure of the catalysts was analyzed using a Tecnai G2 F20 transmission electron microscope (TEM) with an operating voltage of 200 KV.

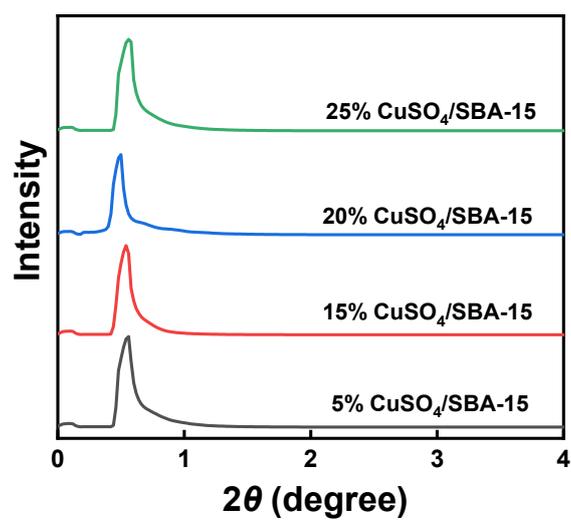


Figure S1. Small-angle XRD patterns of CuSO<sub>4</sub>/SBA-15

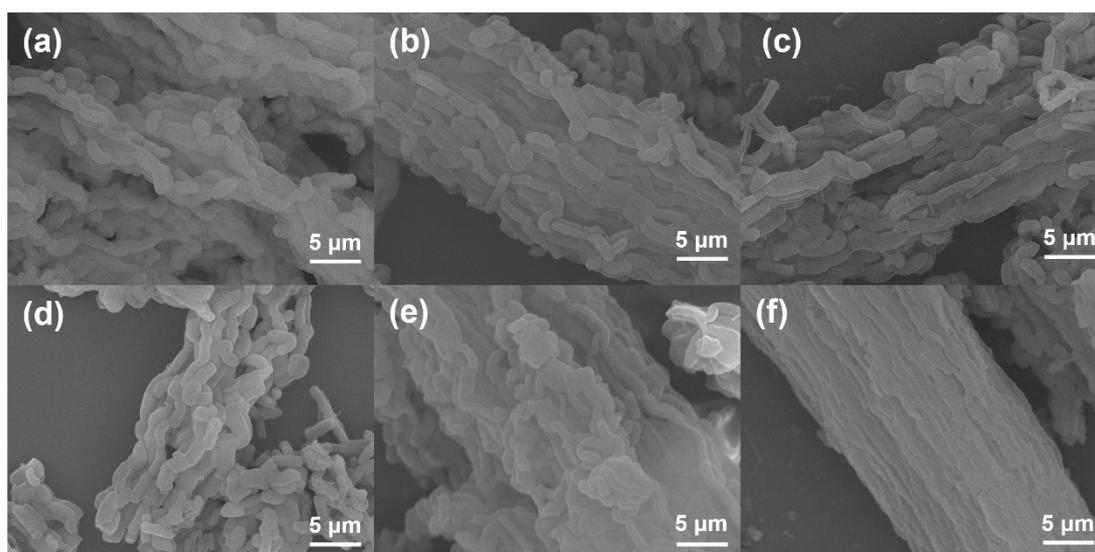


Figure S2. SEM images of (a) SBA-15, (b) 5%CuSO<sub>4</sub>/SBA-15, (c) 10%CuSO<sub>4</sub>/SBA-15, (d) 15%CuSO<sub>4</sub>/SBA-15, (e) 20%CuSO<sub>4</sub>/SBA-15 and (f) 25%CuSO<sub>4</sub>/SBA-15

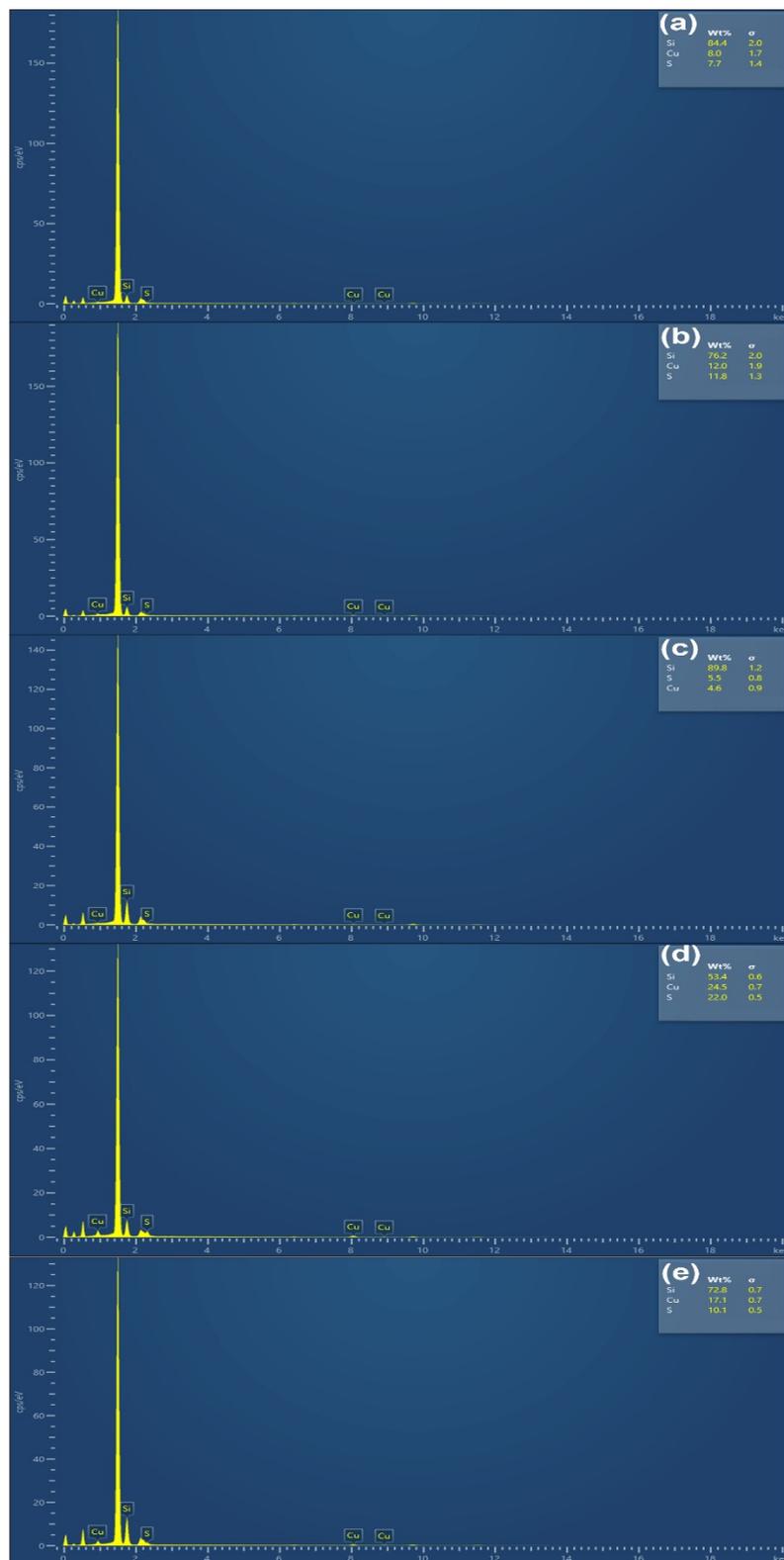


Figure S3. EDS elemental analysis of  $\text{CuSO}_4/\text{SBA-15}$  catalysts: (a) 5%  $\text{CuSO}_4/\text{SBA-15}$ , (b) 10%  $\text{CuSO}_4/\text{SBA-15}$ , (c) 15%  $\text{CuSO}_4/\text{SBA-15}$ , (d) 20%  $\text{CuSO}_4/\text{SBA-15}$  and (e) 25%  $\text{CuSO}_4/\text{SBA-15}$ .

Table S1. Effect of reaction time on the yield of BHT.

Reaction time (h)	Yield (%)
0.5	12.8
1.5	70.2
2.5	80.2
3.5	84.4
4.5	85.4

Table S2. Effect of reaction temperature on the yield of BHT.

Reaction temperature (°C)	Yield (%)
40	45.9
60	69.4
80	81.7
100	76.7
120	70.1

Table S3. Activity of various supported CuSO<sub>4</sub>/SBA-15 catalysts.

Catalyst	Yield (%)
CuSO <sub>4</sub>	0
5%CuSO <sub>4</sub> /SBA-15	72.9
10%CuSO <sub>4</sub> /SBA-15	85.5
15%CuSO <sub>4</sub> /SBA-15	77.8
20%CuSO <sub>4</sub> /SBA-15	71.3
25%CuSO <sub>4</sub> /SBA-15	70.1

Table S4. Cycling stability of the catalyst.

Reaction cycle	Yield (%)
1	85.5
2	81.7
3	81.3
4	72.9
5	83.7

Table S5. Catalytic activity of various catalysts.

Catalyst	Yield (%)
/	0
CuSO <sub>4</sub>	3.2
CuSO <sub>4</sub> /SBA-15	85.5
sulfated SBA-15	71.6

Table S6. Catalytic activity of different mesoporous silica carriers.

Catalyst	Yield (%)
CuSO <sub>4</sub> /SBA-15	85.5
CuSO <sub>4</sub> /mesoporous SiO <sub>2</sub> -1	84.6
CuSO <sub>4</sub> /mesoporous SiO <sub>2</sub> -2	73.5

Table S7. Physicochemical properties of different carriers.

Sample Name	BET Surface	Pore Volume	Average Pore Size
	Area(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)	(nm)
SBA-15	832	1.09	5.22
mesoporous SiO <sub>2</sub> -1	236	0.28	2.3
mesoporous SiO <sub>2</sub> -2	61	0.12	2.1

Table S8. Cycling stability of CuSO<sub>4</sub>/mesoporous SiO<sub>2</sub>-1.

Reaction cycle	Yield (%)
1	83.8
2	57.1
3	19.2
4	12.9

Table S9. Cycling stability of CuSO<sub>4</sub>/mesoporous SiO<sub>2</sub>-2.

Reaction cycle	Yield (%)
1	73.5
2	62.2
3	23.3
4	10.9

Table S10. Activity of various Lewis acid loaded catalysts.

Catalyst	Yield (%)
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /SBA-15	83.8
CuSO <sub>4</sub> /SBA-15	85.5
Ce(SO <sub>4</sub> ) <sub>2</sub> /SBA-15	82.6

Table S11. Cycling stability of  $\text{Fe}_2(\text{SO}_4)_3/\text{SBA-15}$ .

Reaction cycle	Yield (%)
1	83.8
2	84.2
3	76.2
4	40.2

Table S12. Cycling stability of  $\text{Ce}(\text{SO}_4)_2/\text{SBA-15}$ .

Reaction cycle	Yield (%)
1	82.6
2	78.2
3	73.4
4	35.5