

H₂ storage and CO₂ capture on a nanoscale metal organic framework with high thermal stability

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Supporting Information:

Methods:

Synthesis and activation of NMOF

Nanocrystallized Al-MOF (NMOF) was synthesized as follows. Exact amounts of Al(NO₃)₃·9H₂O (2.50 g) and 1,4-H₂NDC (1.44 g) were dissolved in DMF solution (65 ml). The reactants were stirred before the clear solution was poured in a Teflon-coated stainless steel autoclave. The bomb was heated to 220 °C and maintained at that temperature for 3 days. The sample was recovered by filtration, washed thoroughly with DMF and further dried in vacuum at 50 °C overnight.

The sample was firstly activated at 200 °C overnight prior to characterization and testing, unless otherwise noted.

Synthesis and activation of microcrystals (MMOF)

Synthesis of microcrystalline Al(OH)(NDC) (MMOF) was performed under hydrothermal conditions following the recipe described in ref 1. The as-made sample was dried in vacuum at 50 °C overnight. The resulting dry solid was referred to as MMOF. The PXRD pattern of as-made MMOF sample is identical to the pattern of Al(OH)(NDC) in ref 1.

The sample was firstly activated in vacuum at 200 °C overnight (named MMOF-200). When the activation temperature of MMOF increased from 200 °C to 300 °C, we observed that a little of white substance was released and deposited on the sample cell. So we suggested that some residual reactants or byproducts might exist in the MMOF crystals. And the hydrogen uptake capacity of MMOF-300 (heated in vacuum at 300°C) was enhanced (see **Fig. S2**), indicating that these impurities really affected the H₂ adsorption behavior.

As we know, pure 1,4-H₂NDC can be solved by DMF solvent. We put MMOF sample as synthesized into a Teflon-coated stainless steel autoclave with DMF solvent and heated the bomb at 220 °C for 1 day. We hoped that these impurities could be fully solved by DMF. In **Fig. S2**, we found that the H₂ uptake capacity of MMOF-300s (activated using DMF at 220 °C and heated in vacuum at 300 °C) was further improved. But the H₂ adsorbed amount of MMOF-300s was still lower than that of NMOF (heated at 200 °C).

Up to now, we failed to obtain fully pure MMOF samples. The amount of the impurities is very few, which has very remarkable effect on the hydrogen adsorption behaviors of MMOF at 77 K.

So we suggested that our solvothermal synthesis procedure with DMF solvent is more efficient than the hydrothermal recipe for 1,4-H₂NDC as a reactant.

Low-pressure gas adsorption measurements

Nitrogen adsorption and desorption isotherms were measured at 77 K using an Autosorb-1 system after the samples were firstly degassed at 200 °C overnight. Specific surface areas (SSA) were determined by the BET method.

Low pressure hydrogen adsorption analyses were performed using the same Autosorb-1 system over a pressure range of 0-820 mm Hg at 77 K with the universal Dewar filled with only liquid nitrogen. To obtain controllable temperatures such as 87 K and 97 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.

Low pressure carbon dioxide, methane, nitrogen and oxygen adsorption analyses were performed using the same Autosorb-1 system over a pressure range of 0-780 mm Hg at 273 K with an ice water bath and the room temperature.

Determination of isosteric heats of adsorption

The isosteric heats (Q_{st}) of hydrogen, carbon dioxide, and methane adsorption on the NMOF were calculated as a function of surface coverage, by Clausius-Clapeyron equation:

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

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

High-pressure hydrogen storage and adsorption kinetics measurements

The high-pressure hydrogen storage performance and the hydrogen adsorption kinetics were investigated using a gas reaction controller (GRC) from Advanced Materials Corporation at 77 K under an initial hydrogen pressure of 30 atm. Prior to each measurement, the materials were activated

in vacuum at 200 °C overnight using turbomolecular pump units to remove any physisorbed water or volatile impurities.

Other physical measurements

All scanning electron microscopy (SEM) images were obtained using a JSM-6360 LV SEM instrument operating at 20 kV. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G² Spirit at an acceleration voltage of 120 kV. Powder X-ray diffraction patterns (PXRD) were collected in a X'Pert PRO X-ray diffractometer operating at 40 kV and 40 mA with a Cu K α radiation ($\lambda=1.5418$ nm). Temperature-dependent X-ray diffraction experiments were performed in air on the sample set within the furnace of a Rigaku X-ray diffractometer. Diffraction patterns were recorded within a 2θ range of 5°-40° continuously, because the most intense diffraction peaks of NMOF are located in this 2θ range. The temperature ramp between two patterns was 5 °C min⁻¹. TG curves were recorded on a thermogravimetric analyzer (TherMax 500) at a heating rate of 5 °C min⁻¹, in air flow. FT-IR spectra were recorded on a Nicolet 380 infrared spectrometer using KBr pellets, in the 400-4000 cm⁻¹ frequency range.

Calculation of selectivity for CO₂, CH₄, N₂, and O₂

The initial slope was first calculated for CO₂, CH₄, N₂, and O₂ uptakes. The ratio of the slopes was used to calculate the selectivity at 273K.

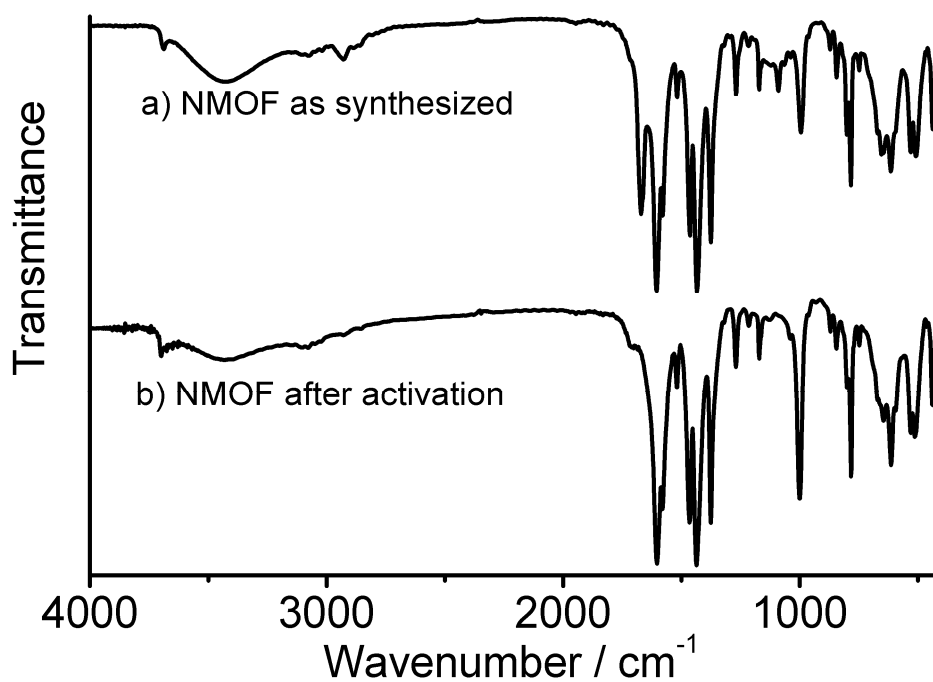


Fig. S1 Infrared spectra of NMOF samples.

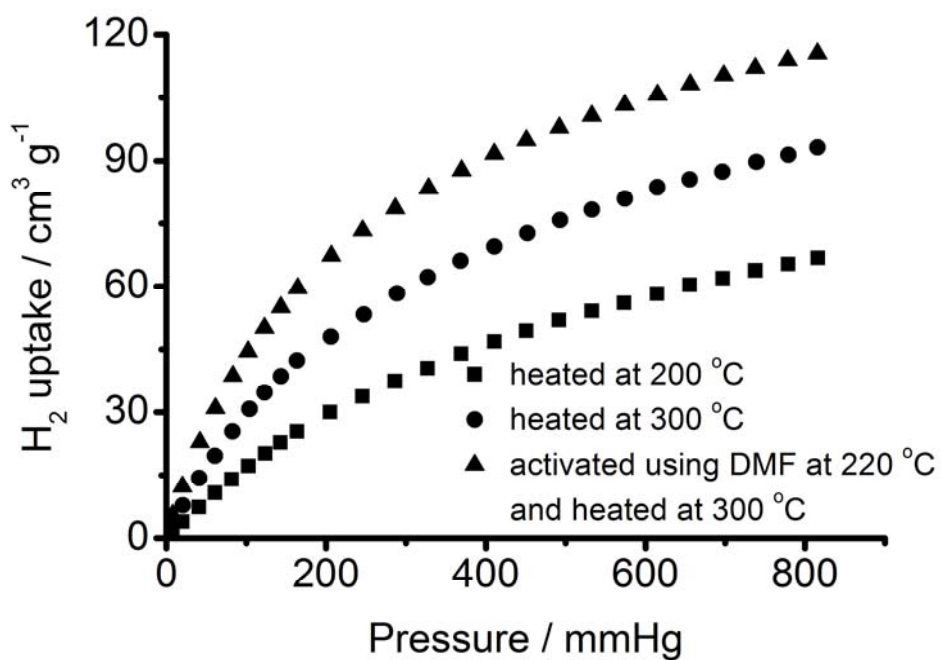


Fig. S2 H₂ adsorption isotherms (at 77 K) of three MMOF samples treated using different methods.

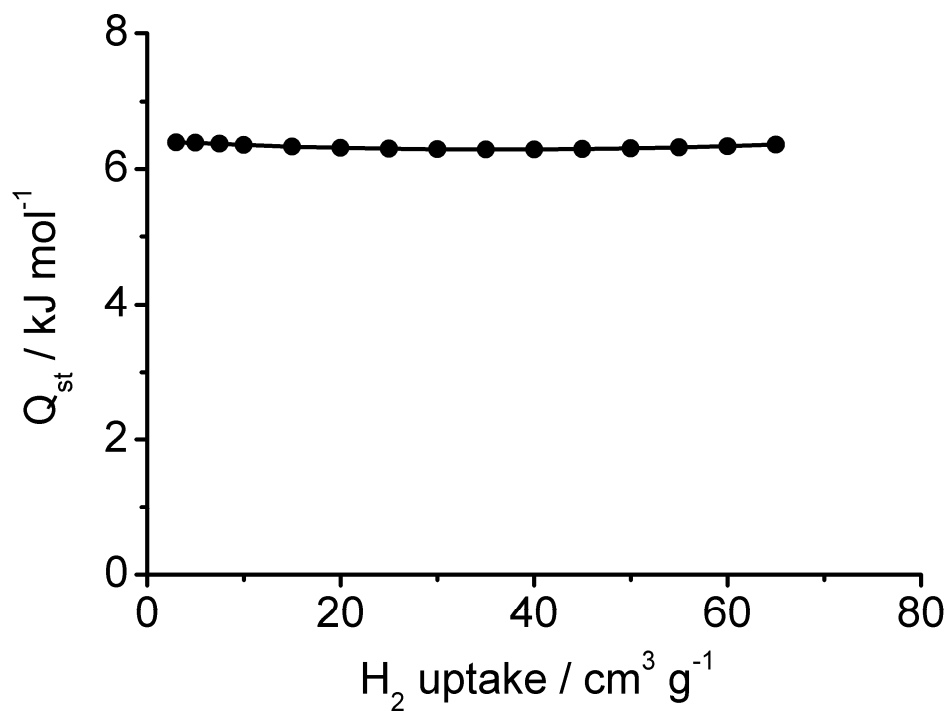


Fig. S3 Heat of adsorption isotherm at different H_2 loadings.

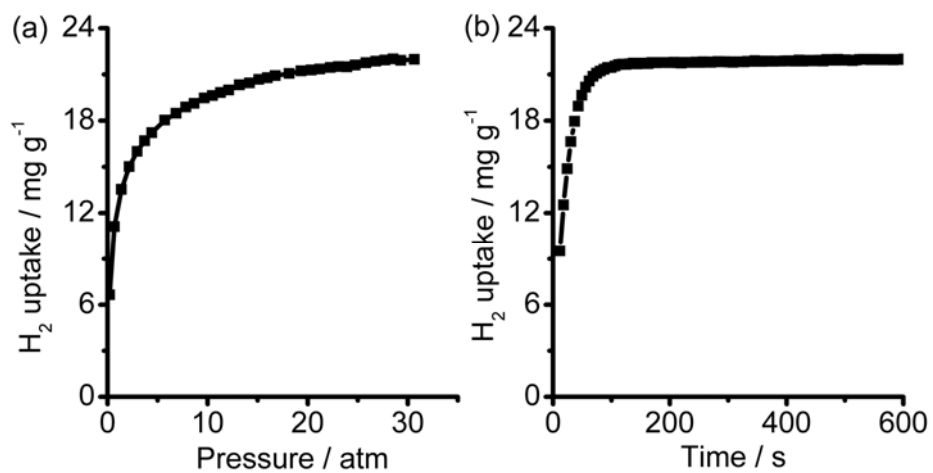


Fig. S4 (a) High-pressure hydrogen adsorption isotherm and (b) kinetics profile for NMOF at 77 K.

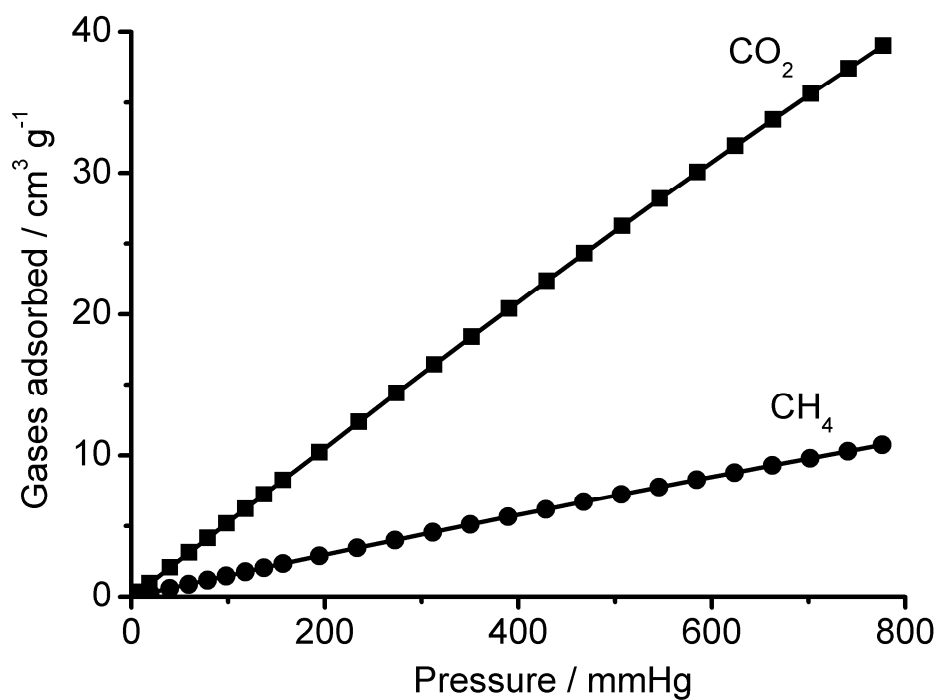


Fig. S5 CO₂ and CH₄ sorption isotherms of NMOF at 298 K.

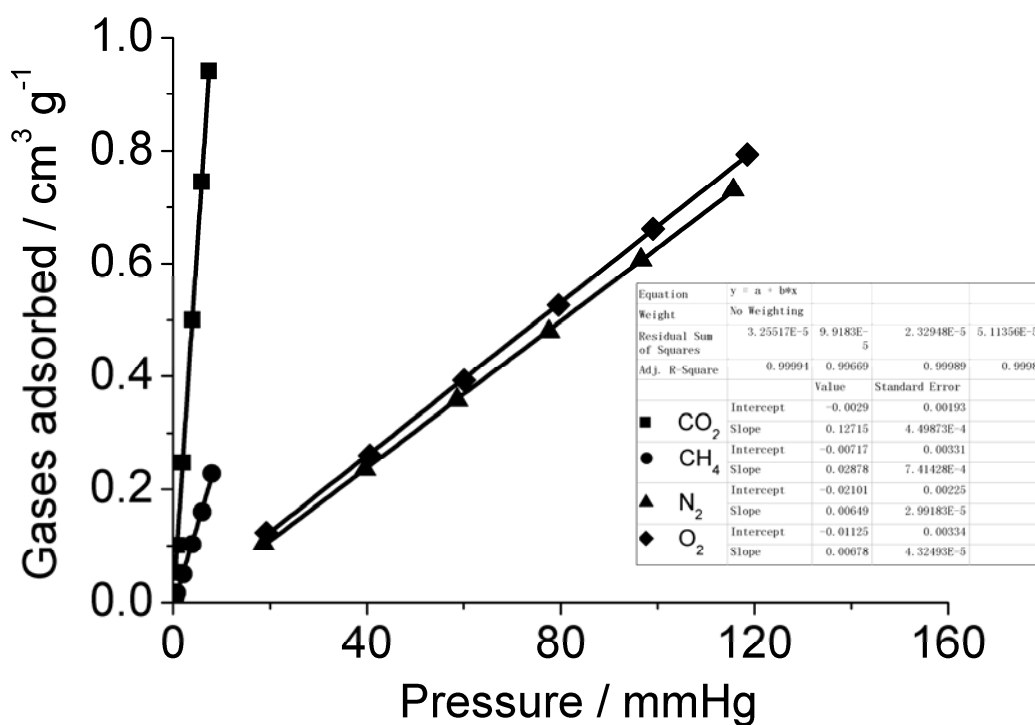


Fig. S6 Initial slope calculation for CO₂, CH₄, N₂, and O₂ isotherms collected at 273 K.

Reference: 1. A. Comotti, S. Bracco, P. Sozzani, S. Horike, R. Matsuda, J. Chen, M. Takata, Y. Kubota and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 13664.