Supporting Information:

I. The adsorption measurement apparatus

The adsorption measurement apparatus mainly consists of gas supplier (12), adsorption cell (6), reference cell (7), liquid nitrogen tank (5), cool trap (3), pressure transducer (8, Pfeifer Vacuum, Germany), molecular pump (10, Pfeifer Vacuum, Germany), rotary pump (11, Vacuum Pump Co., Wuxi) and on-line data analysis system (9, designed in the lab). The variation of pressure with time, $p(t)$, was detected by a pressure transmitter and recorded in a computer via Labcards. The adsorption cell is initially in vacuum (0.01Pa) for both equilibrium and dynamic adsorption measurements. However, the pressure in the adsorption cell was increased stepwise until 0.14 MPa for collecting isotherms, while only the initial pressure of the reference cell was controlled in dynamic experiments and five levels of initial pressure were tested in the dynamic experiments. The pressure sensor is of precision 0.2%. The temperature of the reference cell was kept constant within $\pm$ 0.2K, and the temperature of the adsorption cell was kept constant at 77 K with liquid nitrogen of constant level. The absolute relative error calculated for the adsorption amount was within 2.0□.
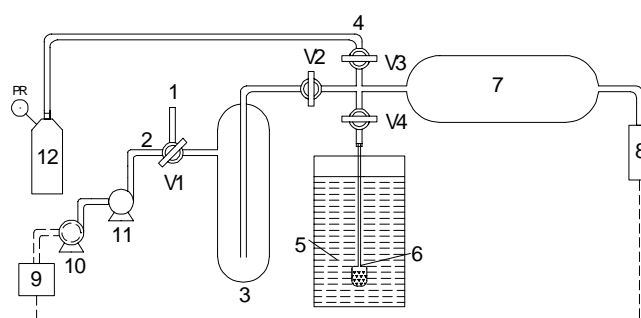

Fig. 1. Schematic diagram of the adsorption measurement apparatus.

II. The mathematical treatment of the dynamic adsorption curves

To quantify the isotope difference in dynamic adsorption, a mathematical model was developed for the experimental setup. It was assumed that the adsorbent surface is homogeneous; the interaction between adsorbed molecules is negligible; both H_2 and D_2 are ideal gases at low pressure. Then we have

$$\frac{d\theta}{dt} = k_a p(1-\theta) - k_d \theta \tag{1}$$

where θ is the ratio of the amount adsorbed at time t to that at equilibrium, p is the instantaneous gas pressure in the bulk phase, k_a is the rate constant of adsorption, and k_d is the rate constant of desorption. The second term of the right hand side of Eq. (1) is negligible at low θ value and the equation becomes

$$\frac{d\theta}{dt} = k_a p(1-\theta) \tag{2}$$

Referring to Fig. 1, the amount adsorbed, n, is calculated as:

$$n = \frac{p_1 V_1}{RT_1} - \frac{p}{R}\left(\frac{V_1}{T_1} + \frac{V_{ad}}{T_2}\right) \tag{3}$$

It is obtained from Eq. 3

$$p = \frac{p_1 V_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)} - \frac{nRT_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)} \tag{4}$$

Since $n = n_0 \theta$ Eq. (4) becomes

$$p = \frac{p_1 V_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)} - \frac{n_0 RT_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)}\theta \tag{5}$$

where p_1, V_1 and T_1 are the initial gas pressure, volume and temperature in the reference cell, V_{ad} and T_2 are the volume and temperature of the adsorption cell, R is the gas constant, and n_0

is the equilibrium amount adsorbed. It yields by substituting Eq. (5) into Eq. (2) that

$$\frac{d\theta}{dt} = k_a(1-\theta)\left(\frac{p_1 V_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)} - \frac{n_0 R T_1}{\left(V_1 + V_{ad}\dfrac{T_1}{T_2}\right)}\theta\right)$$

$$= k_a c_1(1-\theta)\left(1 - \frac{c_2}{c_1}\theta\right) \tag{6}$$

where

$$c_1 = \frac{p_1 V_1}{V_1 + V_{ad}\dfrac{T_1}{T_2}}$$

$$c_2 = \frac{n_0 R T_1}{V_1 + V_{ad}\dfrac{T_1}{T_2}} \tag{7}$$

If $T_1 = T_2$, then

$$c_1 = \frac{p_1 V_1}{V_2}, \quad c_2 = \frac{n_0 R T_1}{V_2} \tag{7a}$$

where V_2 is the sum of V_1 and V_{ad}. However, the temperature of adsorption cell ($T_2 = 77K$) is much lower than that of reference cell ($T_1 = 298K$). To allow for the effect of the temperature gradient along the connection tube, the volume of adsorption cell V_{ad} is divided into two parts: one is of temperature 77K, and the other part of volume V_0, is of temperature 298K. V_0 is principally the volume of connection tube, but with a revision determined by a vacant experiment. Thus, Eq. (7) becomes

$$c_1 = \frac{p_1 V_1}{(V_1 + V_0) + (V_{ad} - V_0)\dfrac{T_1}{T_2}}$$

$$c_2 = \frac{n_0 R T_1}{(V_1 + V_0) + (V_{ad} - V_0)\dfrac{T_1}{T_2}} \tag{7b}$$

Defining $c = \dfrac{c_2}{c_1} = \dfrac{n_0 R T_1}{p_1 V_1} = \dfrac{n_0}{n_{tot}}$, Eq. (6) reformed to

$$\frac{d\theta}{(1-\theta)(1/c - \theta)} = k_a c c_1 dt = k_a c_2 dt \tag{8}$$

where n_{tot} is the total amount of feed gas. After integrating Eq. (8), we get

$$\ln \frac{1-\theta}{\frac{1}{c} - \theta} = k_a (c_2 - c_1) t + C' \tag{9}$$

The rate constant of adsorption, k_a, can be determined from the slope of the plot of $\ln \dfrac{1-\theta}{\frac{1}{c} - \theta}$

versus t since the difference (c_2-c_1) can be evaluated from Eqs. (7a) and 7b.