

*Electronic Supplementary Information for*

**One building block approach for defect-enhanced conjugated microporous polymer:  
Defect utilization for recyclable and catalytic biomass conversion**

Kyoungil Cho,<sup>a</sup> Sang Moon Lee,<sup>b</sup> Hae Jin Kim,<sup>b</sup> Yoon-Joo Ko,<sup>c</sup> and Seung Uk Son<sup>\*a</sup>

<sup>a</sup>*Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea*

<sup>b</sup>*Korea Basic Science Institute, Daejeon 34133, Korea*

<sup>c</sup>*Laboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities (NCIRF),  
Seoul National University, Seoul 08826, Korea*

**Experimental Sections**

SEM images were obtained using a FE-SEM (JSM6700F). TEM images were obtained using a JEOL 2100F. IR spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. Powder XRD patterns were obtained using a Rigaku MAX-2200 (filtered Cu-K $\alpha$  radiation). N<sub>2</sub> adsorption-desorption isotherm curves were obtained at 77K using a BELSORP II-mini analyzer and a Micromeritics ASAP2020. Pore size distribution analysis was conducted based on the DFT method. Solid state <sup>13</sup>C NMR spectra were obtained at CP/TOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities of Seoul National University. A 4 mm magic angle spinning probe was used with a spinning rate of 5 kHz. Normal <sup>1</sup>H NMR spectra of products were obtained using a 400 MHz and 500 MHz Varian spectrometers. Elemental analysis was conducted using a CE EA1110 analyzer. TGA curves were obtained using a Seiko Exstar 7300.

**Synthesis of H-TA-CMP (by one building block approach) and CMP (by two building blocks approach)**

1,4-Dibromo-2,5-diethynylbenzene was prepared by the synthetic procedures in the literature.<sup>1</sup> Silica spheres with an average diameter of 260 nm were prepared by the Stöber method described in the literature.<sup>2</sup> In our study, the synthetic procedures for silica spheres were as follows. In a flame-dried 500 mL round bottom flask, ethanol (200 mL), distilled water (18 mL), and ammonia solution (28~30%, 7 mL) were added. After tetraethyl orthosilicate (TEOS, 14 mL, 63 mmol) was added, the mixture was stirred for 2.5 h at room temperature. The silica spheres were separated by centrifugation, washed with ethanol, and dried under vacuum. In a flame-dried 50 mL Schlenk flask with a condenser, silica spheres (0.30 g), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (8.4 mg, 12  $\mu$ mol), and CuI (2.3 mg, 12  $\mu$ mol) were added. After dimethylformamide (DMF, 20 mL) and triethylamine (TEA, 10 mL) were added, the mixture was sonicated for 1 h. After 1,4-dibromo-2,5-diethynylbenzene (0.10 g, 0.36 mmol) was added, the reaction mixture was stirred at 80°C for 2, 4, 6, and 12 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with dichloromethane, acetone, and methanol (three times each), and dried under vacuum. The resultant SiO<sub>2</sub>@TA-CMP obtained by reaction for 4 h was added to a mixture of HF solution (48~51%, 5 mL), water (15 mL), and methanol (10 mL). The mixture was stirred for 2 h at room temperature. *Caution: the HF solution is extremely toxic and has to be handled with special gloves in the hood. Excess HF retrieved from the reaction mixture during the work up processes can be neutralized by addition to 3 M NaOH solution.* The solid (H-TA-CMP) was separated by centrifugation, washed with a mixture of water (30 mL) and

methanol (10 mL) four times and methanol only three times, and dried under vacuum.

For preparation of CMP materials by two building blocks approach, 1,3,5-triethynylbenzene was prepared by the synthetic procedures in the literature.<sup>3</sup> 1,3,5-triethynylbenzene (36 mg, 0.24 mmol) and 1,4-dibromobenzene (85 mg, 0.36 mmol) were used instead of 1,4-dibromo-2,5-diethynylbenzene. Other synthetic procedures were the same as those used for H-TA-CMP.

### ***Synthesis of H-TA-CMP-ASO<sub>3</sub>H and H-control-SO<sub>3</sub>H***

Post-synthetic modification of CMP materials based on thiol-yne click reaction has been reported in the literature.<sup>4</sup> We referred to the related procedures in the literature.<sup>4</sup> For the synthesis of H-TA-CMP-ASO<sub>3</sub>H, H-TA-CMP (0.576 g) and sodium 3-mercapto-1-propanesulfonate (Aldrich Co, 5.61 g, 31.5 mmol) were added to a flame-dried 250 mL Schlenk flask with a condenser. After 2,2'-azobis(2-methylpropionitrile) (AIBN, 5.17 g, 31.5 mmol) and DMF (200 mL) were added, the reaction mixture was stirred at 90°C for 1 day under argon. After being cooled to room temperature, the solid was separated by filtration, washed with hot THF, methylene chloride, acetone, and methanol, and dried under vacuum. To transform sodium sulfonate to sulfonic acid, the H-TA-CMP-ASO<sub>3</sub>Na was added to a mixture of water (30 mL), H<sub>2</sub>SO<sub>4</sub> (5 mL), and methanol (10 mL). The mixture was stirred for 2 h at room temperature. The solid (H-TA-CMP-ASO<sub>3</sub>H) was separated by centrifugation, washed with a mixture of water (30 mL) and methanol (10 mL) four times and methanol only (40 mL) two times, and dried under vacuum. According to elemental analysis, the S content was 4.56wt%, corresponding to 0.713 mmol SO<sub>3</sub>H/g.

For the synthesis of H-control-SO<sub>3</sub>H, H-TA-CMP (0.150 g) and distilled methylene chloride (30 mL) were added to a flame-dried 100 mL Schlenk flask with a condenser. The post-synthetic modification of CMP materials by treatment of ClSO<sub>3</sub>H was reported in the literature.<sup>5</sup> We referred to the related procedures in the literature.<sup>5</sup> After the mixture was cooled to 0°C using an ice bath, chlorosulfonic acid (1.8 mL) was added dropwise for 5 min. The mixture was stirred for 1.5 h at room temperature. After the mixture was cooled to 0°C using an ice bath, methanol was added slowly to quench excess chlorosulfonic acid until the generation of bubbles finished. The solid (H-control-SO<sub>3</sub>H) was separated by centrifugation, washed with methanol (40 mL) four times and acetone (40 mL) once, dried under vacuum. According to elemental analysis, the S content was 5.16wt%, corresponding to 1.61 mmol SO<sub>3</sub>H/g.

### ***Experimental procedures for catalytic reactions***

D-fructose (0.304 g, 1.69 mmol) and H-TA-CMP-ASO<sub>3</sub>H (0.713 mmol SO<sub>3</sub>H/g based on elemental analysis-S: 4.56 wt%, 47 mg, 0.034 mmol SO<sub>3</sub>H, 2.0 mol% SO<sub>3</sub>H to fructose), biphenyl (internal standard, 0.130 g, 0.844 mmol), and distilled DMSO (5 mL) were added to a 20 mL vial. *Note: although the <sup>1</sup>H NMR spectra of products are pure, there can be <sup>1</sup>H NMR-undetectable by-products. Thus, to be convincing analysis, the internal standard-based analysis should be carefully performed.* The reaction mixture was heated at 60, 80, 120, and 140°C. Yields of HMF were analysed by <sup>1</sup>H NMR based on the internal standard analysis. <sup>1</sup>H NMR of HMF (DMSO-d<sub>6</sub>, 500

MHz):  $\delta = 4.51$  (d,  $J = 5.5$  Hz, 2H), 5.55 (t,  $J = 5.9$  Hz, 1H), 6.61 (d,  $J = 3.5$  Hz, 1H), 7.50 (d,  $J = 3.6$  Hz, 1H), 9.56 (s, 1H) ppm.  $^1\text{H}$  NMR of biphenyl (DMSO- $d_6$ , 500 MHz):  $\delta = 7.38$  (t,  $J = 7.4$  Hz, 2H), 7.48 (t,  $J = 7.8$  Hz, 4H), 7.67 (d,  $J = 7.2$  Hz, 4H) ppm. We obtained the yields of HMF based on the  $^1\text{H}$  peak of HMF at 5.55 ppm and  $^1\text{H}$  peak of internal standard at 7.38 ppm.

For the recyclability tests, D-fructose (0.304 g, 1.69 mmol) and H-TA-CMP- $\text{ASO}_3\text{H}$  (0.712 mmol  $\text{SO}_3\text{H/g}$  based on elemental analysis-S: 4.56wt%, 47 mg, 0.033 mmol  $\text{SO}_3\text{H}$ , 2.0 mol%  $\text{SO}_3\text{H}$  to fructose), biphenyl (internal standard, 0.130 g, 0.844 mmol), and distilled DMSO (5 mL) were added to a 20 mL vial. The reaction mixture was stirred at 100°C for 5 h. After being cooled to room temperature, the catalyst was retrieved by centrifugation, washed with methanol three times, acetone three times, dichloromethane three times, and hexane three times, dried under vacuum, and used for the next runs. In the case of catalytic reaction of H-control- $\text{SO}_3\text{H}$ , H-control- $\text{SO}_3\text{H}$  (S: 5.16wt%, 21 mg, 0.034 mmol  $\text{SO}_3\text{H}$ , 2.0 mol%  $\text{SO}_3\text{H}$  to fructose) was used instead of H-TA-CMP- $\text{ASO}_3\text{H}$ . In the case of H-control- $\text{SO}_3\text{H}$ , the conversion of reactants was relatively faster than the case of H-TA-CMP- $\text{ASO}_3\text{H}$ , possibly due to the desulfonation (refer to Fig. S6 in the SI) and the catalysis by the generated  $\text{H}_2\text{SO}_4$ . Thus, reaction time of 2 h was applied instead of 5 h. Other procedures were the same as those used for H-TA-CMP- $\text{ASO}_3\text{H}$ .

## References

1. D. Wang and T. Michinobu, *J. Polym. Sci., Part A: Polym. Chem.* 2011, **49**, 72-81.
2. W. Stöber, A. Fink and E. Bohn, *J. Colloid Inter. Sci.* 1968, **26**, 62-69.
3. M. I. Mangione and R. A. Spanevello, A. Rumero, D. Herdia, G. Marzari, L. Fernandez, L. Otero and F. Fungo, *Macromolecules* 2013, **46**, 4754-4763.
4. (a) X. Han, M. Xu, S. Yang, J. Qian and D. Hua, *J. Mater. Chem. A* 2017, **5**, 5123-5128; (b) H. Urakami, K. Zhang and F. Vilela, *Chem. Commun.* 2013, **49**, 2353-2355; (c) B. Kiskan and J. Weber, *ACS Macro Lett.* 2012, **1**, 37-40.
5. N. Park, Y. N. Lim, S. Y. Kang, S. M. Lee, H. J. Kim, Y. -J. Ko, B. Y. Lee, H. -Y. Jang and S. U. Son, *ACS Macro Lett.* 2016, **5**, 1322-1326.

**Fig. S1** N<sub>2</sub> sorption isotherm curves and pore size distribution diagrams (based on DFT method) of H-TA-CMPs and CMPs prepared by one building block approach and two building blocks approach, respectively.

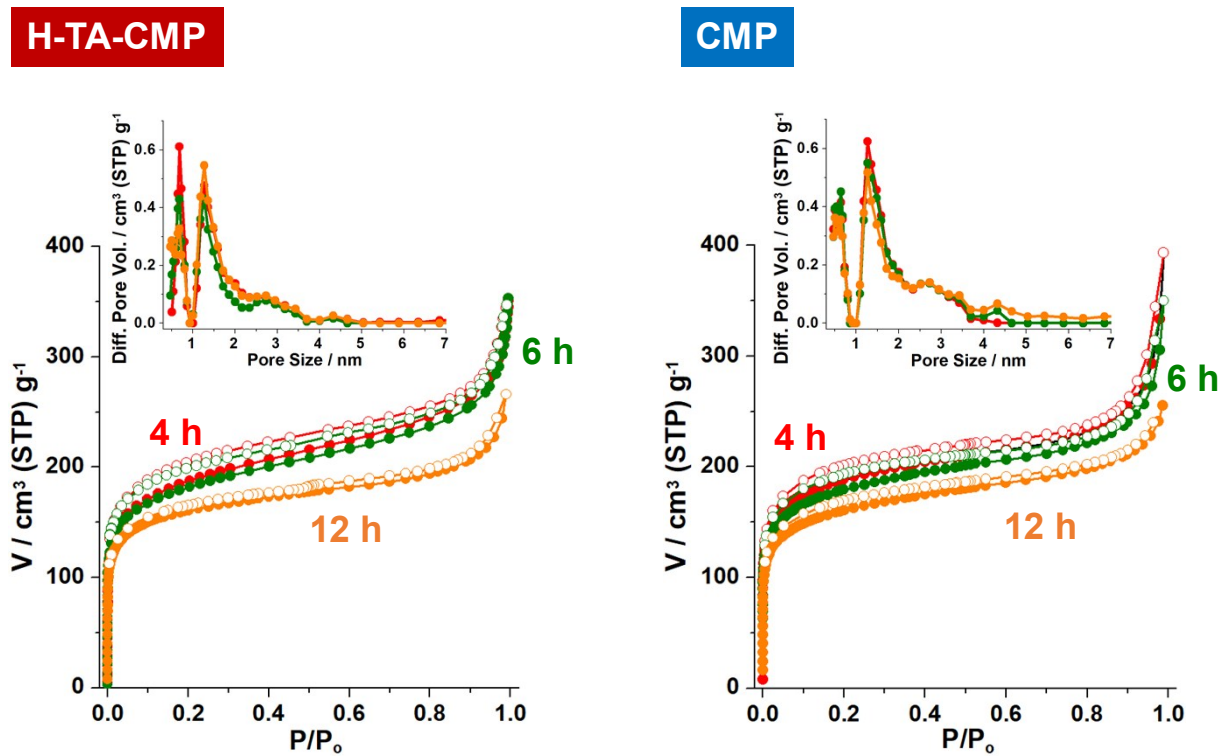
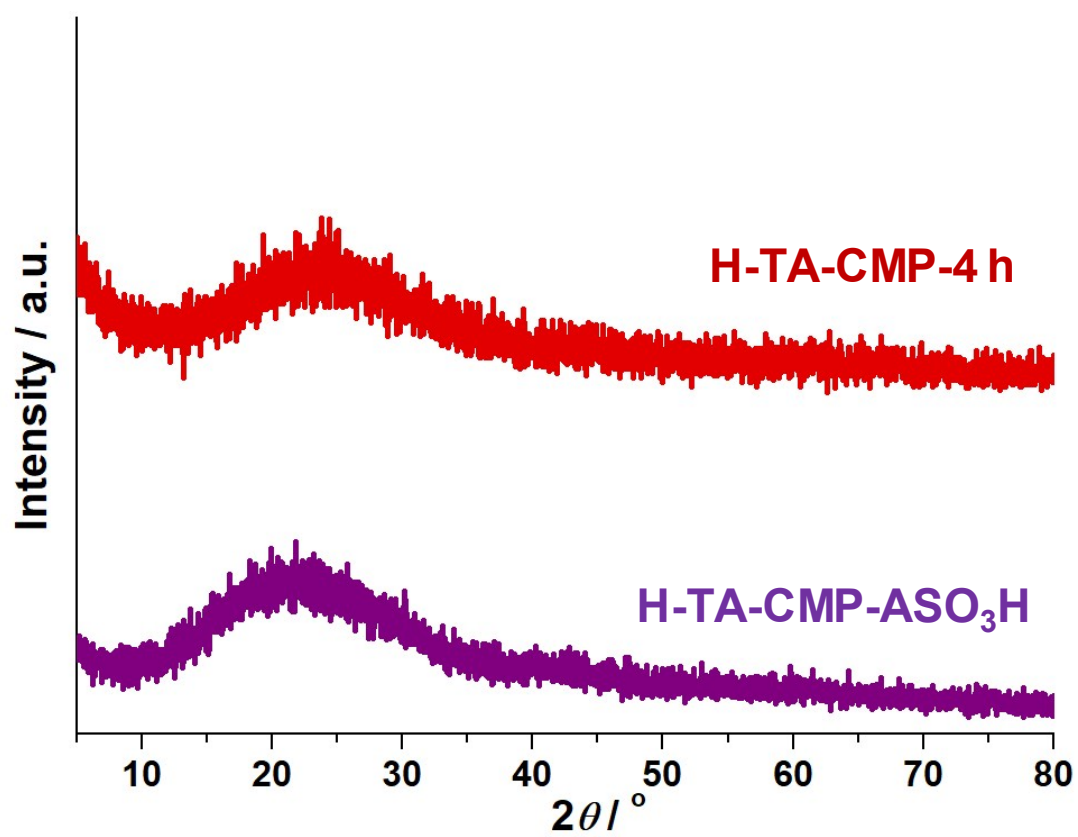


Fig. S2 PXRD patterns of H-TA-CMP and H-TA-CMP-ASO<sub>3</sub>H.



**Fig. S3** TGA curve of H-TA-CMP (4 h).

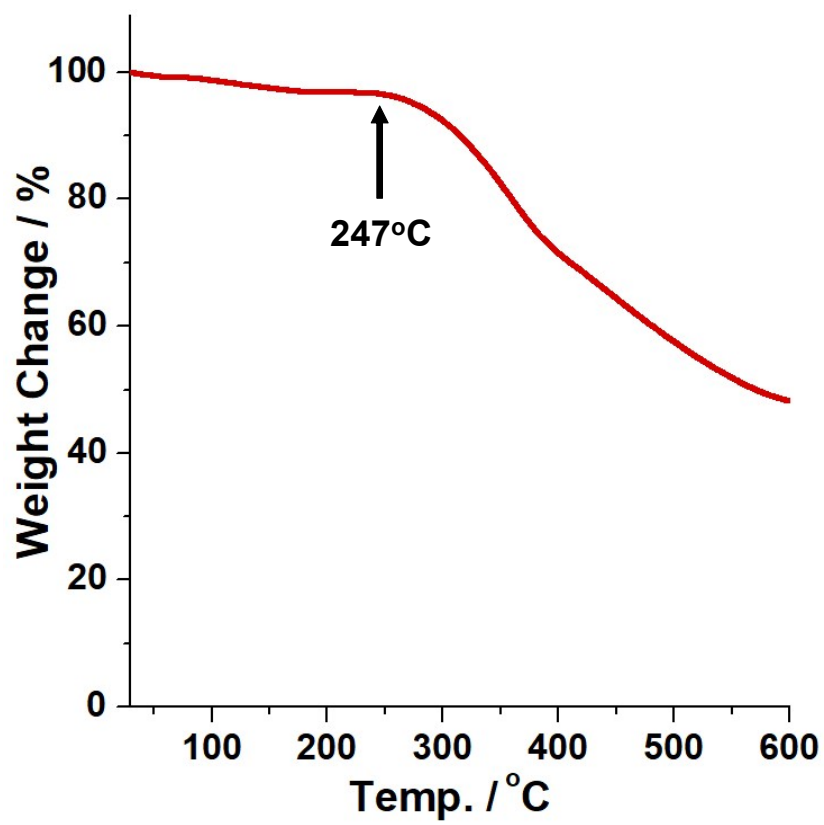
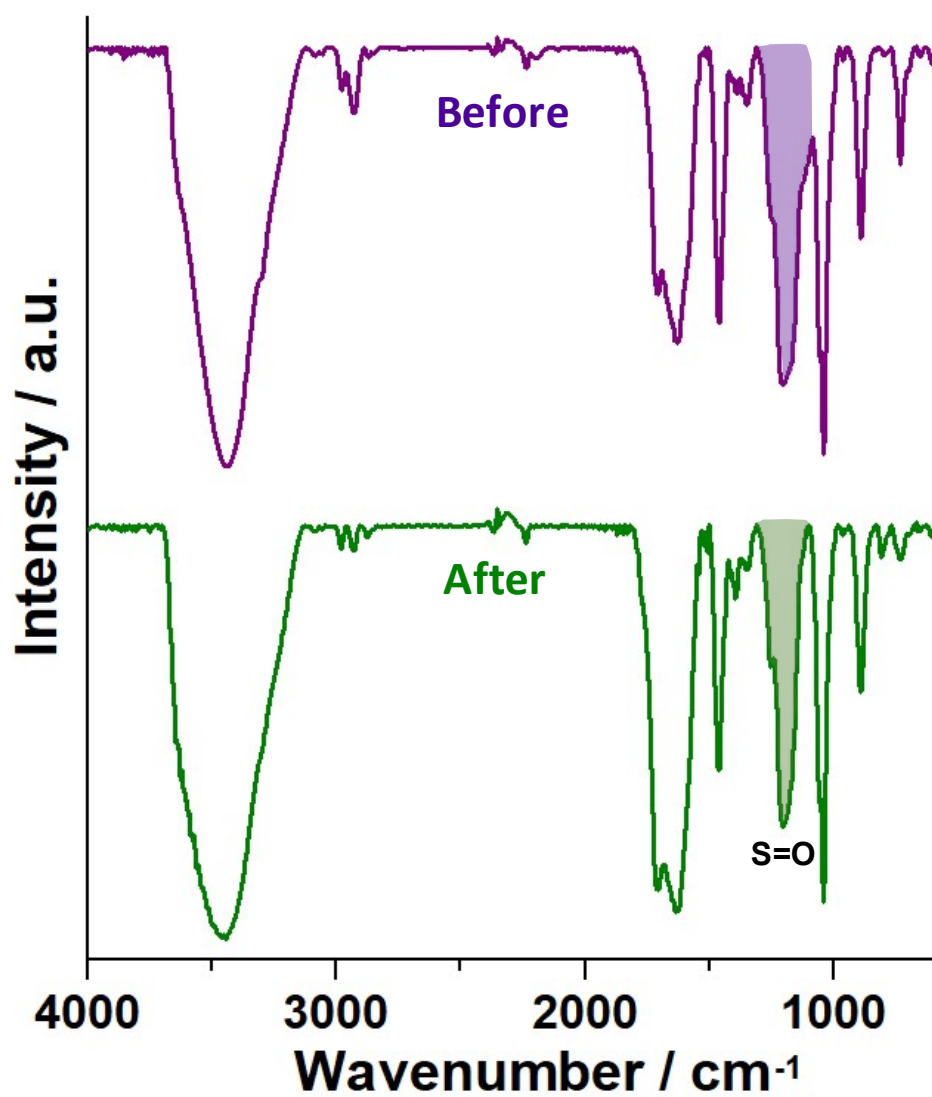
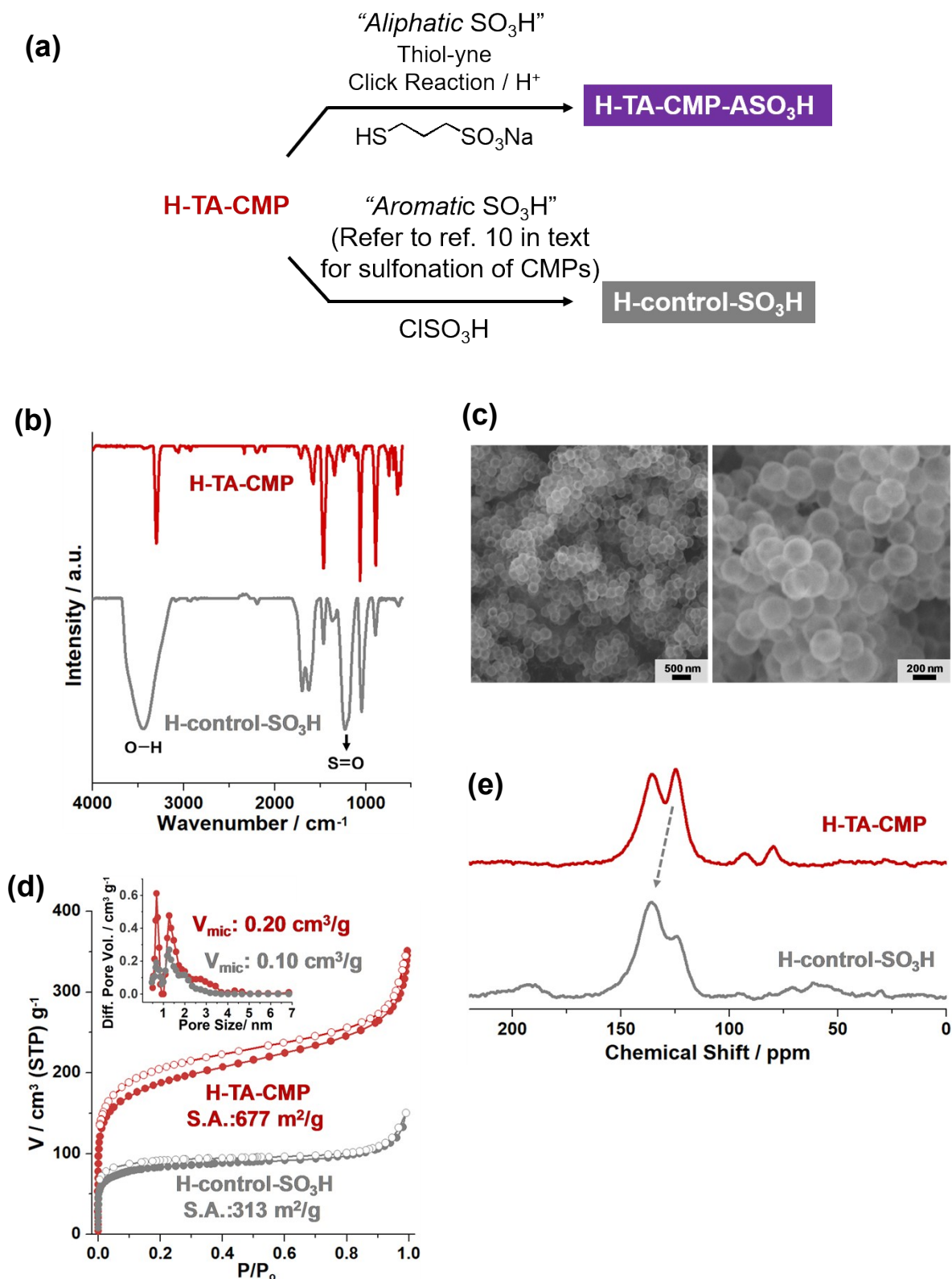


Fig. S4 IR spectra of H-TA-CMP-ASO<sub>3</sub>H before and after five successive catalytic reactions.



**Fig. S5** Characterization data of H-control-SO<sub>3</sub>H: (a) Synthetic schemes (Refer to Experimental Section for detail procedures), (b) IR spectra, (c) SEM images, (d) N<sub>2</sub> isotherm curves obtained at 77K, pore size distribution diagrams by the DFT method, and (e) solid state <sup>13</sup>C NMR spectra of H-control-SO<sub>3</sub>H.





**Fig. S6** (a) Reaction scheme of the desulfonation of aromatic sulfonic acids and (b) IR spectra of H-control-SO<sub>3</sub>H before and after five successive catalytic reactions.

