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Modify structure transition and improve gas (H_2, CO_2) adsorption property of metal organic framework MIL-53 by encapsulation of BNH_x

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All reagents were obtained from commercial sources of analytical grade and used as received, unless otherwise noted.

Materials Preparation

Synthesis of MIL-53:

MIL-53(Al) was synthesized using terephthalic acid as a linker, following the protocol described in the literature.[1] In a typical experiment, a mixture of $Al(NO_3)_3 \cdot 9H_2O$ (20 mmol) and H_2BDC (10 mmol) was suspended in water (30 mL) and heated at 220 °C for 3 days. After filtration, a white microcrystalline product was obtained. The as-synthesized sample was then heated at 430 °C for 5 days to remove the solvents and other guest molecules in the pores. The resulting void-cleaned sample was then stored in an Unilab91200 glove box (MBraun Co., Germany) filled with purified argon for further use.

Synthesis of BNH_x@MIL-53:

Boron and nitrogen resources are from ammonia borane. 0.2 g NH_3BH_3 (97% Sigma-Aldrich) was dissolved in 10 ml THF (99.9% Acros), the resulting solution was transferred by syringe to a known mass of activated MIL-53. The mixture was stirred for one hour to allow the complete penetration of NH_3BH_3 into the MIL-53 network, then the mixture was heated at 35 °C under vacuum condition for several hours. After vacuum treatment the product was heated to 450 ^oC for 8 h at a heating rate of 10 $^oC\ min^{-1}$ under Ar gas flow. Then the final product BNH_x@MIL-53 was obtained. Boron content in nanocomposites was confirmed by elementary analysis.

Low-pressure gas adsorption measurements

N_2 and CO_2 adsorption and desorption isotherms were measured by Autosorb-1 system at 77 K and 273 K , respectively. All samples were firstly degassed at 200 °C for 6 hours.

Low pressure hydrogen adsorption tests were performed using the same Autosorb-1 system over a pressure range of 0-820 mmHg at 77 K with the universal Dewar filled with only liquid nitrogen. To obtain controllable temperatures such as 87 K for calculating the heats of H_2 adsorption, a customized Optistat®DN cryostat was used, which has been developed specially for Autosorb-1 analyzers by Quantachrome Instruments, in cooperation with OXFORD Instruments (Abingdon, U.K.). The Cryostat Option (interfaced Autosorb-1, ITC503 and the OptistatDN Cryostat bath) allows one to run gas adsorption experiments over a wide range of controllable temperatures, from 77 K to 200 K, by using only liquid nitrogen as coolant. The isosteric heats (Q_{st}) of hydrogen adsorption on the metal organic frameworks were calculated as a function of surface coverage, by the Clausius-Clapeyron equation:[2]

$$Q_{st} = -R * d(\ln P)/d(1/T)$$

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where *R* is the gas constant, *T* the temperature and *P* the gas pressure.

Other physical measurements

Powder X-ray diffraction patterns (XRD) were collected in a X'Pert PRO X-ray diffractometer operating at 40 kV and 40 mA with a Cu Kα radiation (λ=1.5418 nm). FT-IR spectra were recorded on a Nicolet 380 infrared spectrometer using KBr pellets, in the 400-4000 cm^{-1} frequency range. Elementary analysis were carried out on a 3520 ICP AES instrument (ARL Co., USA). ^{11}B magic-anglespinning (MAS) solid-state NMR experiments were conducted at room temperature on a Bruker Avance 500 NMR spectrometer and the ^{11}B NMR signals were referenced to $BF_3 \cdot Et_2O$ at 0 ppm.

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Before decomposition, the FTIR spectra of sample **1** and **2** demonstrate the existence of both MIL-53 and ammonia borane (**Fig. S1 a**). Peaks appear at 3290, 2340, 1170 and 1080 cm^{-1} are belonging to ammonia borane. Peaks appear at 3290 and 2340 cm^{-1} in ammonia borane are due to stretching of N-H and B-H bonds, respectively.

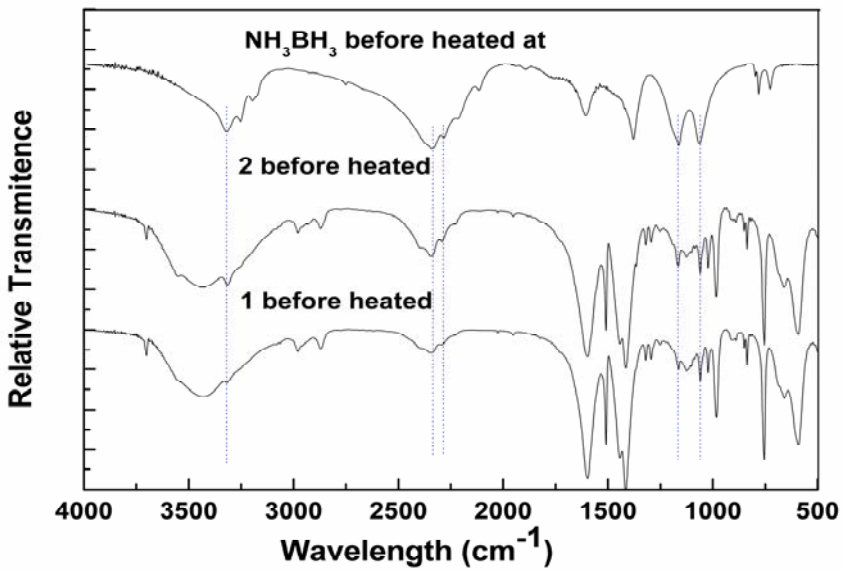

Fig. S1 a. FTIR characterization on all samples before heated at 450 °C for 8 hours..

After decomposition, no characteristic B-H stretch at 2300 cm^{-1} was detectable, only weak N-H stretch can be detected at 3300 cm^{-1}.

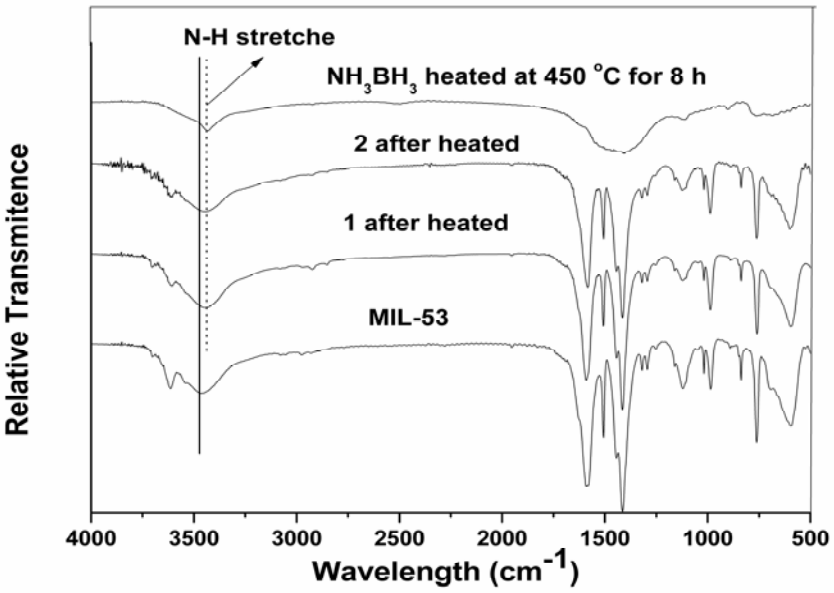

Fig. S1 b. FTIR characterization on all samples after heated at 450 °C for 8 hours..

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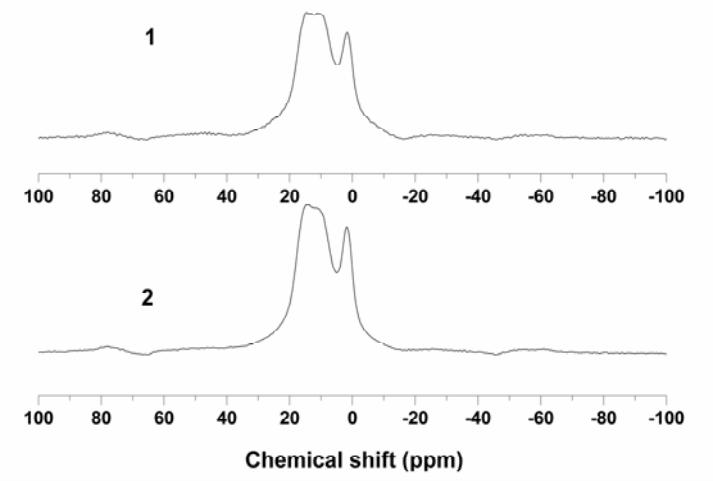
Fig. S2. ^{11}B solid-state NMR tests for sample **1** and **2**.



Heat of Sorption Calculation for H_2 Uptakes

The enthalpy of H_2 adsorption into the activated sample was calculated using a modified version of the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \qquad \textbf{(A)}$$

（T_i = temperature for isotherm i; P_i = pressure for isotherm i; R = 8.313 J K^{-1} mol^{-1}）

The pressure as a function of the amount of hydrogen adsorbed was determined using the Langmuir-Freundlich fit for the isotherms:

$$\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \qquad \textbf{(B)}$$

(Q = moles adsorbed; Q_m = moles adsorbed at saturation; P = pressure; B and t = constants)

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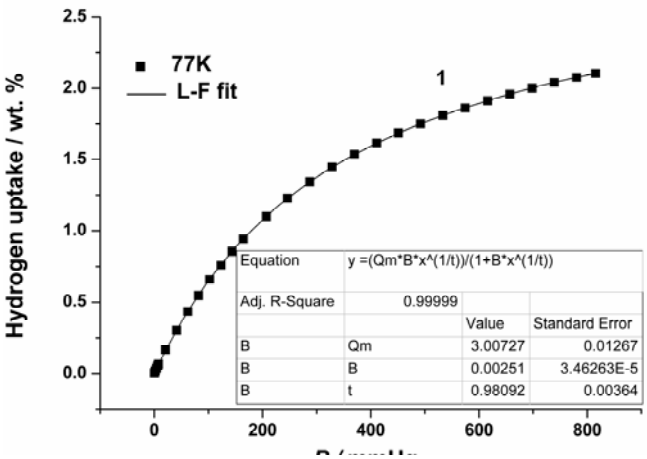
Equation B can be rearranged to $P = \left(\frac{Q/Q_m}{B - B \times Q/Q_m}\right)^t$

Heats of adsorption can be obtained by adding the P values derived from (B) into equation A.

Fig. S3. (a) H_2 adsorption isotherms for sample **1** at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.



(b) H_2 adsorption isotherms for sample **1** at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

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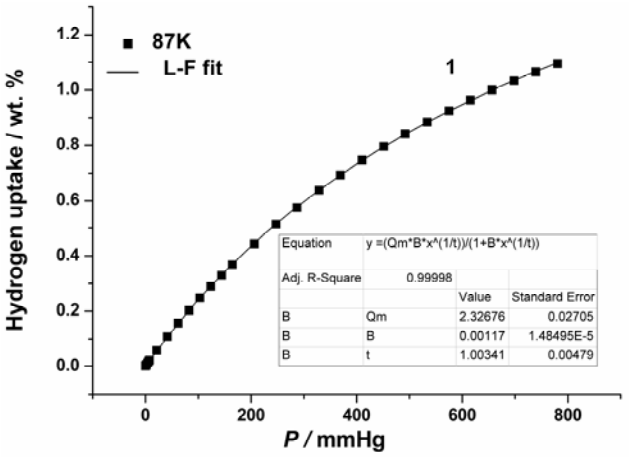
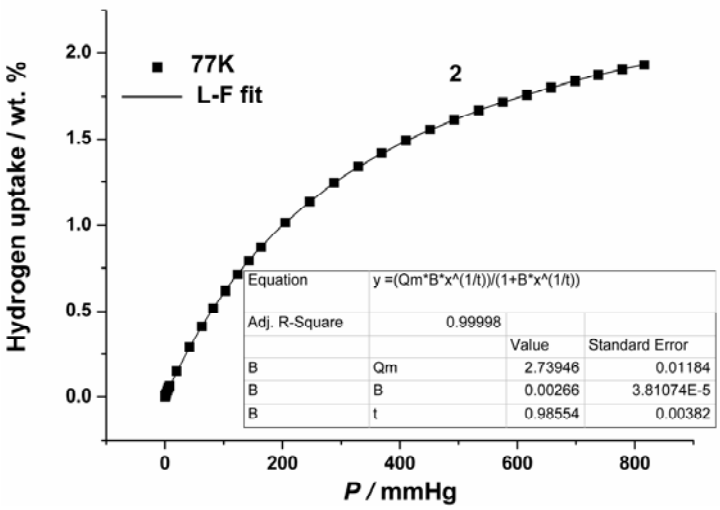


Fig. S4. (a) H_2 adsorption isotherms for sample **2** at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.



(b) H_2 adsorption isotherms for sample **2** at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

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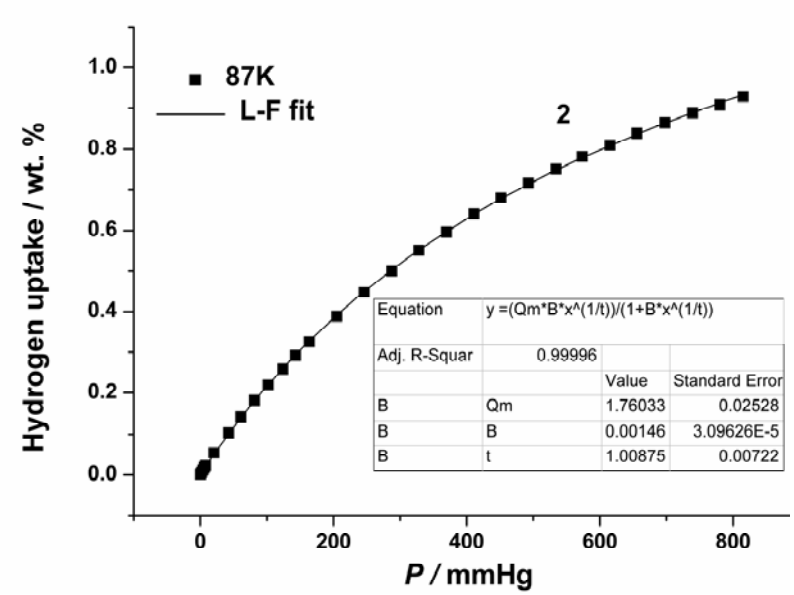
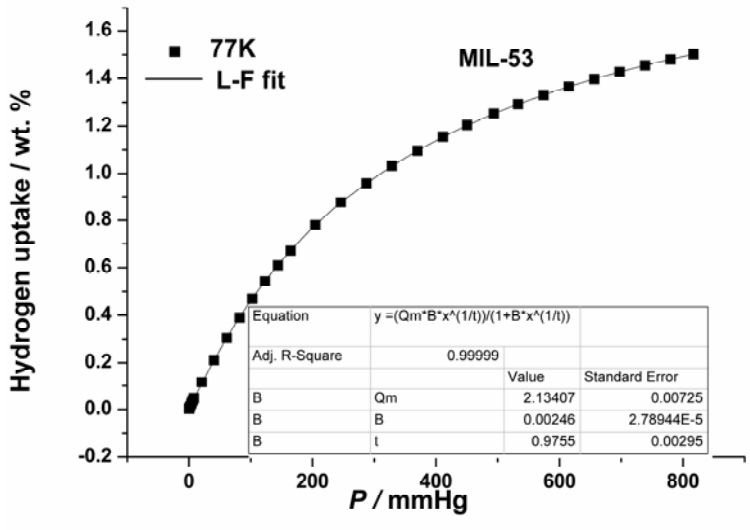
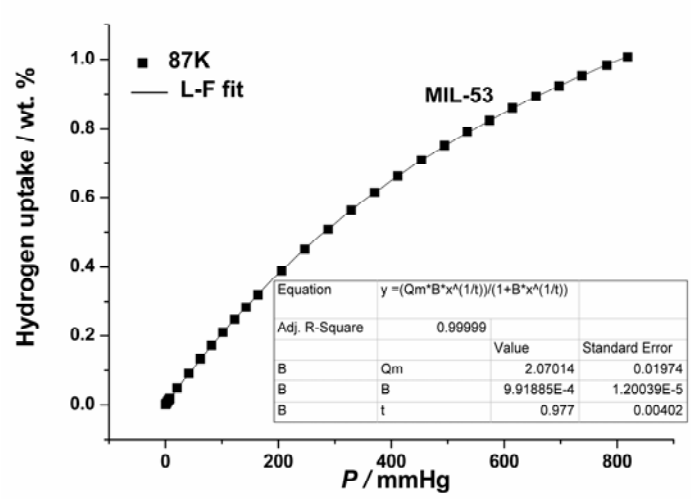


Fig. S5. (a) H_2 adsorption isotherms for sample **MIL-53** at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.



(b) H_2 adsorption isotherms for sample **MIL-53** at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.



1 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Ferey, *Chemistry-a European Journal*, 2004, **10**, 1373.

2 S. M. Cohen, Z. Q. Wang, K. K. Tanabe, *Chemistry-a European Journal* **2010**, *16*, 212.