Electronic Supplementary Information

Methyl modified MOF-5: a water stable hydrogen storage material

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I. Materials and Methods

Materials

$Zn(NO_3)_2 \cdot 6H_2O$ (98%, Aldrich), diethylene glycol (99%, Acros) and methylterephthalonitrile (98%, Acros) were used as received. 2,5-Dimethylterephthalic acid (>97%, TCI) was recrystallized from 2-methyl-1-propanol. *N,N'*-diethylformamide (DEF) (99%, Acros) and $CHCl_3$ were dried over and distilled from CaH_2 and P_2O_5 before use, respectively. MOF-5 was synthesized according to a literature procedure.[1]

Synthesis of Methylterephthalic acid

Methylterephthalic acid was synthesized according to a procedure reported by Anzalone *et al.*.[2] Methylterephthalonitrile (35.2 mmol, 5.00 g.) was added to a solution of NaOH (141 mmol, 5.63 g) and 0.1 mL water in 100 mL of diethylene glycol (DEG). The reaction mixture was heated to 200 ^{o}C with a heating rate of 1 ^{o}C min^{-1} and kept at 200 ^{o}C for 42 h. During this time, 60 mL of DEG was added to the reaction mixture. After cooling, the reaction mixture was adjusted to about pH=1 with a 37% HCl solution. The precipitate was collected by filtration, and the crude product was washed with cold ethanol and dried at 80 ^{o}C in vacuum. Crude methylterephthalic acid (5.24 g, 83 % yield) was recrystallized from acetone/hexane (10:1). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 2.54 (s, 3H, C$\underline{H}_3$), 7.80-7.88 (3H, Ar$\underline{H}$), 12.17 (s, 2H, COO$\underline{H}$). ^{13}C NMR (DMSO-d_6, 400 MHz): δ(ppm) 168.7, 167.2, 139.4, 134.9, 133.6, 132.5, 130.6, 127.1, 21.4. IR: 1673 cm^{-1} (C=O). MS (EI), *m/z* (rel.): 180 (61), 162 (100), 134 (64), 89 (25), 77 (44), 28 (63).

Synthesis of CH_3MOF-5

4 mL of a methylterephthalic acid solution in DEF (0.1 M) and 4 mL of a Zn $(NO_3)_2 \cdot 6H_2O$ solution in DEF (0.3 M) were mixed in a 20 mL glass vial. The vial was

sealed and heated in an oven at 100 ^{o}C for 49 h. When cooled to r.t. the supernatant was decanted and discarded. Cubic crystals were collected and immersed in DEF (3 mL) for 24 h (2×), followed by immersing the crystals in $CHCl_3$ (4 mL) for 24 h (3×). The solvent-exchanged product was heated at 160 ^{o}C in vacuum for 24 h, and stored in a glove box (yield: 75 mg, 69%). Element analysis (EA): Calc. for $Zn_4O(C_9H_6O_4)_3$: C, 40.0%, H, 2.22%. Found C, 40.2%, H, 2.24%. FT-IR: 2982, 1605, 1565, 1497, 1405, 1380, 1293, 1209, 1099, 911, 828, 788, 763.

Synthesis of DiCH$_3$MOF-5

DiCH$_3$MOF-5 was synthesized using a similar procedure as described for CH$_3$MOF-5. 4 mL of a 2,5-dimethylterephthalic acid solution in DEF (0.1 M) and 4 mL Zn $(NO_3)_2 \cdot 6H_2O$ solution in DEF (0.3 M) were mixed in a 20 mL a glass vial. The vial was sealed and heated in an oven at 100 ^{o}C for 29 h. A similar solvent exchange procedure was used as described for CH$_3$MOF-5. The solvent-exchanged product was heated at 160 ^{o}C in vacuum for 24 h, and stored in a glove box (yield: 40 mg, 35%). Element analysis (EA): Calc. for $Zn_4O(C_{10}H_8O_4)_3$: C, 42.2%; H, 2.81%. Found: C, 41.0%; H, 2.89%. FT-IR: 2967, 2930, 1558, 1499, 1409, 1356, 1286, 1193, 1154, 1038, 910, 851, 795, 760.

II. Characterization

XRD patterns of all samples were recorded on a X'Pert X-ray diffractometer operated at 45 kV and 40 mA with monochromated Cu Kα radiation within a 2-theta range of 5-60^{o}. A sample was placed into an airtight sample-holder in order to limit exposure to air and moisture. IR spectra of the samples were collected on PerkinElmer Spectrum 100 FT-IR Spectrometer. TG curves of samples were obtained on a PerkinElmer Pyris Diamond Thermogravimetic Differential Thermal/Analyzer. Samples were investigated from room temperature to 600 ^oC with a heating rate of 10 ^oC min^{-1} under an airflow (200 mL min^{-1}). Element Analyses were performed on a Thermo Scientific InterScience Flash 2000 Organic Elemental Analyzer. The pore textural properties, including BET surface area and pore volume, were recorded on a Mocromeritics ASAP 2010 adsorption analyzer at 77 K. Prior to the adsorption measurements, the samples were *in-situ* degassed in vacuum at 135 ^oC. The dead volume of the sample cell was determined in a separate experiment. *In-situ* pretreatment coupled to a separate dead volume measurement after the analysis was employed in order to avoid the helium entrapment phenomenon. The weight of sample obtained after the pretreatment was used in the various calculations. BET surface areas were calculated in the adapted pressure range of P/P_0=0.01-0.1.

III. Hydrogen storage measurement

Hydrogen storage measurements at different pressures were performed on a home-made Sievert's setup at 77 K. Samples were heated to 150 ^oC for 12 h. under high vacuum (10^{-6} mbar) prior to each measurement. Hydrogen (ultra-high-purity grade, 99.999%) was additionally purified by leading it through a bed of zeolite spheres at 77 K before being loaded into the sample holder. The pressure change was monitored and recorded after the hydrogen reservoir was connected to the sample holder. The samples were weighed in a glovebox after the measurements.

References

1 B. Panella, M. Hirscher, H. Puetter, U. Mueller. *Adv. Funct. Mater.*, 2006, **16**, 520.
2 L. Anzalone, J. A. Hirsch, *J. Org. Chem.*, 1985, **50**, 2131.

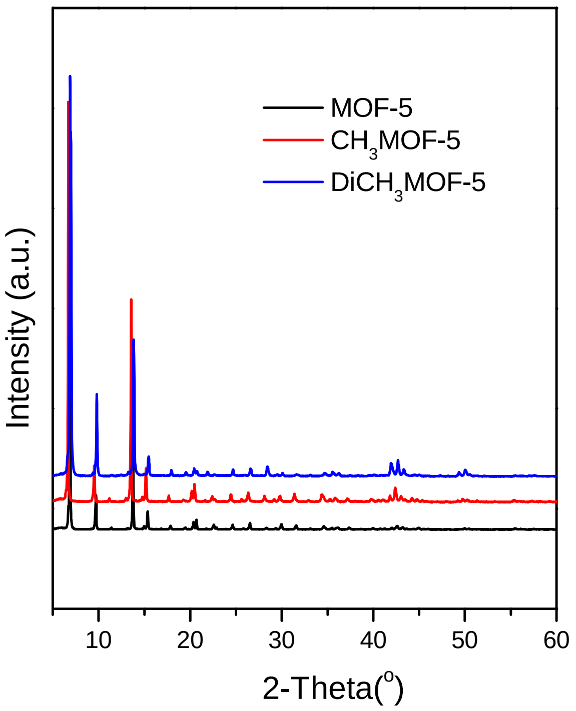

Figure S1. PXRD patterns of MOF-5 and methyl modified MOF-5s.

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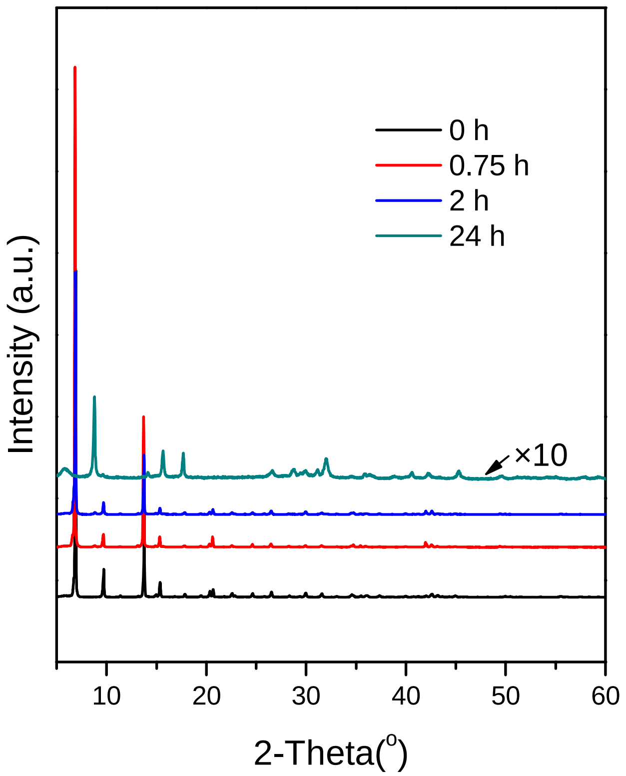

Figure S2. PXRD patterns of MOF-5 exposed to ambient air for 0h, 0.75h, 2h and 24h, respectively.

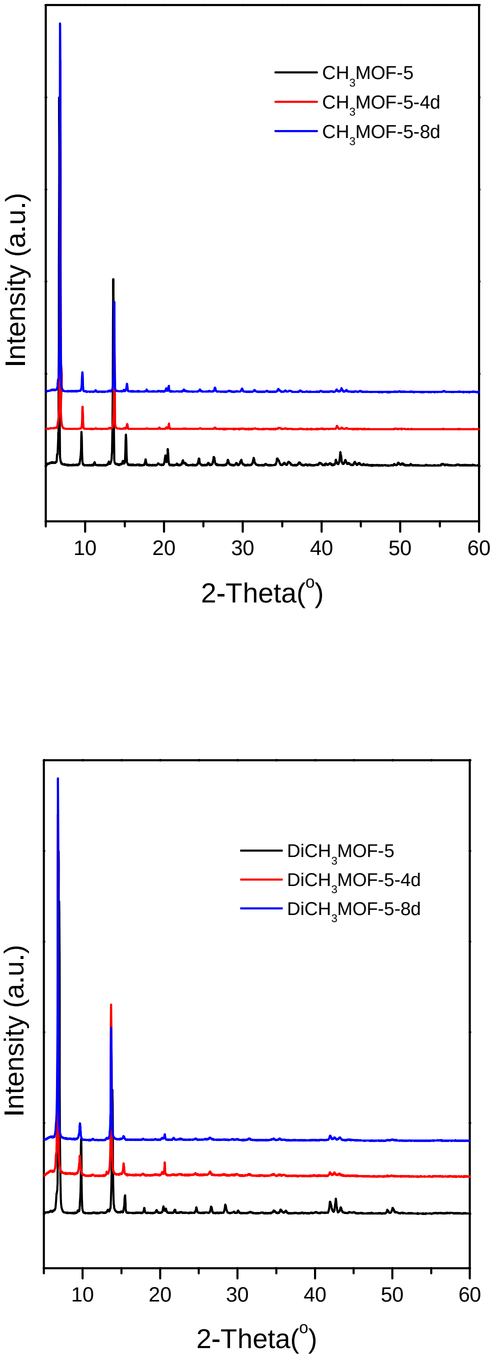

Figure S3. PXRD patterns of methyl modified MOF-5s after 4 days (4d) and 8 days (8d) exposure to ambient air.

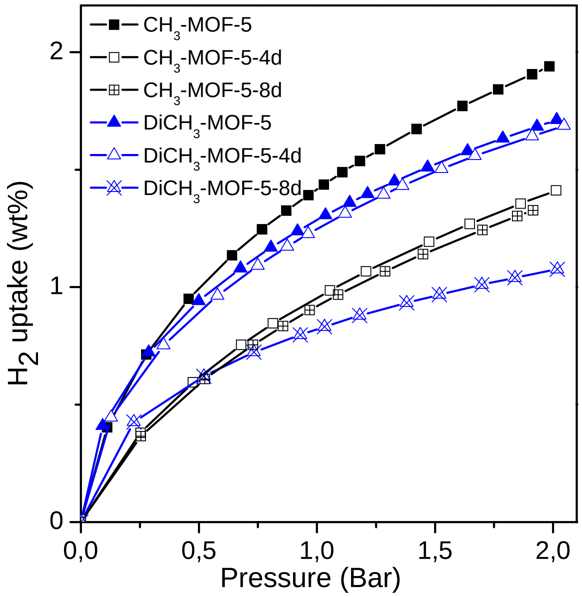

Figure S4. H_2 uptake capacities of methyl modified MOF-5s before and after 4 days (4d) and 8 days (8d) exposure to ambient air.