

Supporting Information

Conversion of Fructose into 5-Hydroxymethylfurfural Catalyzed by Recyclable Sulfonic Acid–Functionalized Metal–Organic Frameworks

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Preparation of MOFs

MIL-101(Cr): A solution containing $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.00 g, 10 mmol), 1,4-benzenedicarboxylic acid (1.66 g, 10 mmol), hydrofluoric acid (0.43 mL, 40 % solution in water) and H_2O (48 mL) was introduced in a 100 mL Teflon-liner. The mixture was heated to 220 °C in an autoclave for 8 h. The crystalline MIL-101 product in the solution was doubly filtered off using two glass filters with a pore size between 40 and 100 μm to remove the free terephthalic acid. Then a solvothermal treatment was sequentially performed using ethanol (95 % EtOH with 5 % water) at 70 °C for 24 h. The resulting solid was soaked in 1 M of NH_4F solution at 70 °C for 24 h and immediately filtered, washed with hot water. The solid was finally dried overnight at 50 °C under air atmosphere. (Lit. Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem., Int. Ed.* **2008**, 47, 4144–4148.)

UIO-66(Zr): Typical synthesis of UIO-66(Zr) was performed by dissolving ZrCl_4 (1.40 g, 6 mmol) and 1,4-benzenedicarboxylic acid (1 g, 6 mmol) in DMF (60 mL) at room temperature. The thus obtained mixture was sealed and placed in a preheated oven at 120 °C for 16 h. Crystallization was carried out under static conditions. After cooling in air to room temperature, the resulting solid was filtered, repeatedly washed with DMF and dried at room temperature. (Lit. V. Guillerm, F. Ragon, M. Dan-Hardi. *Angew. Chem. Int. Ed.* **2012**, 51, 9267–9271.)

MIL-53(Al): The synthesis was carried out under mild hydrothermal conditions using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5.20 g), 1,4-benzenedicarboxylic acid (BDC, 1.152 g), and deionized water (20 mL). The reaction was performed in a 100 mL Teflon-liner for three days at 220 °C. After filtering off and washing with deionized water, the solid was purified upon heating in air (330 °C, 3 days). At this temperature, the unreacted BDC species and the occluded BDC molecules contained in the structure are expelled. (Lit. T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, 10, 1373–1382.)

PTA/MIL-101(Cr) (PTA 33.8 wt%): A solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4 g, 10 mmol), PTA (3.0 g), and hydrofluoric acid (0.44 mL, 10 mmol) in water (48 mL) was stirred for 10 min and then 1,4-benzenedicarboxylic acid (1.6 g, 10 mmol) was added to the mixture. The solution pH was adjusted to 1 by addition of NaOH. This mixture was placed in an autoclave and heated to 220 °C for 8 h. After cooling, the reaction mixture was filtered and the solid was extracted by a Soxhlet extractor in methanol overnight, dispersed in 96 % ethanol, and heated at 100 °C for 20 h in a Teflon-lined autoclave. The resulting solid was filtered, dried at 60 °C in an oven, and denoted as PTA/MIL-101(Cr) (PTA 33.8 wt%). (Lit. Y. Zhang, V. Degirmenci, C. Li, E. J. M. Hensen, *ChemSusChem* **2011**, 4, 59–64.)

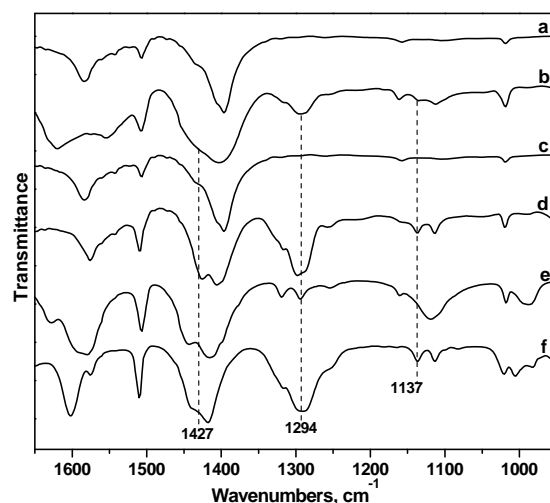


Figure S1. FTIR of (a) MIL-101(Cr), (b) MIL-101(Cr)-SO₃H (15.0%), (c) UIO-66(Zr), (d) UIO-66(Zr)-SO₃H (9.5%), (e) MIL-53(Al), and (f) MIL-53(Al)-SO₃H (8.2%).

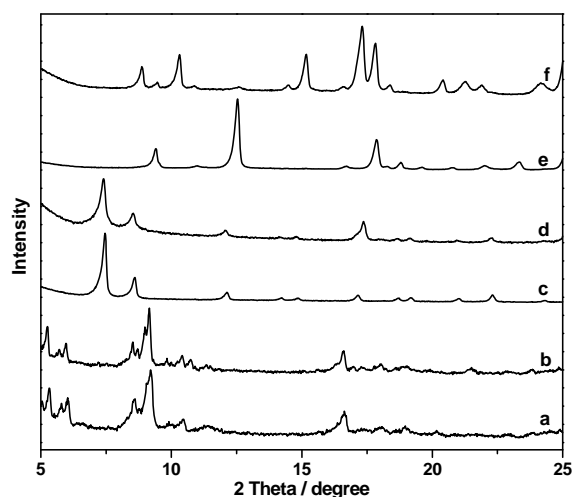


Figure S2. XRD patterns of (a) MIL-101(Cr), (b) MIL-101(Cr)-SO₃H (15.0%), (c) UIO-66(Zr), (d) UIO-66(Zr)-SO₃H (9.5%), (e) MIL-53(Al), and (f) MIL-53(Al)-SO₃H (8.2%).

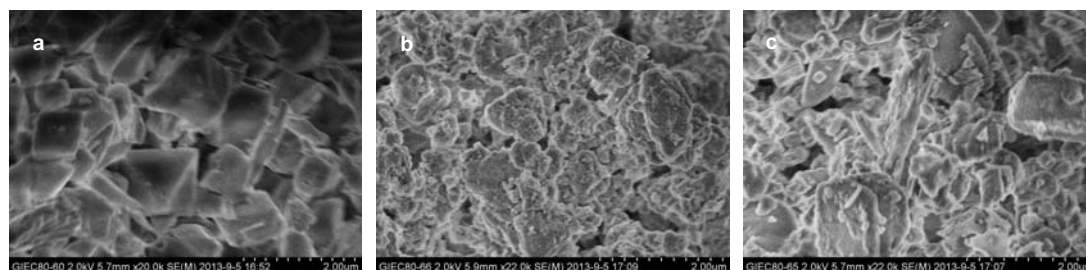


Figure S3. SEM images of (a) MIL-101(Cr)-SO₃H (15.0%), (b) UIO-66(Zr)-SO₃H (9.5%), and (c) MIL-53(Al)-SO₃H (8.2%).