Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Data

Size-controlled synthesis of MIL-101(Cr) nanoparticles with enhanced selectivity for CO_2 over N_2

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Experimental section

Chemicals

Chromium nitrate nonahydrate [$Cr(NO_3)_3 \cdot 9H_2O$, 99%], absolute ethanol (AR), stearic acid (99%) and ammonium fluoride (95%) were bought from Fisher Scientific. 1.4-Benzenedicarboxylic acid (H_2bdc, 98%) was purchased from Lancaster Synthesis. Benzoic acid (99.5%), 4-methoxybenzoic acid (99%), 4-nitrobenzoic acid (99%) and perfluorobenzoic acid (99%) were bought from Aldrich Chemical Co.

Synthesis of MIL-101(Cr) nanoparticles

In a typical experiment, H_2bdc (0.33 mmol) and $Cr(NO_3)_3 \cdot 9H_2O$ (0.33 mmol) were added to water (10 cm^3, 555 mmol). The resulting suspension was stirred for 1 h at room temperature then heated under autogeneous pressure at 180 °C for 4 h in a Teflon-lined autoclave. After cooling to room temperature, the mixture was filtered with Whatman filter paper to remove the recrystallised terephthalic acid. The product was isolated from the filtrate as a green powder following centrifugation at 11000 rpm for 1 h, and then washed three times with EtOH before drying at room temperature.

Nano MIL-101(Cr) with different particle sizes was prepared by the same method, though with addition of a monocarboxylic acid (0.11 mmol) to the reaction mixture.

Synthesis of bulk MIL-101(Cr)

Bulk MIL-101(Cr) was synthesised using a similar method to that reported by Férey and co-workers,[1] except that no HF was used during the synthesis. For a typical synthesis process, $Cr(NO_3)_3 \cdot 9H_2O$ (1 mmol) and H_2bdc (1 mmol) were added to water (4.8 cm^3, 265 mmol) and the mixture stirred for 10 min. The resulting suspension was heated under autogenous pressure at 220 °C for 8 h in a Teflon-lined autoclave and then cooled to room temperature. The mixture was filtered with Whatman filter paper to remove the recrystallised terephthalic acid. The product was isolated as a green powder following centrifugation at 6000 rpm for 5 min, and subsequently washed three times with EtOH.

Purification of MIL-101(Cr) materials

The MIL-101(Cr) samples were further purified by the following two step process using hot ethanol and aqueous NH_4F solutions. Firstly, the solid sample was treated in ethanol at 80 °C for 4 h, then separated by centrifugation and washed three times with ethanol, each time separating by centrifugation before drying at room temperature. The ratio of sample to solvent used was 1 g to 56 cm^3. Secondly, the obtained solid sample was dispersed in an aqueous solution of 30 mM NH_4F at 60 °C for 5 h, then separated by centrifugation and washed five times with hot water to remove traces of NH_4F, each time separating by centrifugation. The resulting material was dried at room temperature. The ratio of sample to the NH_4F solution used was 1 g to 100 cm^3.

Characterization

Powder X-ray diffraction (XRD) patterns of the materials were recorded on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.542 Å). The transmission electron microscope (TEM) images of the materials were taken on the JEOL IEM1200EXII instrument with the operating voltage of 120 kV. The particle sizes were manually analysed using ImageJ software, with more than 200 particles selected for analysis. The sorption isotherms of N_2 at 77 K/ 273 K and CO_2 at 273 K under medium relative pressure were carried out on BELSORP Mini-II (BEL, Japan) instrument. The sample was degassed at 150 °C for 4 h prior to sorption. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller method in the P/P_0 range of 0.05-0.1. The total volume was obtained by calculating the data at the relative pressure of 0.99. The selectivities of the materials for CO_2 were calculated from the single gas isotherms by dividing the CO_2 adsorption capacity by that of N_2 at the relative pressure of 1.

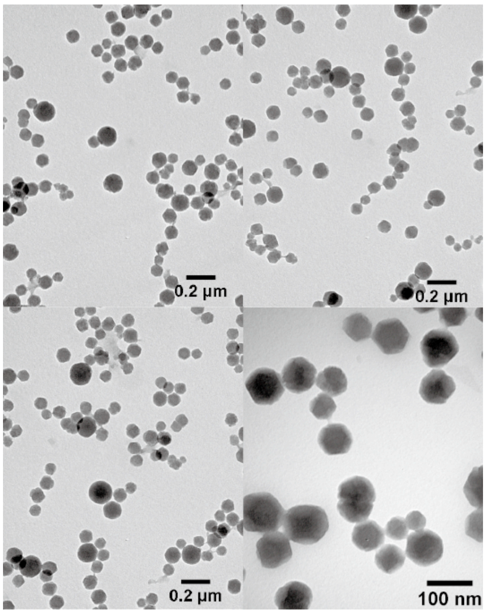

Fig. S1. TEM images of nano MIL-101(Cr) synthesised with perfluorostearic acid.

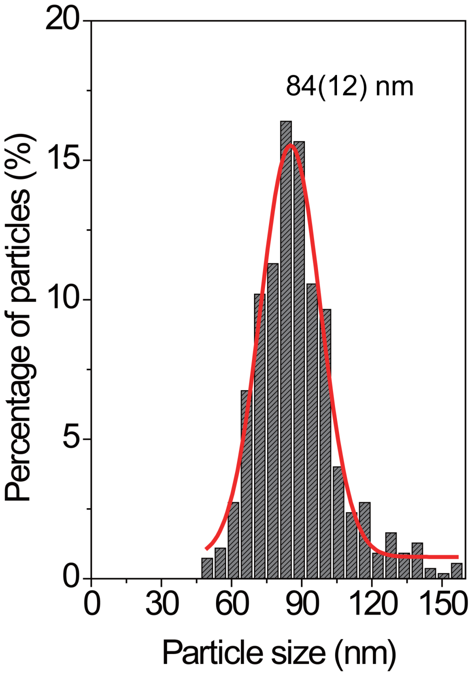

Fig. S2. Particle size distribution of MIL-101(Cr) synthesised with perfluorostearic acid.

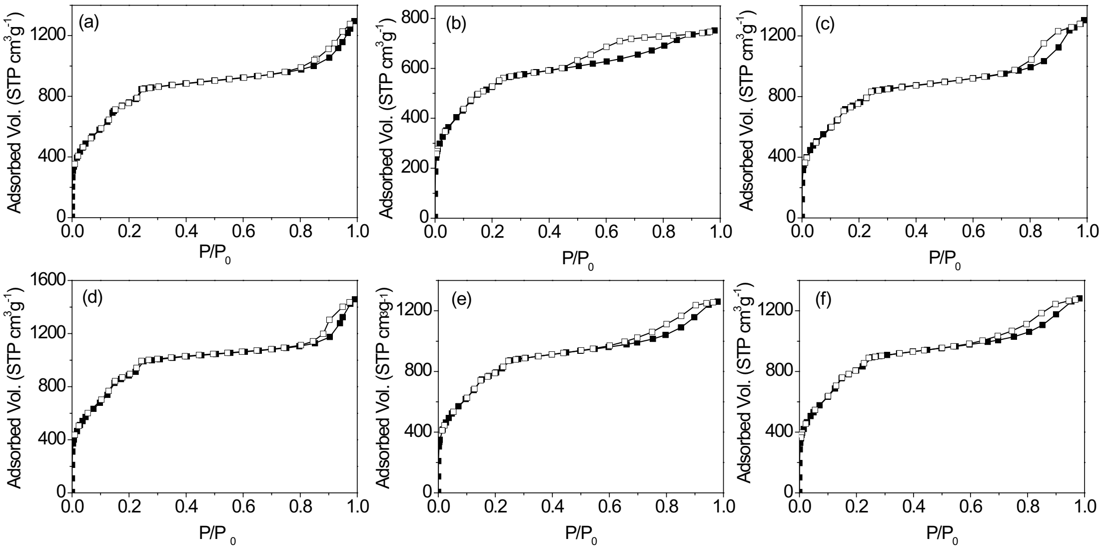

Fig. S3. Nitrogen adsorption-desorption isotherms of the activated nano MIL-101(Cr) samples with/without chemical additives 77 K: (a) without chemical additive; (b) stearic acid; (c) 4-methoxylbenzoic acid; (d) benzoic acid; (e) 4-nitrobenzoic acid; (f) perfluorobenzoic acid.

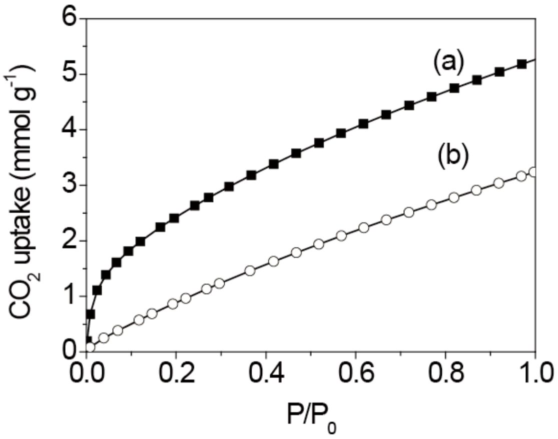

Fig. S4. CO_2 sorption of the nano MIL-101(Cr) material without chemical additives at 273 K (a) after activation and (b) before activation. *P_0* is 101.33 kPa.

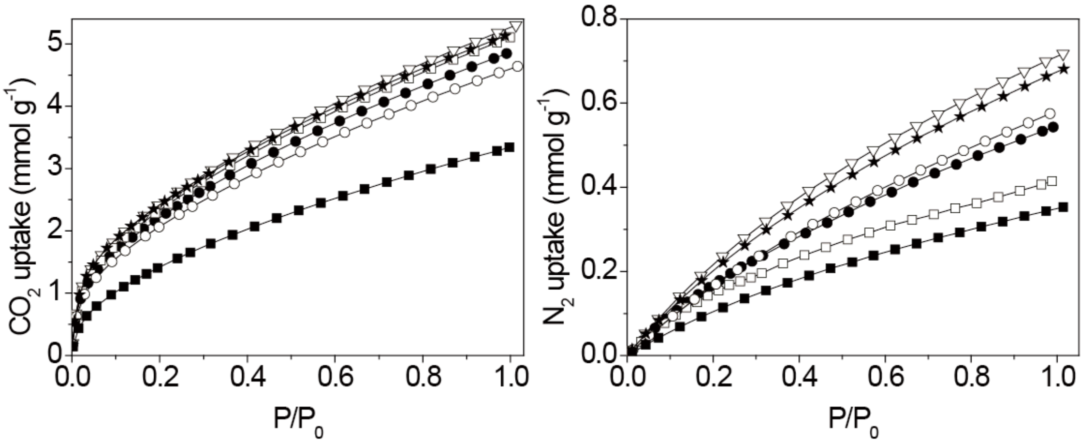

Fig. S5. CO_2 sorption (left) and N_2 sorption (right) of the nano MIL-101(Cr) materials with or without chemical additives at 273 K: (▽) without additive; (●) 4-methoxylbenzoic acid; (★) benzoic acid; (□) 4-nitrobenzoic acid; (○) perfluorobenzoic acid; (■) stearic acid. *P_0* is 101.33 kPa.

References:

1 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science* 2005, **309**, 2040.