Modify structure transition and improve gas ($\text{H}_2$, $\text{CO}_2$) adsorption property of metal organic framework MIL-53 by encapsulation of $\text{BNH}_x$.

Xiaoliang Si, Jian Zhang, Fen Li, Chengli Jiao, Shuang Wang, Shuang Liu, Zhibao Li, Huaiying Zhou, Lixian Sun, Fen Xu.
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. In a typical experiment, a mixture of Al(NO₃)₃•9H₂O (20 mmol) and H₂BDC (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 BNHₓ@MIL-53:**
Boron and nitrogen resources are from ammonia borane. 0.2 g NHₓBH₃ (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 NHₓBH₃ 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 °C for 8 h at a heating rate of 10 °C min⁻¹ under Ar gas flow. Then the final product BNHₓ@MIL-53 was obtained. Boron content in nanocomposites was confirmed by elementary analysis.

**Low-pressure gas adsorption measurements**

N₂ and CO₂ 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 H₂ 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 (Qₛₜ) of hydrogen adsorption on the metal organic frameworks were calculated as a function of surface coverage, by the Clausius-Clapeyron equation:

\[ Qₛₜ = -R^* \frac{d(\ln P)}{d(1/T)} \]
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 ($\lambda=1.5418$ 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$_3$ · Et$_2$O at 0 ppm.
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.

![FTIR characterization on all samples before heated at 450°C for 8 hours.](image)

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$^{-1}$.

![FTIR characterization on all samples after heated at 450°C for 8 hours.](image)

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

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

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

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

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

($Q =$ moles adsorbed; $Q_m =$ moles adsorbed at saturation; $P =$ pressure; $B$ and $t =$ constants)
Equation B can be rearranged to

\[ P = \left( \frac{Q}{Q_m} \right)^\gamma \]

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

**Fig. S3.** (a) H\textsubscript{2} adsorption isotherms for sample 1 at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

(b) H\textsubscript{2} adsorption isotherms for sample 1 at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.
Fig. S4. (a) H₂ adsorption isotherms for sample 2 at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

(b) H₂ adsorption isotherms for sample 2 at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.
(a) H₂ adsorption isotherms for sample MIL-53 at 77 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

(b) H₂ adsorption isotherms for sample MIL-53 at 87 k (black squares) Solid lines correspond to Langmuir-Freundlich fits to the experimental data.