Support information

Robust ultramicroporous MIL-160 Enables Efficient Hydrogen Isotope Separation

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Section 1 Calculations of isosteric heat of adsorption

This study employs the Virial equation (Equation 1-1) to fit the single-component gas adsorption isotherms obtained at 77 K and 87 K, followed by the application of Equation (1-2) to determine the isosteric heats of adsorption (Q_{st}) of the material for both hydrogen and deuterium.

$$ln(P) = ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j \tag{1-1}$$

$$Q_{st} = - R\sum_{i=0}^{m} a_i N^j \tag{1-2}$$

Where P is the pressure in mmHg, N is the amount adsorbed in mg/g, T is the temperature in K, a_i and b_j represents virial coefficients, and m and n specify the number of coefficients needed for a precise description of the isotherms, Q_{st} is the coverage-dependent isosteric enthalpy of adsorption in kJ/mol and R is universal gas constant with the value of 8.314 J $mol^{-1}K^{-1}$.

Section 2 Calculations of IAST Selectivity

The single-component gas adsorption isotherms were fitted using the Dual-Site Langmuir-Freundlich (DSLF) equation:

$$N = A_1 \frac{B_1 \times P^{C_1}}{1 + B_1 \times P^{C_1}} + A_2 \frac{B_2 \times P^{C_2}}{1 + B_2 \times P^{C_2}}$$

Where N is molar loading of species i(mmol·g^{-1}), $A_1$and A_2 are saturation uptakes (mmol·g^{-1}) of species i for sites 1 and 2, B_1 and B_2 are affinity coefficients (kPa^{-1}) for sites 1 and 2, C_1 and C_2 represent the deviations from the ideal homogeneous surface for site 1 and 2, P is bulk gas phase pressure of species i (kPa).

Based on the Ideal Adsorbed Solution Theory (IAST), the partial pressure equations of each component in the gas mixture were solved numerically to determine the molar fraction and adsorption amount of each component in the adsorbed phase. The selectivity coefficient was then calculated according to the definition given in Equation (1-3).

$$S_{ads} = \frac{x_A / x_B}{y_A / y_B} \tag{1-3}$$

where S is the IAST selectivity, x_1 and x_2 represent the equilibrium adsorption capacity of component 1 and component 2, y_1 and y_2 represent the molar ratio of component 1 and component 2 in the original mixed gas.

Section 3 General Methods and Materials

All chemical solvents and reagents were purchased from commercial suppliers and used as received without further purification. Powder X-ray diffraction (PXRD) pattens were recorded on a Mini600 diffractometer over a 2θ range of 4-40°, with a step size of 0.02° and a scanning rate of 4° min^{-1}. The morphological characteristics of the samples were examined using field emission scanning electron microscopy (FE-SEM, Sigma 300) operated at 3 kV with a working distance of 5 mm. Thermogravimetric analysis (TGA) was performed on a Rigaku STA8122 instrument under a continuous nitrogen flow at a heating rate of 10 °C/min.

Section 4 Experimental

Synthesis of MIL-160. MIL-160 was synthesized following a reported procedure [1]. In a 200 mL glass flask, aluminum chloride hexahydrate ($AlCl_3·6H_2O$, 1.04g, 4.31 mmol) and 2, 5-furandicarboxylic acid (H_2fdc, 0.75 g, 4.31 mmol) were dissolved in 72 mL of deionized water. Subsequently, an aqueous solution of sodium hydroxide (NaOH, 0.26 g, 6.5 mmol in 3 mL water) was added dropwise under continuous stirring. The mixture was refluxed at 100 °C for 12 h. After cooling to room temperature, the resulting precipitate was collected by filtration and washed thoroughly with deionized water to remove residual impurity. The obtained solid was then activated under vacuum at 150 °C for 12 h to afford **MIL-160** as a fine powder, with a typical yield of approximately 0.55 g (65%).

Shaping of MIL-160. Polyvinyl alcohol (PVA, 0.9 g) and sodium alginate (0.15 g) were dissolved in a mixed solvent of anhydrous ethanol (28.5 mL) and deionized water (35 mL) under continuous stirring. Subsequently, 3 g of **MIL-160** powder was gradually added to the above solution under vigorous stirring to form a homogeneous slurry. The resulting slurry was then introduced dropwise, using a syringe, into 500 mL of a 0.5% $CaCl_2$ solution. The droplets were allowed to solidify at room temperature for 180 min. After removing the supernatant, the solidified beads were collected by filtration and dried in a vacuum oven at 60 °C for 12 h to afford the molded **MIL-160** pellets (**MIL-160-P**), with a yield of 4.1 g. The dried pellets were gently crushed and sieved, and the particle fraction between 30 and 45 mesh was collected for subsequent tests.

Section 5 Adsorption measurements

The adsorption isotherms of N_2, H_2 and D_2 were measured using an automatic volumetric adsorption apparatus (Micromeritics ASAP 2020 PLUS) at 77K (liquid nitrogen bath) and 87 K (liquid argon bath). Prior to the measurements, the samples were degassed under dynamic vacuum ($\leq$ 10 μmHg) at 150 ^{o}C for 10 h, following six solvent exchanges with methanol over three days. The specific surface area of **MIL-160** was calculated using the Brunauer–Emmett–Teller (BET) method from the N_2 adsorption isotherms.

Section 6 Breakthrough Measurements

Dynamic gas breakthrough measurements were performed using a custom-built breakthrough apparatus with gas mixtures of $D_2/H_2/Ne$ at 100 K and 101 kPa. For a typical experiment with a $D_2/H_2/Ne$ (10/10/80, vol.%) mixture, 4.73 g of dry **MIL-160-P** powder was packed into an 80 cm long column with an internal diameter of 5 mm. The packed column was degassed under dynamic vacuum at 423 K for 10 h, followed by purging with Ne (10 mL min^{-1}) for 2 h at 423 K to ensure complete displacement of residual gases. Prior to each experiment, the adsorption column and pre-cooling lines were immersed in liquid nitrogen for at least 20 min to guarantee thermal equilibration. The gas mixture was then introduced at a flow rate of 10 mL min^{-1}, and the effluent composition was continuously monitored using mass spectrometry. After reaching adsorption equilibrium, desorption was carried out under a Ne purge (5 mL min^{-1}) with a temperature ramp of 2 ^{o}C min^{-1} until 158 K. For regeneration, all samples were treated under a Ne flow (10 mL min^{-1}) at 423 K for 2 h before subsequent experiments.

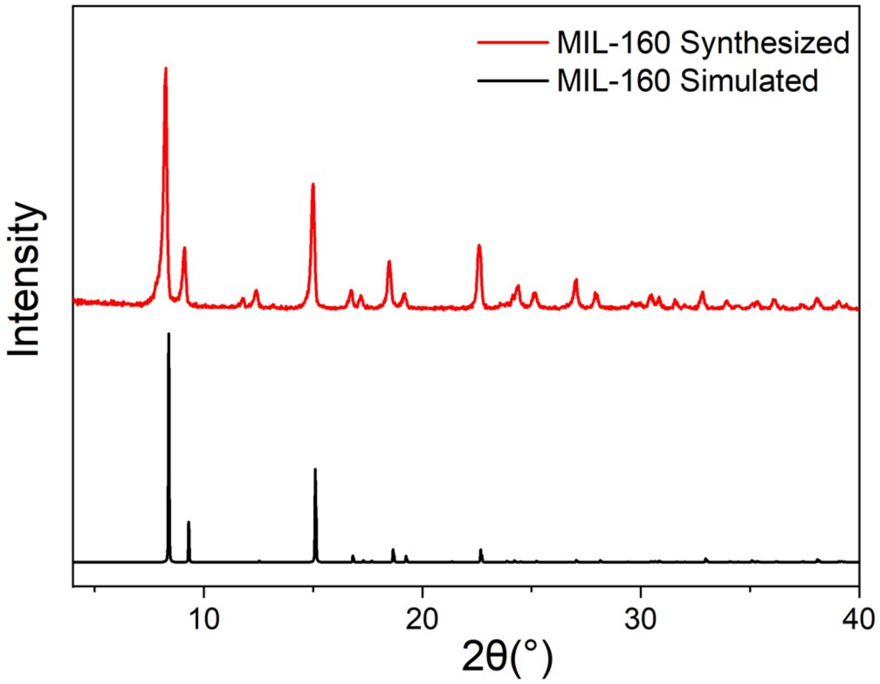

Fig. S1. Comparison of the experimental and simulated PXRD patterns of **MIL-160**.

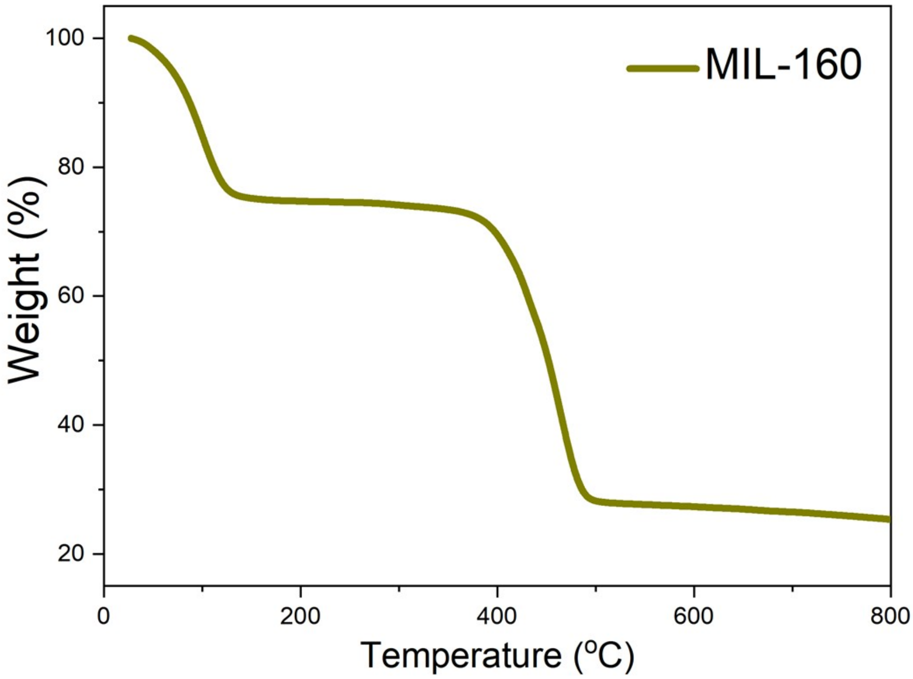

Fig. S2. Thermogravimetric curves of activated **MIL-160** measured under N_2 atmosphere.

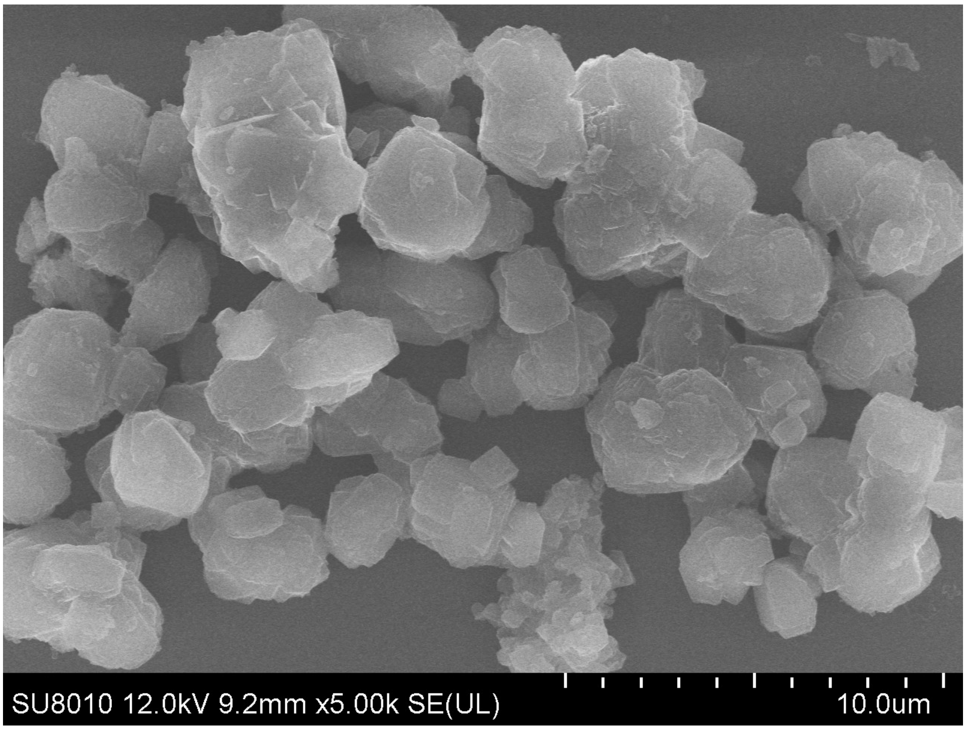

Fig. S3. Scanning electron microscope image of **MIL-160**.

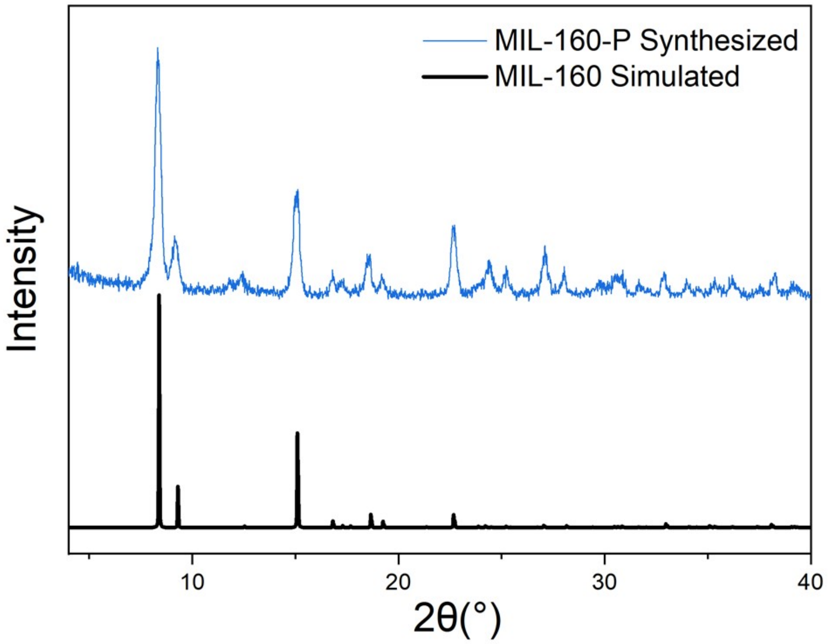

Fig. S4. Comparison of the experimental and simulated PXRD patterns of **MIL-160-P**.

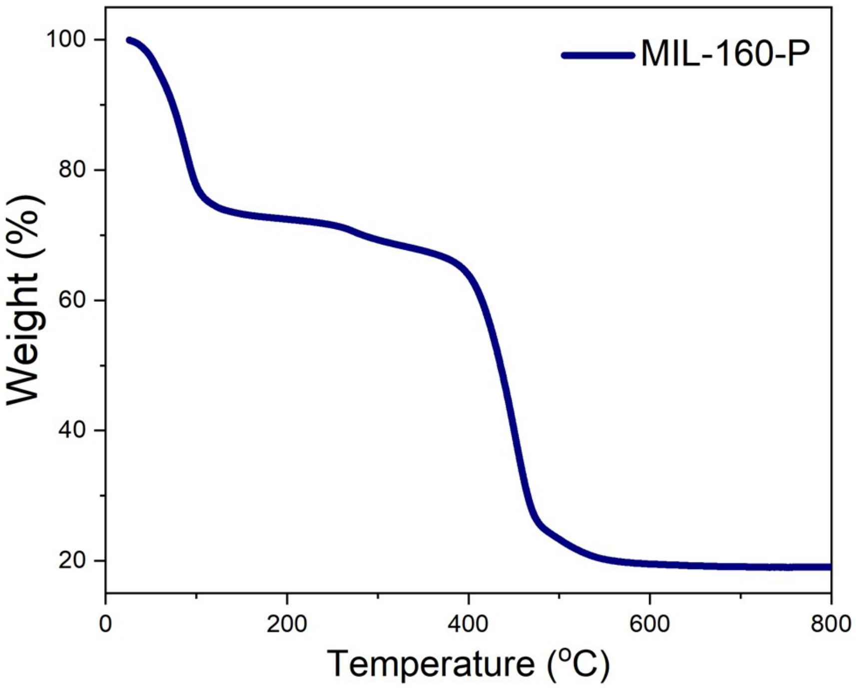

Fig. S5. Thermogravimetric curves of activated **MIL-160-P** measured under N_2 atmosphere.

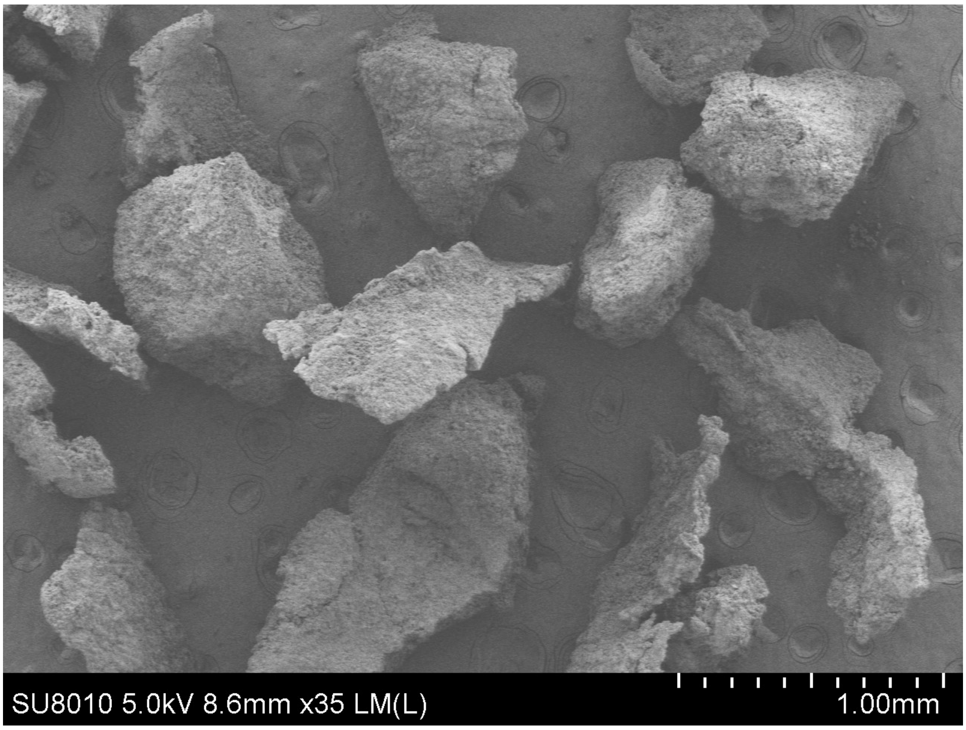

Fig. S6. Scanning electron microscope image of **MIL-160-P**.

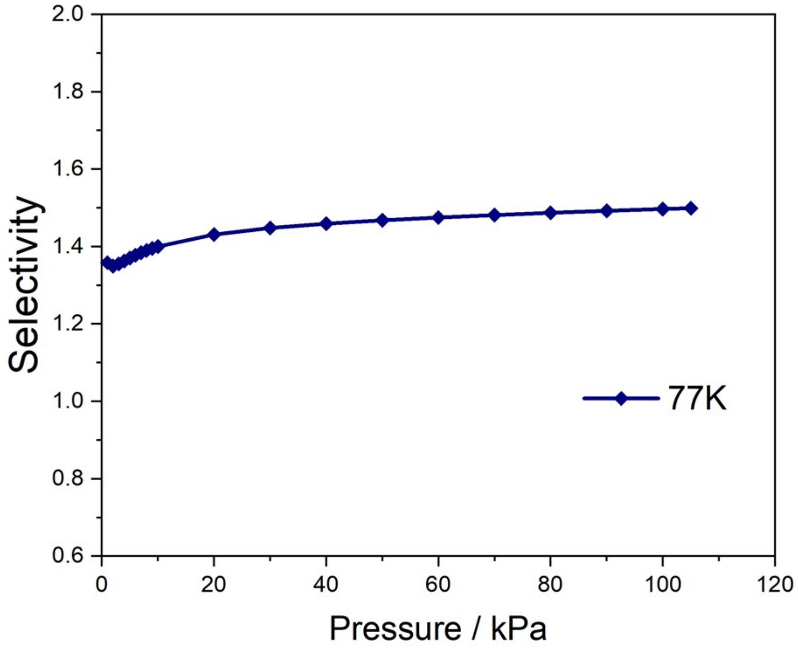

Fig. S7. IAST selectivity of **MIL-160-P** for equimolar D_2/H_2 mixture at 77 K.

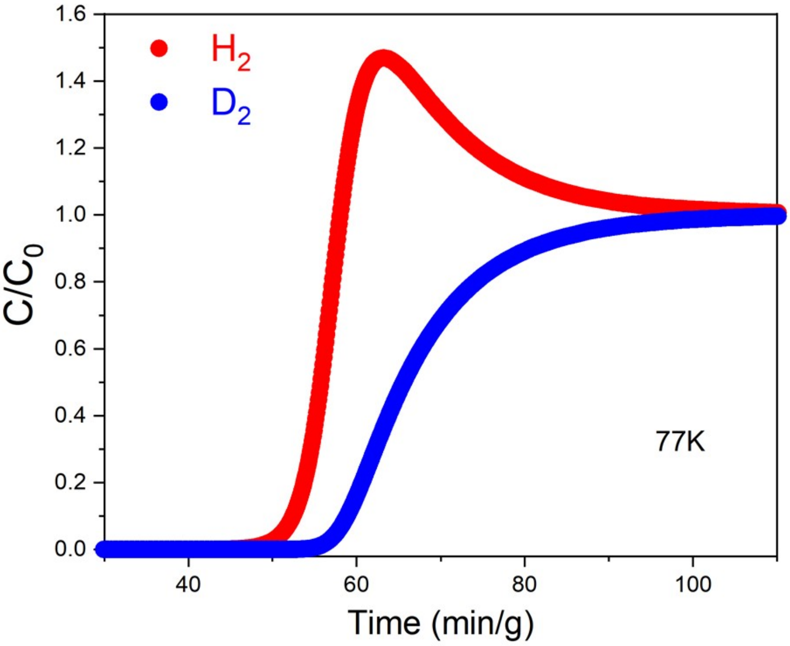

Fig. S8. The dynamic breakthrough curve of **MIL-160-P** at 77 K and 1 bar for the mixed gases of $D_2/H_2/Ne$ (10%/10%/80%, vol%) with a total flow rate of 10 mL min^{-1}.

Reference

1. Y. Ye, S. Xian, H. Cui, K. Tan, L. Gong, B. Liang, T. Pham, H. Pandey, R. Krishna, P. C. Lan, K. A. Forrest, B. Space, T. Thonhauser, J. Li and S. Ma, Metal–organic framework based hydrogen-bonding nanotrap for efficient acetylene storage and separation, *J. Am. Chem. Soc.*, 2021, **144**, 1681–1689.