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Electronic supplementary information (ESI)

Insight into the reversible structural crystalline-state transformation from MIL-53(Al) to MIL-68(Al)

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Experimental section

General methods and materials

Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, ≥98 %, Sigma-Aldrich), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, 99 %, Sigma-Aldrich), terephthalic acid (C_6H_4-1,4-$(CO_2H)_2$, 98 %, Aldrich), and *N*,*N*-dimethylformamide (DMF, $HCON(CH_3)_2$, 99.95 %, Scharlau) were purchased commercially and used without further purification.

MIL-53(Al) synthesis

The conditions used for MIL-53(Al) preparation were acquired from the work reported by Loiseau *et al*.[1] In a typical synthesis, 6.5 g of aluminum nitrate nonahydrate and 1.437 g of terephthalic acid were combined in 25 mL of deionized water. The mixture was transferred into a Teflon™-lined autoclave. The autoclave was placed in an oven heated at 220 °C for 3 d. After cooling down, crystals of MIL-53(Al)as were recovered by centrifugation (10,000 rpm for 15 min), washed 3 times with deionized water and dried at room temperature.

MIL-53(Al) activation

MIL-53(Al)as was calcined at 330 °C for 3 d with heating and cooling rates of 1 °C min^{-1}. After exposure to atmosphere, the product obtained was MIL-53(Al)np.

MIL-68(Al) synthesis

MIL-68(Al) was synthesized according to the procedure described by Yang *et al*.[2] Aluminum chloride hexahydrate (0.244 g) and terephthalic acid (0.25 g) were dissolved in DMF (15 mL) in a round flask. The flask was placed under reflux and heated at 130 °C. After 18.5 h, the product was cooled down, centrifuged (10,000 rpm, 15 min) and rinsed 3 times with fresh DMF. Finally, MIL-68(Al)as was dried at ambient conditions.

Transformations between MIL-53(Al) and MIL-68(Al)

Transformation from MIL-53(Al) to MIL-68(Al)

This transformation was accomplished from MIL-53(Al)as and MIL-53(Al)np obtaining MIL-68(Al)_1 and MIL-68(Al)_2, respectively. In both cases, MIL-53(Al) powder (*ca*. 0.15 g) was immersed in DMF (80 mL) under reflux and stirring at 130 °C for 3 d. Products were collected by centrifugation (10,000 rpm for 15 min) and dried at ambient conditions.

Conversion from MIL-68(Al) to MIL-53(Al)

MIL-68(Al)_1 and MIL-68(Al)_2 (*ca*. 0.12 g) were converted to the MIL-53(Al)np structure under vacuum (0.1-0.15 mbar) at 260 °C for 24 h with a heating rate of 10 °C min^{-1}. The materials formed were termed MIL-53(Al)np_1 and MIL-53(Al)np_2, respectively.

Characterization

Fourier transform infrared (FTIR, Shimadzu IRAffinity-1) spectra of bulk powder were recorded within a wavenumber range of 4000 and 400 cm^{-1} using the KBr disk method and averaging 20

scans at a resolution of 4 cm^{-1}. Thermogravimetric analyses (TGA, Mettler Toledo TGA/DSC 1 SF/755) of the distinct samples were performed between 25 and 900 °C in air with a heating rate of 5 °C min^{-1}. Scanning electron microscopy (SEM, FEI Inspect F50) images were taken in a voltage range of 2-15 kV on samples previously coated with platinum. Powder X-ray diffraction (PXRD, D-Max Rigaku and Bruker D8 Advance) patterns were gathered with a copper anode at room temperature. CuKα radiation with λ = 1.5418 Å was selected by a graphite monochromator. Molecular graphics were done with Diamond[3] using the cif files of MIL-68(Sc),[4] MIL-53(Al)as (CCDC 220475)[1] and MIL-53(Al)np (CCDC 220477).[1] Solid-state nuclear magnetic resonance (NMR, Bruker Avance III WB400) studies were carried out packing the samples in standard 4 mm zirconia rotors spun at the magic angle in N_2 at 12 kHz. Conventional ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra were acquired with a contact pulse of 3 ms and a recycle delay of 10 s. A total of 1024 scans were collected for each spectrum. The spectrometer operated at 100.6 MHz. N_2 physisorption isotherms were measured at -196 °C (Micromeritics TriStar 3000). Samples of MIL-68(Al) were previously degassed at 260 °C for 8 h with a heating rate of 10 °C min^{-1}. In the case of MIL-53(Al) materials, the degassing temperature was 200 °C. Brunauer-Emmett-Teller (BET) specific surface areas were calculated from isotherm data.

Figures and tables

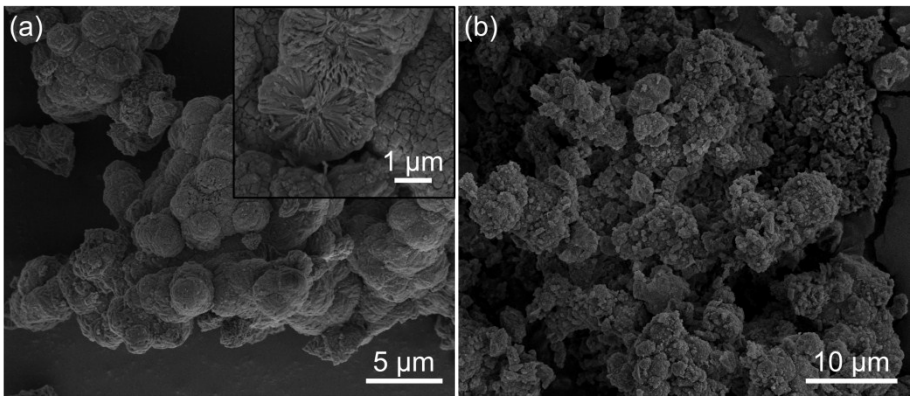


Fig. S1. SEM images of (a) MIL-68(Al)as and (b) MIL-68(Al)as outgassed at 260 °C for 24 h.

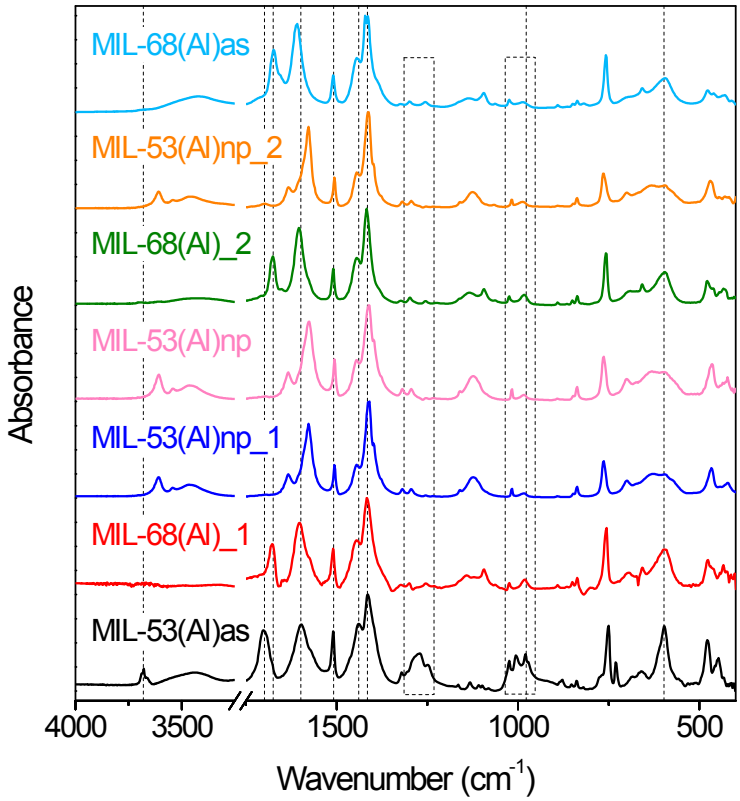
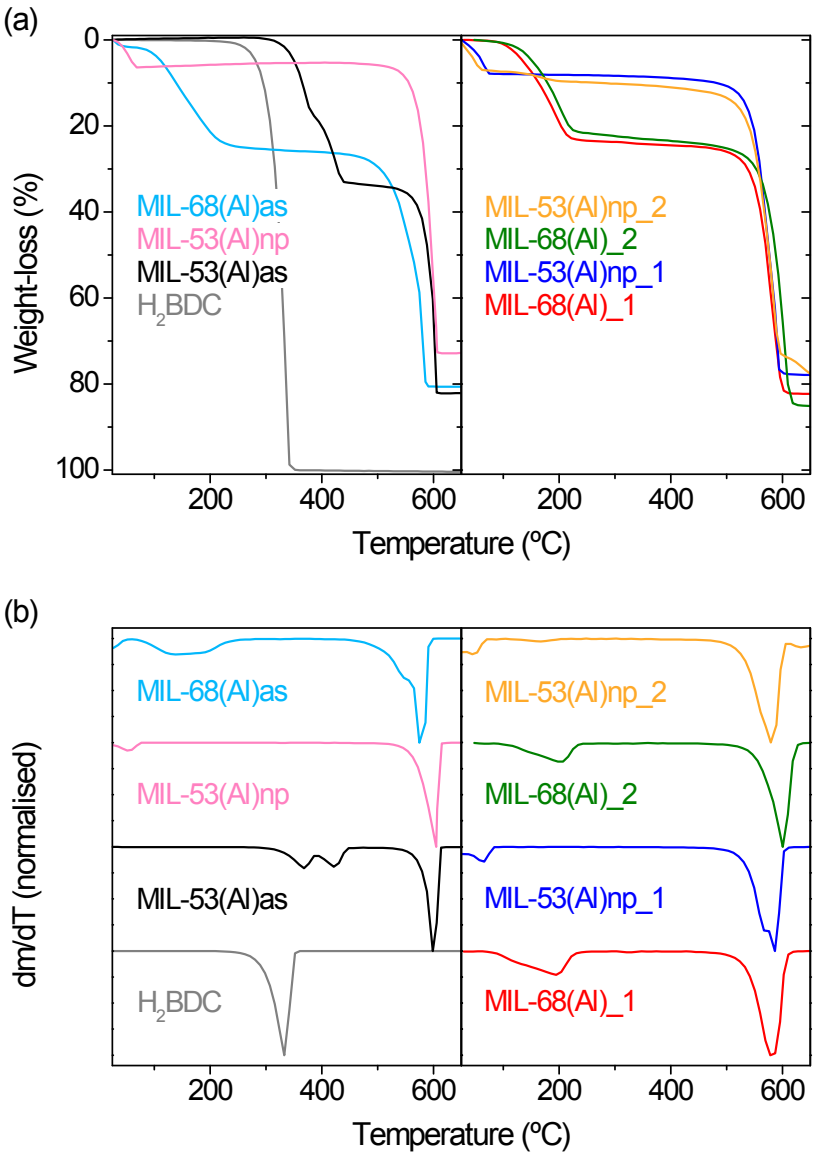


Fig. S2. FTIR spectra of the products of the reversible transformation from MIL-53(Al) to MIL-68(Al) and that of MIL-68(Al)as. The signs placed at 1598 and 1510 cm^{-1} in MIL-53(Al)as (1609 and 1511 cm^{-1} in MIL-68(Al)as) were attributed to the asymmetric stretching of the carboxylates coordinated to aluminium (COO-Al).[5] The bands corresponding to the symmetric stretching appeared at 1440 and 1415 cm^{-1} (1445 and 1417 cm^{-1} in MIL-68(Al)as).[5] The band arisen at 980 cm^{-1}, strong for MIL-53(Al)as but weak for MIL-68(Al)as (988 cm^{-1}), was due to the bending vibration of the $AlO_4(OH)_2$ μ_2-hydroxo groups while the band at 3682 cm^{-1} in MIL-53(Al)as was assignable to the stretching vibration.[6, 7] The intensity of the bands within the wavenumber ranges of 1336-1218 cm^{-1} and 1054-937 cm^{-1} was higher for MIL-53(Al)as than for MIL-68(Al)as and MIL-53(Al)np. The peak placed at 598 cm^{-1} in MIL-53(Al)as was more intense and sharper than that in MIL-68(Al)as (sited at 595 cm^{-1}). MIL-53(Al)as contained disordered

terephthalic acid molecules in its pores. This is confirmed by the band at 1701 cm^{-1} corresponding to the carbonyl (C=O) group. MIL-68(Al)as also had a weak band at *ca*. 1701 cm^{-1} from the presence of a small amount of terephthalic acid inside the pores. This band was slightly overlapped by the intense band related to the carbonyl function of DMF (1674 cm^{-1}) trapped in the triangular pores.[2] The bands placed at 3682 and 1609 cm^{-1} in MIL-53(Al)as were displaced to lower wavenumbers in MIL-53(Al)np (3608 and 1577 cm^{-1}, respectively). Compared to MIL-53(Al)as, two weak signals appeared at 3543 and 1635 cm^{-1} whereas two shoulders arose at 1123 and 631 cm^{-1} in MIL-53(Al)np.



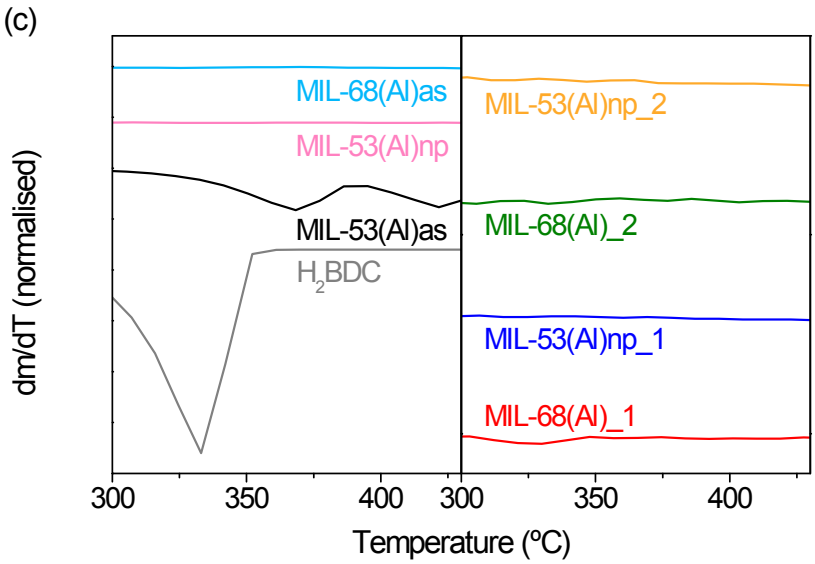


Fig. S3. (a) TGA and (b) DTG curves of the products of the reversible transformation from MIL-53(Al) to MIL-68(Al) and those of MIL-68(Al)as and terephthalic acid (H_2BDC). (c) Enlargement of DTG curves between 300 and 430 °C. MIL-53(Al)as decomposed in three steps. The two events below 480 °C (33.7 %) corresponded to the removal of 0.7 free terephthalic acid molecules per formula unit.[1] The weight loss above 480 °C was ascribed to MOF degradation, leading to an alumina residue. The thermogram of MIL-53(Al)np presented two losses. The first step (25-100 °C; 6.2 %) was attributed to water release. Then, a plateau was maintained up to structure decomposition (480 °C). MIL-68(Al)as degraded in four steps. The departure of water molecules caused the loss at low temperature (25-60 °C; 1.7 %). The event between 60 and 300 °C (23.8 %) was assigned to the release of DMF molecules trapped in the pores. The minuscule step in the range of 300-370 °C (0.4 %) was related to the elimination of terephthalic acid. The weight loss above 430 °C was due to decomposition. Both MIL-68(Al)_1 and MIL-68(Al)_2 had two weight losses before decomposition corresponding to DMF (80-300 °C; 23.8 and 22.1 %, respectively) and terephthalic acid (300-430 °C; 0.9 and 1.1 %, respectively). Both MIL-53(Al)np_1 and MIL-53(Al)np_2 adsorbed water after exposure to environment (25-100 °C; 8.1 and 7.5 %, respectively), as MIL-53(Al)np.

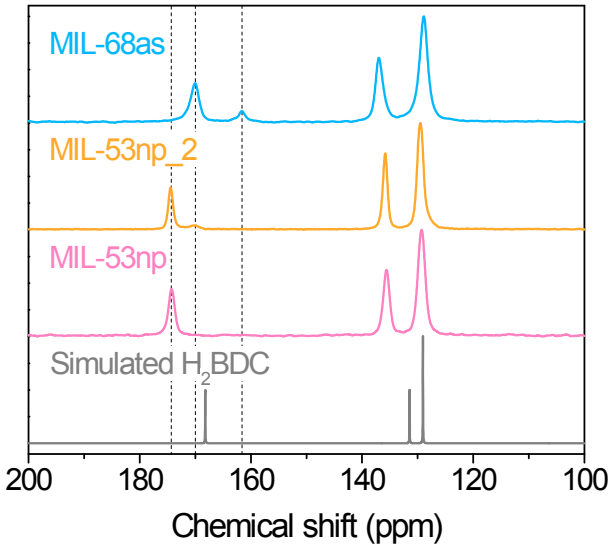


Fig. S4. ^{13}C CP-MAS NMR spectra of MIL-53(Al)np, MIL-53(Al)np_2, MIL-68(Al)as and simulated ^{13}C NMR spectrum of H_2BDC.[8-10] MIL-53(Al)np, MIL-53(Al)np_2 and MIL-68(Al)as share similar signals at chemical shifts of 129 and 136 ppm for MIL-53(Al)s (129 and 137 ppm for MIL-68(Al)as) corresponding to the aromatic (-CH) and quaternary carbons, respectively.[1] The signal at 174 ppm in MIL-53(Al)s is assigned to the carbons of the carboxylate groups disturbed by water molecules.[1] The signal at the chemical shift of 162 ppm in MIL-68(Al)as is related to the carbon of the amide group (-CON-) from DMF. This signal is not present in MIL-53(Al)np_2, indicating a full removal of DMF upon outgassing treatment.

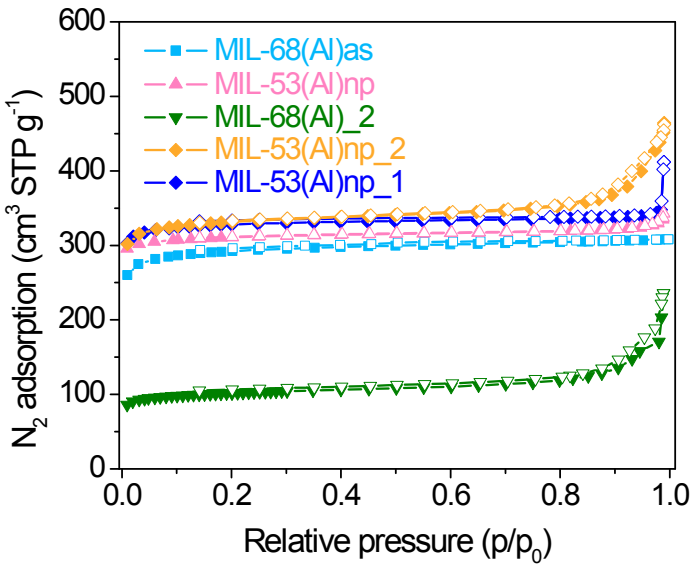


Fig. S5. N_2 sorption isotherms at -196 °C of some products obtained in this work. Filled and empty symbols for adsorption and desorption branches, respectively. MIL-68(Al)as and MIL-53(Al)np feature type I isotherms, typical of microporous materials. The corresponding BET surface areas are close to those of the same MILs found in the literature (see table S1). The small discrepancy can be due to an insufficient activation which rendered remaining guest molecules in the pores (DMF for MIL-68(Al)as and terephthalic acid for MIL-53(Al)np).

Table S1. BET surface areas of some products obtained in this work in comparison to those of the MIL-68(Al) and MIL-53(Al)np found in the literature.

MOF	S_{BET} (m^2 g^{-1})	Reference
MIL-68(Al)as	1121	This work
MIL-53(Al)np	1051	This work
MIL-68(Al)_2	391	This work
MIL-53(Al)np_2	1167	This work
MIL-53(Al)np_1	1253	This work
MIL-68(Al)	1430	[2]
	976	[11, 12]
	1283	[13]
MIL-53(Al)np	1140	[1]
	1074.1-1165.0	[14]
	1132	[15]
	819	[16]
	1163	[17]
	1041	[18]
	1235	[19]

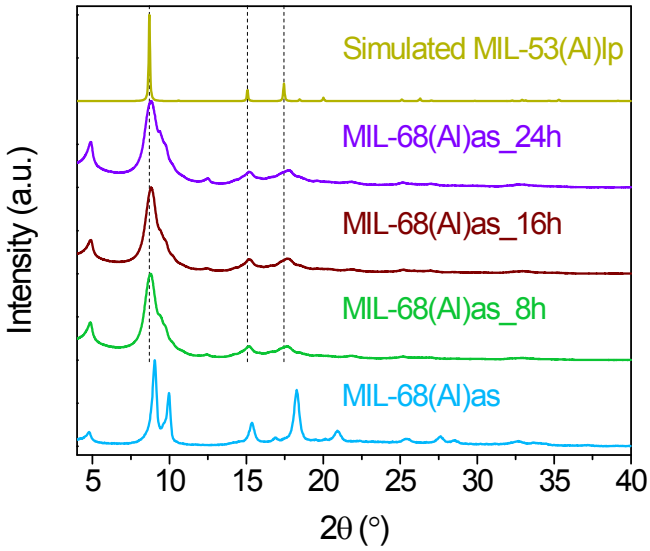


Fig. S6. PXRD patterns of MIL-68(Al)as, simulated MIL-53(Al)lp (CCDC 220476)[1] and the products of the conversion from MIL-68(Al) to MIL-53(Al) starting from MIL-68(Al)as after outgassing at 260 °C for 8, 16 and 24 h.

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