Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Support Information

The Effect of Pore Sizes on D_2/H_2 Separation Conducted by MOF-74 Analogue

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1. IAST selectivity calculations

The dual-site Langmuir equation (DSL) was used to fit the hydrogen and deuterium adsorption isotherms of Ni_2(dobdc), Ni_2(dobpdc), Ni_2(olz) and Ni_2(dotpdc) frameworks at 77 K and 87 K, respectively. Equation is given by:

$$N = A_1\frac{b_1 \times P}{1 + b_1 \times P} + A_2\frac{b_2 \times P}{1 + b_2 \times P} \quad (1)$$

where N represents the adsorbed amount per mass of adsorbent in mmol·g^{-1}, A_1 and A_2 are the adsorption saturation capacity for site 1 and site 2 in mmol/g, respectively. b_1 and b_2 are dimensionless Langmuir parameters for site 1 and site 2, and P represents the pressure of the bulk at equilibrium with the adsorbed phase in kPa. The fitting of H_2 and D_2 sorption isotherms are given in **Fig. S6–S9.**

Using the ideal adsorption solution theory (IAST) [1], the adsorption capacity of the binary mixture can be estimated from the pure gas adsorption isotherm, and then the selectivity can be calculated. S is defined according to the following formula:

$$S = \frac{x_1/x_2}{y_1/y_2} \quad (2)$$

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.

2. Isosteric heat of adsorption calculations

The Clausius-Clapeyron equation was used to estimate the isosteric heat of adsorption:

$$Q_{st} = RT^2(\frac{\partial lnp}{\partial T})_q$$

Where Q_{st} (kJ·mol^{-1}) is the isosteric heat of adsorption at a specific surface loading of adsorbate, R (kJ·mol^{-1}·K^{-1}) is the universal gas constant, T (K) is the temperature, p (kPa) is the pressure, and q (mmol·g^{-1}) is the adsorbate amount adsorbed on the surface. Before using this equation, it is necessary to obtain the exact pressure

corresponding to a certain adsorption amount, therefore, we first use the dual-site Langmuir-Freundlich (DSLF) equation to fit the single-component adsorption equilibrium isotherm, and then calculate the adsorption enthalpy based on the data points on the fitted curve. The calculated value of adsorption enthalpy is slightly different from that reported in the previous literature, which may be caused by the difference in test conditions and fitting methods. The calculation results are given in **Table S1**.

Table S1 Isosteric heat of adsorption for D_2 (red) and H_2 (blue) as a function of coverage for Ni_2(dobdc), Ni_2(dobpdc), Ni_2(olz) and Ni_2(dotpdc).

Adsorption enthalpy (KJ/mol)	Ni_2(dobdc)	Ni_2(dobpdc)	Ni_2(olz)	Ni_2(dotpdc)
H_2	11.8	11	11.8	11.1
D_2	13.8	12.9	12.9	12.6

3. Additional diagrams

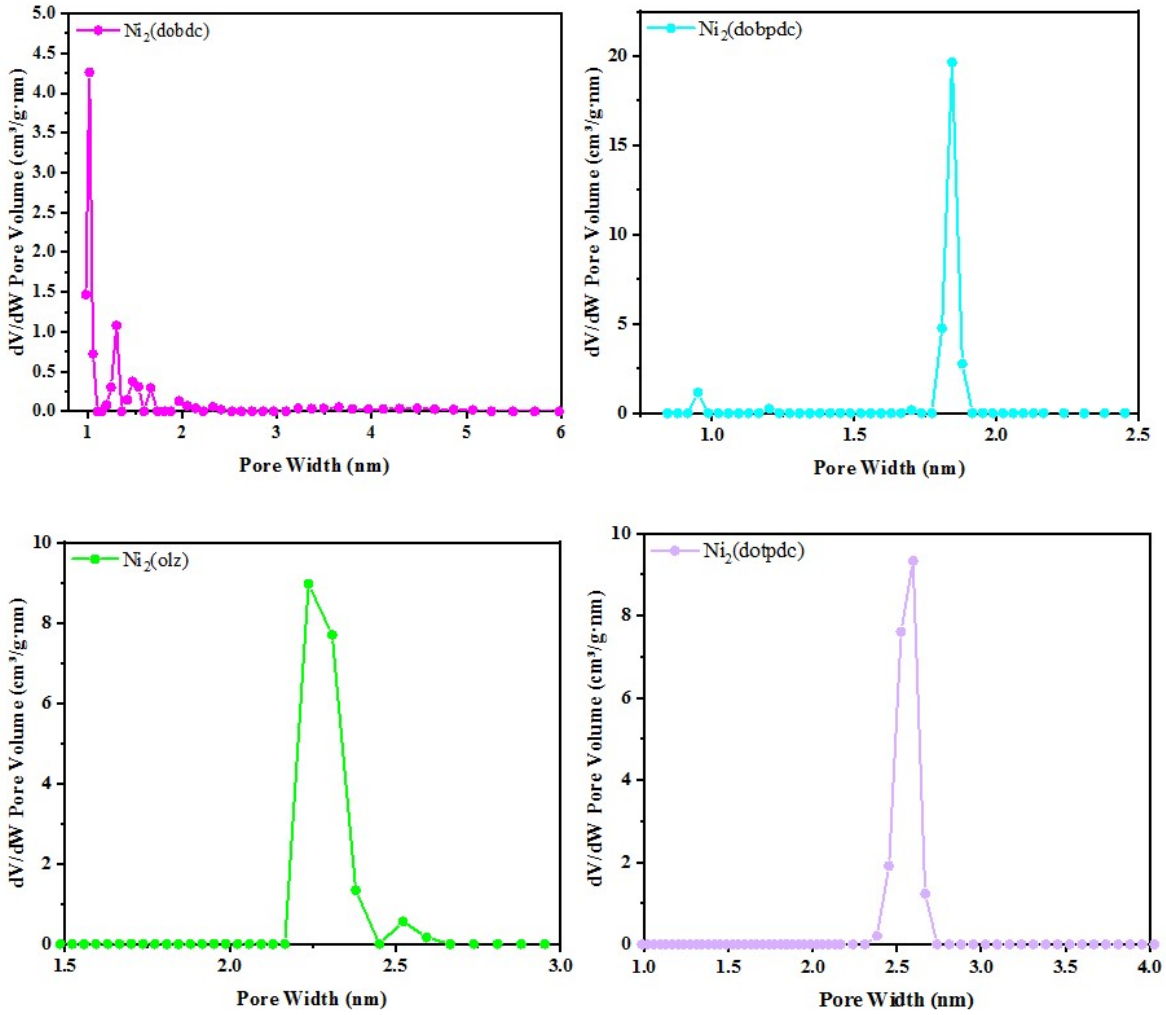

Fig. S1 The pore size distributions of Ni_2(dobdc), Ni_2(dobpdc), Ni_2(olz) and Ni_2(dotpdc) frameworks were analysed using the NLDFT method.

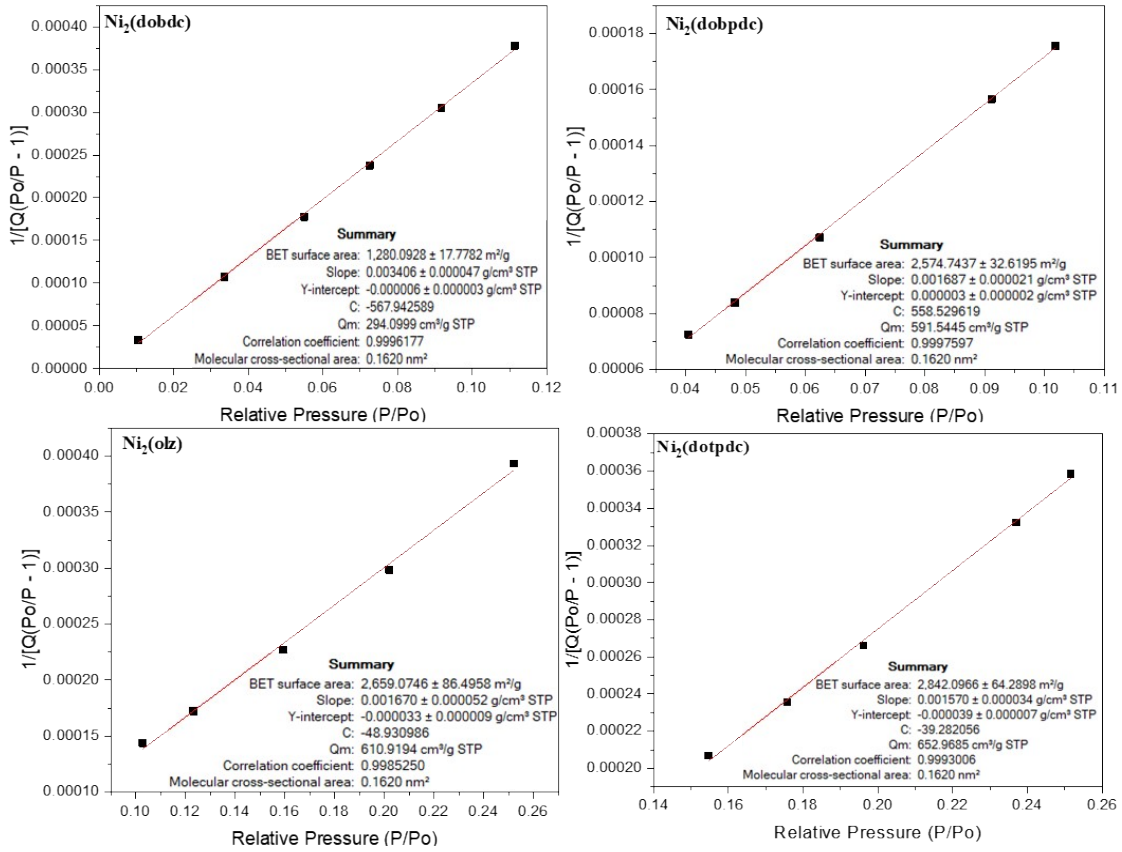

Fig. S2 BET linear fits of Ni_2(dobdc), Ni_2(dobpdc), Ni_2(olz) and Ni_2(dotpdc).

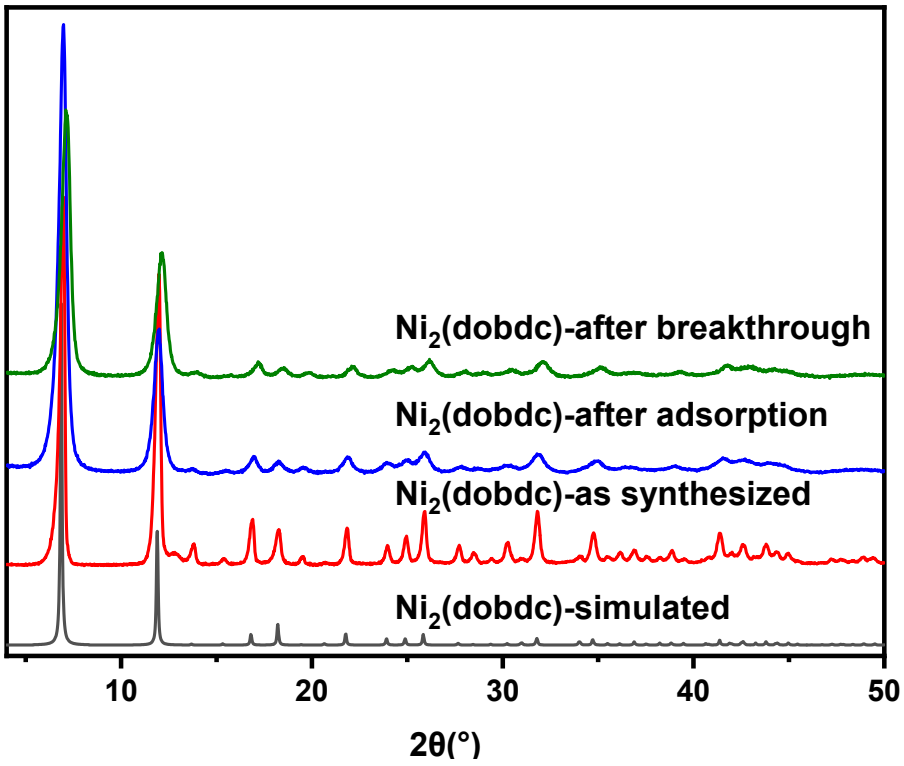

Fig. S3 PXRD patterns of Ni_2(dobdc).

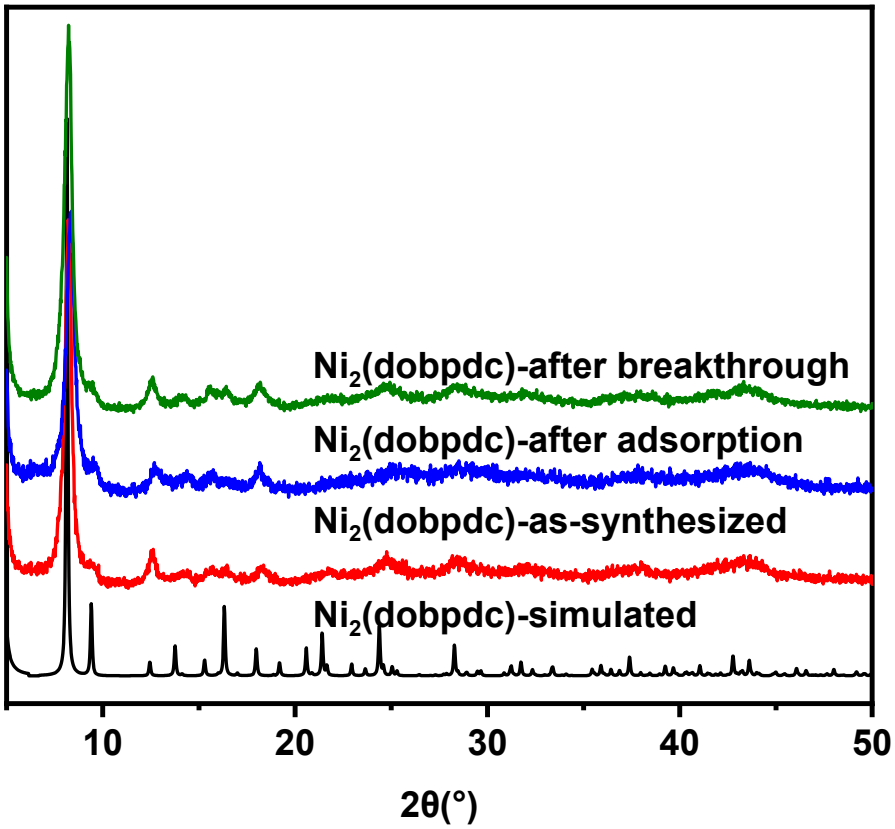

Fig. S4 PXRD patterns of Ni_2(dobpdc)

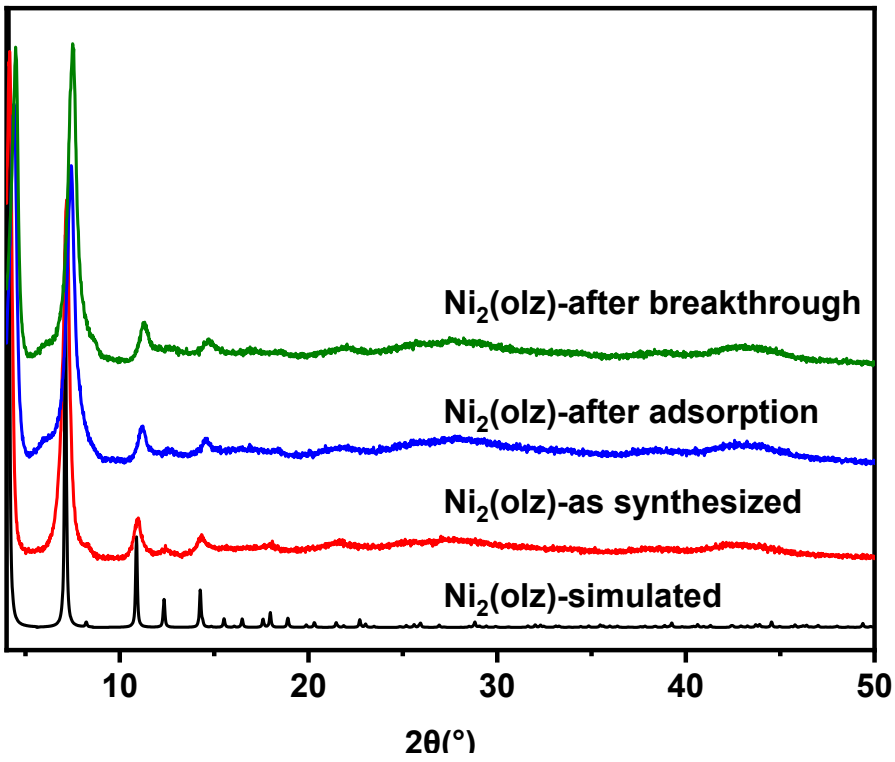

Fig. S5 PXRD patterns of Ni_2(olz).

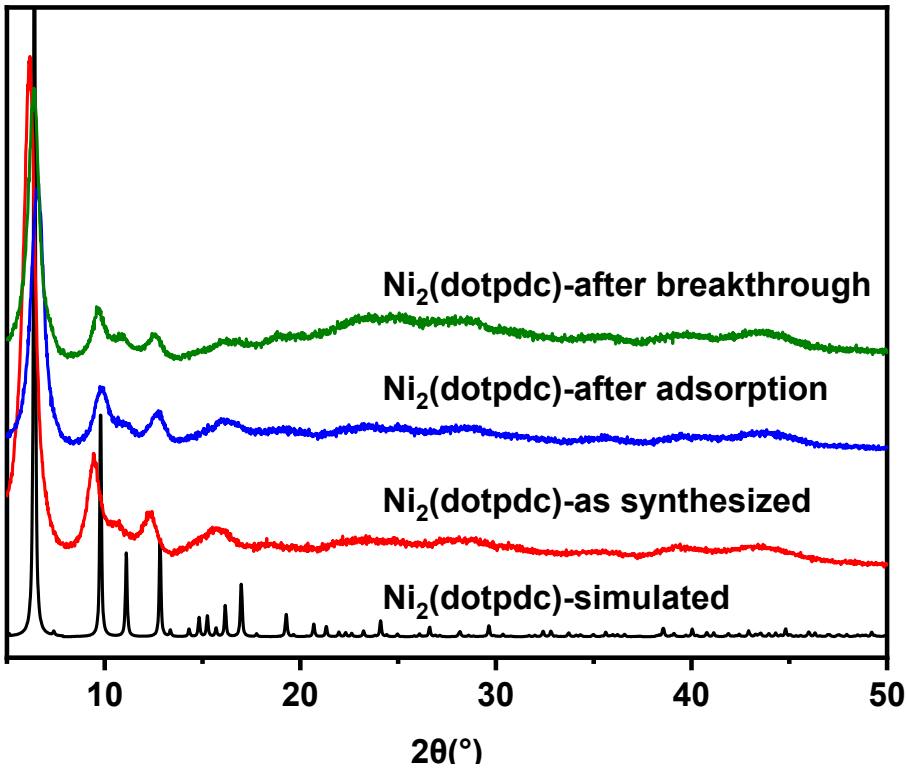

Fig. S6 PXRD patterns of Ni_2(dotpdc).

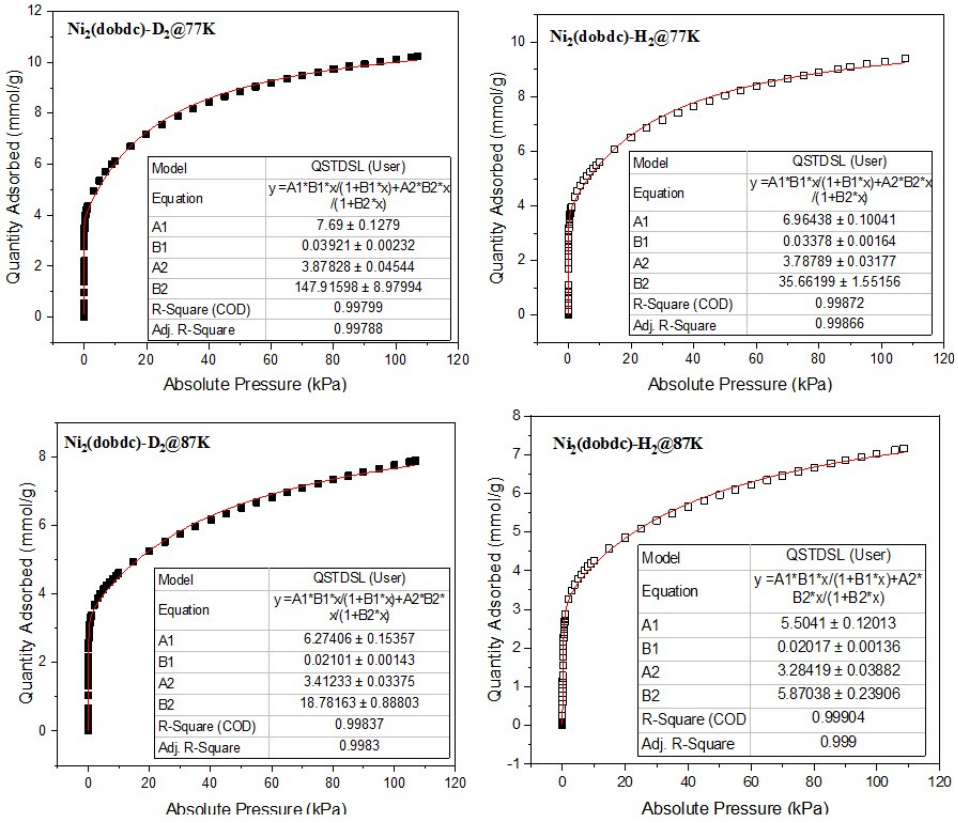

Fig. S7 The dual-site Langmuir fitting of pure-component isotherm for Ni_2(dobpdc).

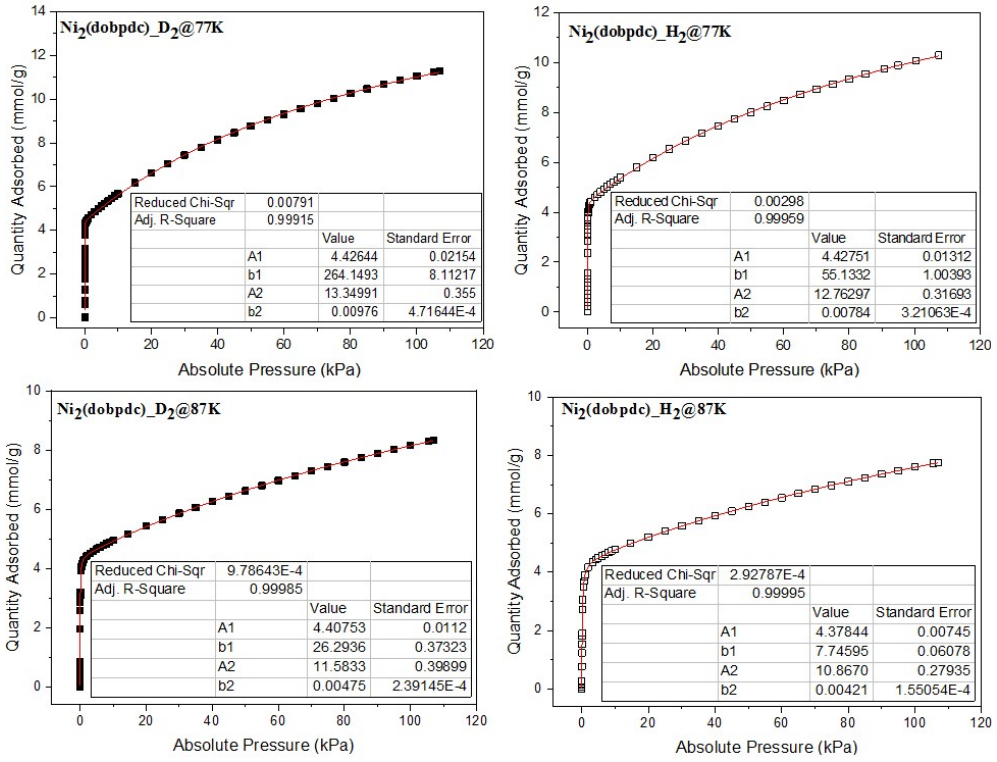

Fig. 8 The dual-site Langmuir fitting of pure-component isotherm for Ni_2(dobpdc).

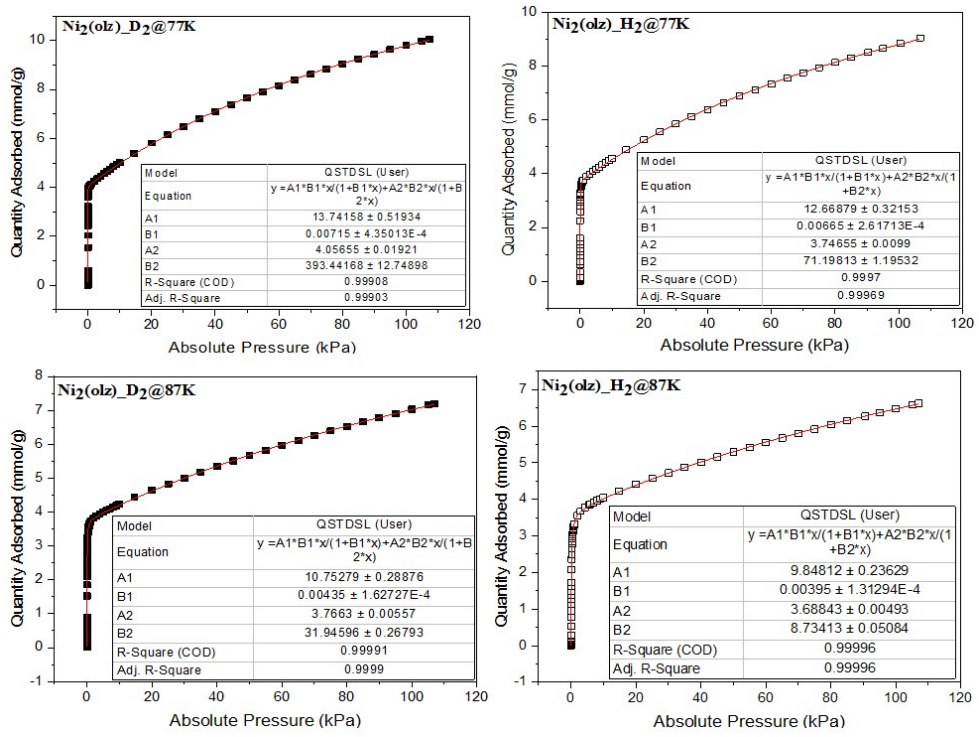

Fig. S9 The dual-site Langmuir fitting of pure-component isotherm for Ni_2(olz).

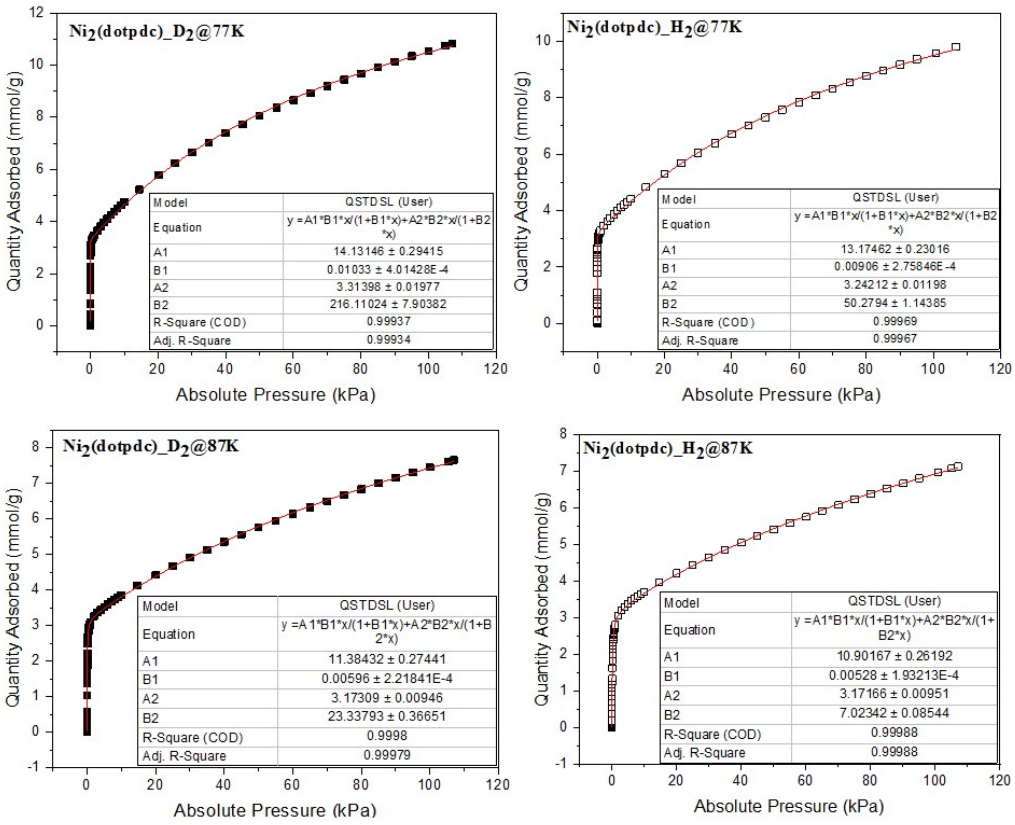

Fig. S10 The dual-site Langmuir fitting of pure-component isotherm for Ni_2(dotpdc).

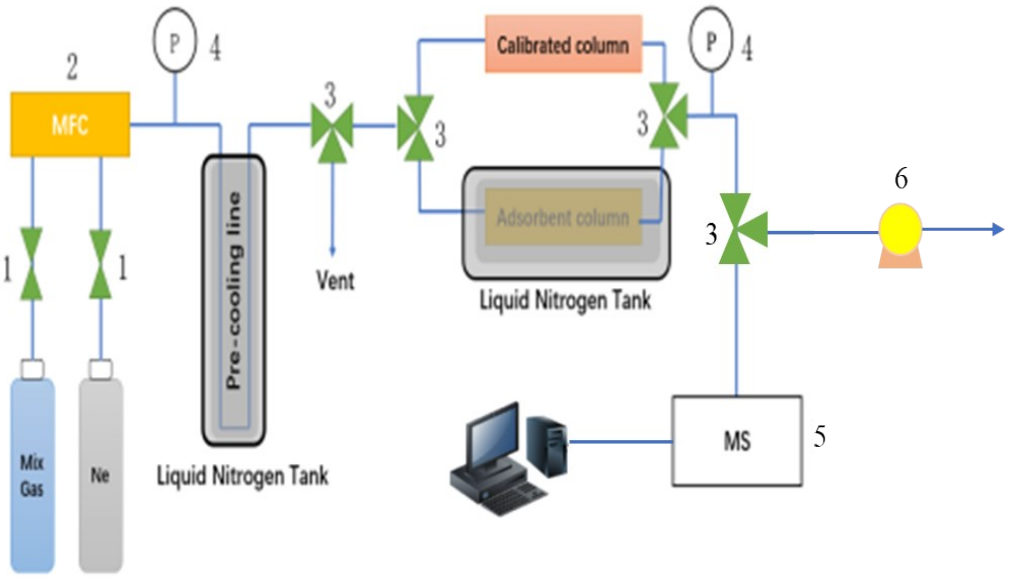

Fig. S11 Schematic illustration of the breakthrough setup used in this study.

1. cylinder two-way valve; 2. gas mass flow controller; 3. three-way valve; 4. pressure gauge; 5. mass spectrometer; 6 vacuum pump.