Sulfonic Acid-functionalized Covalent Organic Framework for Efficient Catalytic Hydration of α-Alkenes to Secondary Alcohols

Hua Yuan,[a] Bowen Shi,[a] Hao Huang,[a] Huijing Jiang,[a] Jiali Feng,[a] Ruilong Li,[a]* Gangguo Zhao,[b] and Aijing Ma[b]*

[a] Ningxia Coal Industry Co., LTD, China Energy Investment, Yinchuan, Ningxia 750011, China

[b] State Key Laboratory of Advanced Separation Membrane Materials, Tianjin Key Laboratory of Green Chemical Technology and Process Engineering, School of Chemical Engineering and Technology, Tiangong University, Tianjin 300387, China

* Corresponding authors: 15010217@ceic.com (Ruilong Li), maaijing@tiangong.edu.cn (Aijing Ma)

1. Synthesis of TAPT-DHTP COF and TAPT-DHTP-SO_3H COF catalysts

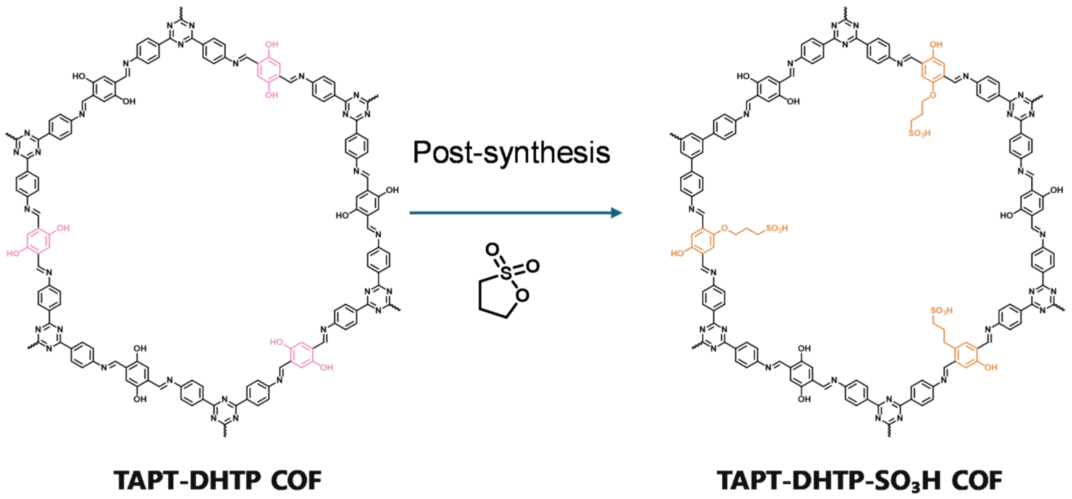
Synthesis of TAPT-DHTP COF

A mixture of 1,3,5-tris(4-aminophenyl)-1,3,5-triazine (TAPT, 0.04 mmol) and 2,5-dihydroxyterephthalaldehyde (DHTP, 9.9 mg, 0.06 mmol) was added in a 10 mL ampoule. A mixed solvent of ethylene glycol dimethyl ether (0.5 mL) and mesitylene (0.5 mL) was added, and the suspension was sonicated for 5 min to ensure homogeneous dispersion. Subsequently, aqueous acetic acid (6 M, 0.1 mL) was added dropwise as a catalyst. The ampoule was evacuated, sealed under liquid nitrogen, and heated at 120 °C for 72 h under static conditions. After cooling to room temperature naturally, the resulting dark red blocky precipitate was collected by centrifugation, washed twice with tetrahydrofuran and once with acetone to remove unreacted species and solvents, and finally dried under vacuum at 80 °C for 12 h to afford TAPT-DHTP COF as a dark red powder.

Post-synthetic modification to TAPT-DHTP-SO_3H COF

The as-synthesized TAPT-DHTP COF (300 mg) was dispersed in anhydrous tetrahydrofuran (40 mL) and stirred under argon at room temperature for 10 min. NaH (400 mg, 60% dispersion in mineral oil) was added slowly in portions, and the mixture was heated to 80 °C and stirred for 1 h. After cooling to room temperature, 1,3-propanesultone (3 mL) was added dropwise under continuous stirring. The reaction was allowed to proceed at room temperature for 24 h, after which the mixture was quenched with water. The solid product was collected by vacuum filtration and washed thoroughly with methanol. The crude solid was then suspended in dilute sulfuric acid aqueous solution ($pH \approx 2.5$, 100 mL), sonicated for 30 min, and allowed to stand overnight at room temperature. The product was collected by vacuum filtration, washed successively with deionized water and methanol until the filtrate became neutral, and dried under vacuum at 60 °C for 12 h to yield TAPT-DHTP-SO_3H COF.

2. Synthesis Procedure and Related Characterization of TAPT-DHTP-SO$_3$H COF Catalyst



Scheme S1. Synthesis Procedure of TAPT-DHTP-SO$_3$H COF Catalyst.

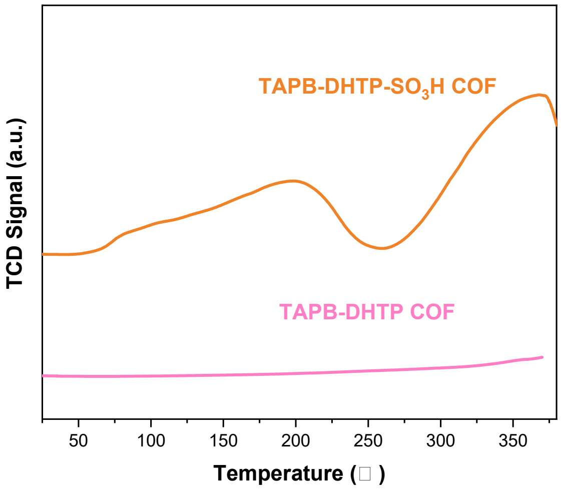


Figure S1. The NH_3-TPD curves of TAPB-DHTP COF and TAPB-DHTP-SO$_3$H COF.

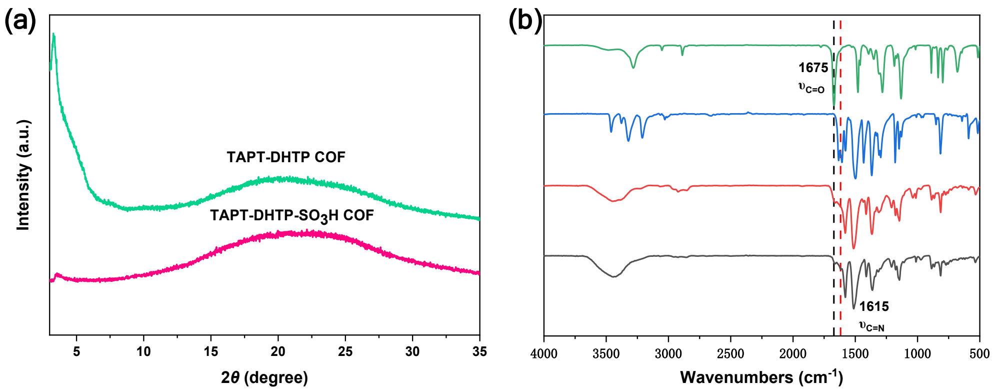


Figure S2. (a) PXRD of TAPT-DHTP COF and TAPT-DHTP-SO$_3$H COF. (b) FT-IR spectra of TAPT-DHTP COF and TAPT-DHTP-SO$_3$H COF.

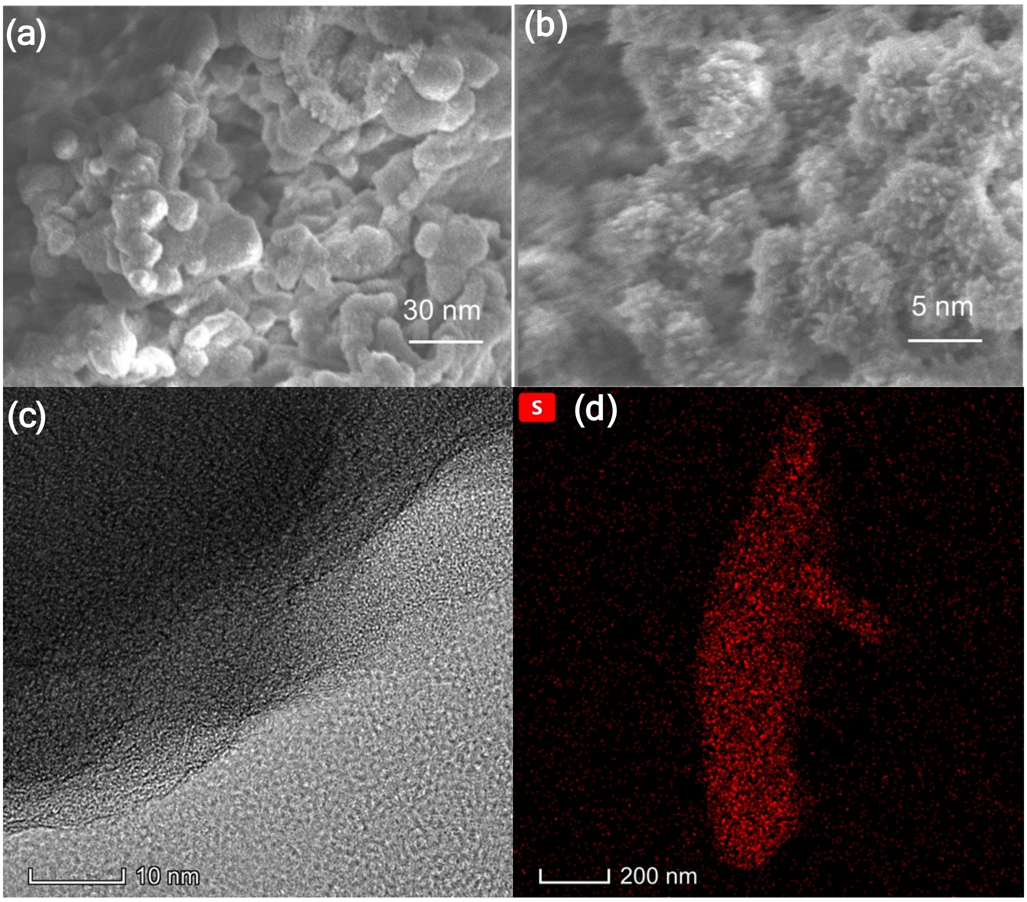


Figure S3. SEM images of (a) TAPT-DHTP COF and (b) TAPT-DHTP-SO$_3$H COF. (c-d) TEM images of TAPT-DHTP-SO$_3$H COF.

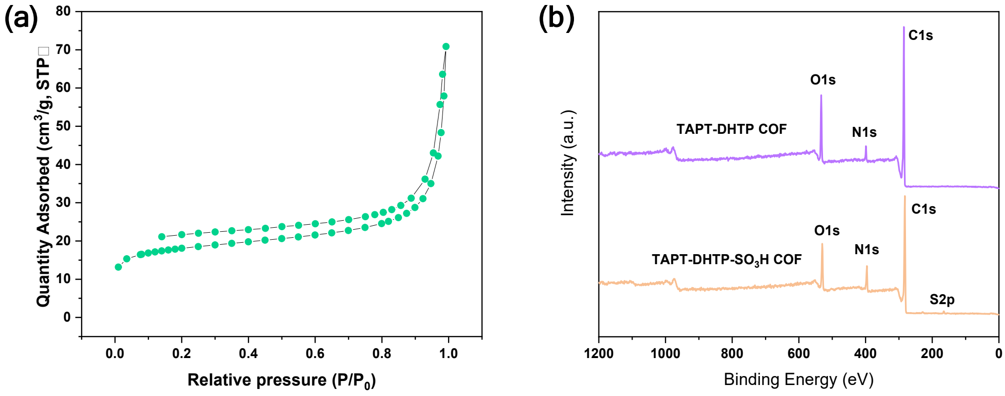


Figure S4. (a) BET curve of TAPT-DHTP-SO$_3$H COF, (b) XPS curves of TAPT-DHTP COF and TAPT-DHTP-SO$_3$H COF.

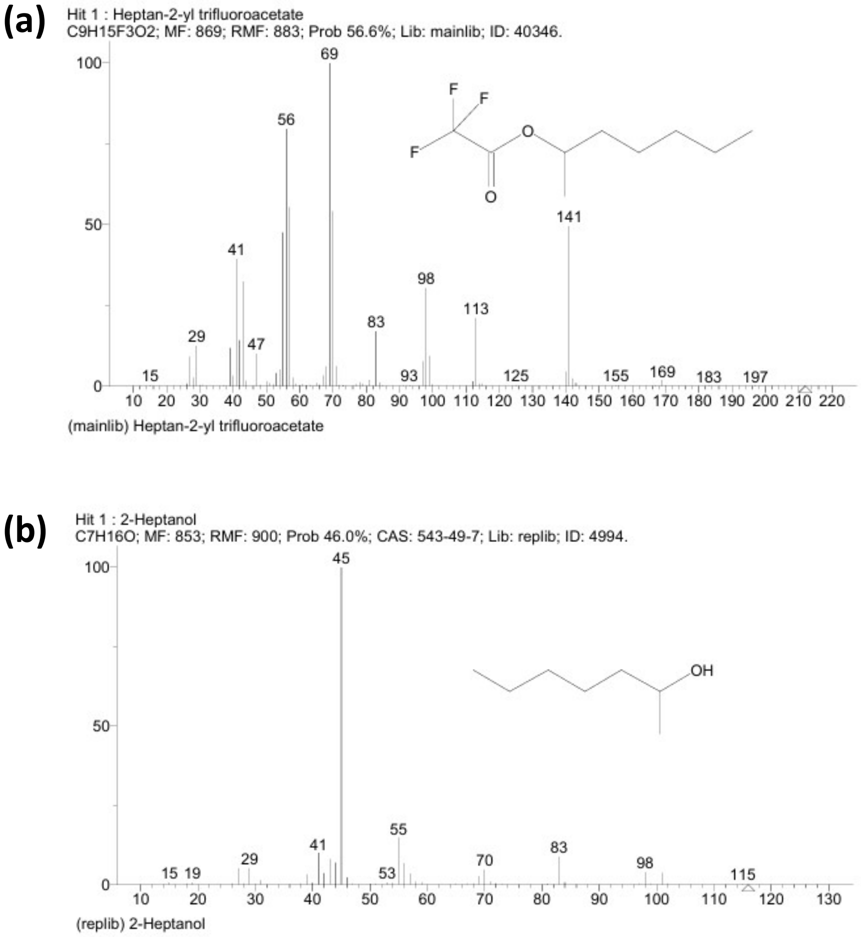


Figure S5. The GC-MS analysis of trifluoroethyl ester intermediate and 2-Heptanol.