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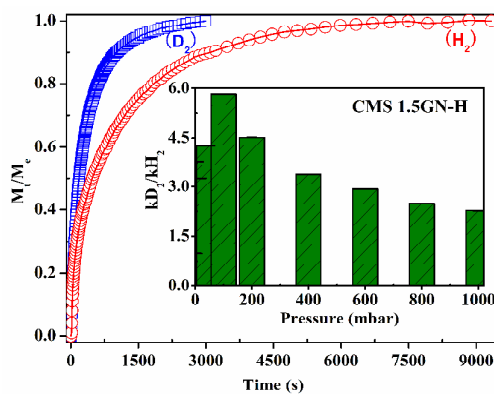
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TOC Graphic:



An exceptional quantum sieving is demonstrated on CMS 1.5GN-H where D_2 diffuses

5.83 times faster than H_2 at 77 K.

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COMMUNICATION

An exceptional kinetic quantum sieving separation effect of hydrogen isotopes on commercially available carbon molecular sieves

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The quantum sieving effect of H₂/D₂ at 77 K on commercially available carbon molecular sieves (1.5GN-H and 3KT-172) was studied. An exceptional reverse kinetic quantum effect is observed on 1.5GN-H where D₂ diffuses much faster than H₂ with ratio up to 5.83 at low pressure, and the difference is still very evident even as the pressure up to 1 bar. D₂ also diffuses faster than H₂ on 3KT-172 with ratio up to 1.86. However, the reverse kinetic sieving disappears in a polymer-based carbon (PC). The present kinetic quantum sieving effect of H₂ and D₂ at 77 K on 1.5GN-H is the highest to date.

The heavier isotopes of hydrogen, deuterium, is an important raw material for nuclear fusion. It has also been extensively applied in various fields such as the medical treatments and geography as an effective chemical tracer.¹ However, natural abundance of mole fraction deuterium in the composition of hydrogen isotope is only up to 0.015 wt%,^{1b, 2} and the small concentration of deuterium must be effectively separated from mixtures of hydrogen isotopes with a conception of environmental safety and durable economy in our mind.

Usually, these traditional molecular sieves are applied for the separation and purification of gas mixtures based on the different molecular sizes which can not be applicable to the situation of isotopes separation due to their identical properties like size, shape, and thermodynamic.^{1c, 2b, 3} The conventional separation methods for hydrogen isotopes based on small difference in mass such as chromatography, cryogenic distillation, proton exchange, thermal diffusion, and electrolysis are also suffering from high energy consumption and low efficiency.⁴ The development of an effective method for separation of hydrogen isotopes is still great challenge. In this respect, quantum sieving based on the quantum effect and restricted rotation proposed by Beenakker *et al.*⁵ at 1995s can be applied to effectively separate hydrogen isotopes by preferential adsorption at low temperatures in an appropriate solid microporous material. Quantum sieving has been considered to be a promising technique with low energy consumptions in the separation of hydrogen isotopes.^{1a, 1c, 6} It has been proposed that if the difference between pore size and molecular hard core become comparable to the de Broglie wavelength of molecules, quantum effect on the molecular adsorption and transport in these confined pores would be very important.⁵ The heavier isotope of deuterium with slightly smaller de Broglie wavelength and lower zero-point

energy than hydrogen will lead to the stronger adsorption strength in these confined pores of microporous materials.⁷

To date, many molecular simulation and experimental studies have demonstrated the existence of quantum sieving effect for H₂ isotopes in microporous materials such as carbon molecular sieve (CMS), activated carbon fibers, carbon nanotubes, nanohorns, zeolites, metal-organic frameworks (MOF), and covalent-organic frameworks (COF).^{1c, 2b-d, 7a, 7d, 8} However, adsorption isotherms for H₂/D₂ have only been experimentally measured for small numbers of these materials and the ultimate adsorbed D₂/H₂ ratio in molar amount is often less than 1.2 basis at 77 K,^{2a, 9} indicating that the equilibrium quantum sieving is not an alternative to the conventional separation methods. Therefore, we have reasons to believe that the effective separation of H₂ and D₂ in microporous carbons is probable largely based on the kinetic quantum sieving effect rather than equilibrium. Although several studies have also provided a large selectivity up to 7.5 as temperature at 40 K and pressure near at zero coverage, and the equilibrium selectivity can be even up to 10 at 20 K,^{2b, 7d, 8a} such experimental conditions are generally difficult to achieve in ordinary lab. Recently, the group of Hirscher¹⁰ have reported an exciting result on the equilibrium selectivity of D₂/H₂ in a typical MOF containing opening metal sites where the selectivity can be even up to 12 at 60 K. However, most of researches ignored the influence of different kinetic diffusions between H₂ and D₂, and the kinetic quantum sieving on the separation of H₂/D₂ using adsorption method is rarely studied to date. In our previous work, we have experimentally observed for the first time that D₂ diffuses significantly faster than H₂ up to 1.9 times at 77 K in a CMS (Takeda 3 Å) with adsorption.^{9a} Later, we have again observed this reverse diffusion of D₂ and H₂ on a zinc/copper mixed MOF material as the result of kinetic quantum sieving effect.^{9b} Bhatia *et al.*^{7b} have also demonstrated the reverse diffusion in Takeda 3 Å using the quasielastic neutron scattering (QNS) technique in which D₂ diffuses faster than H₂ below 100 K. Using the QNS method, the group of Contescu^{7a} also observed an extreme kinetic quantum sieving effect in a polyfurfuryl alcohol-derived activated carbon with D₂ diffusing up to 10 times faster than H₂ at 40 K. Very importantly, some simulations have also indicated the promising potential of kinetic quantum sieving in the separation of H₂ and D₂ at milder conditions than traditional methods.^{7c, 11} Since quantum effects vary significantly with the pore structures of adsorbent, the kinetic adsorption measurements should be performed on a series of comparable but

distinctively different samples to illustrate the outstanding kinetic quantum sieving effect.

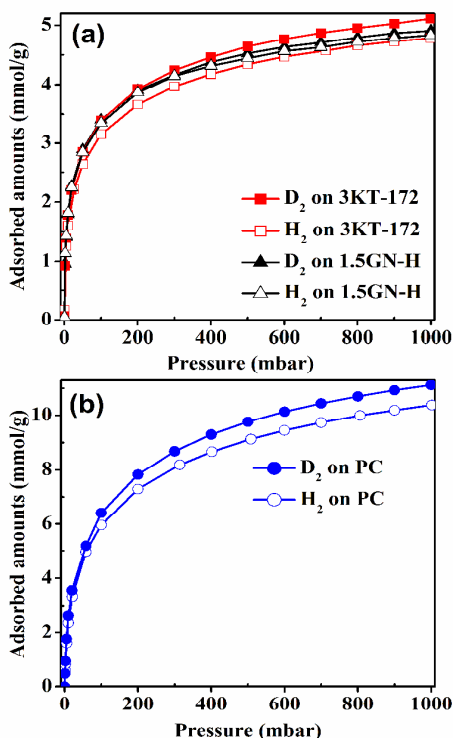


Fig. 1, Equilibrium adsorption isotherms for H₂ and D₂ at 77 K on (a) two commercially available CMS materials of 3KT-172 and 1.5GN-H, and (b) a poly(vinylidene chloride)-based carbon (PC).

Herein, we report novel kinetic quantum sieving effects of H₂ and D₂ on two commercially available CMS materials (1.5GN-H and 3KT-172) at 77 K through adsorption method under the same equipments, procedures and conditions. Moreover, the adsorption properties of H₂/D₂ on a poly(vinylidene chloride)-derived carbon (PC)¹² were also compared. **Fig. 1** depicts adsorption isotherms of H₂/D₂ at 77 K on the three kinds of materials. All the isotherms are typical type I in the IUPAC classification scheme.¹³ It is very obvious that adsorption trends of H₂/D₂ on all samples are very similar to each other. As can be deduced from CO₂ adsorption isotherms at 273 K and 1 bar on 1.5GN-H and 3KT-172 shown in **Fig. 2**, the aperture structures of the two CMS materials only have small difference with the micropore volumes of 0.1957 cm³/g for 3KT-172, and 0.1839 cm³/g for 1.5GN-H which were determined from the classical Dubinin-Radushkevich (DR) equation (**Fig. S1**, ESI†). The pore size distribution (PSD) curve in **Fig. 2** calculated from CO₂ adsorption isotherms based on the well-known Dubinin-Radushkevich-Stoeckli model¹⁴ implied that the 1.5GN-H has a slightly narrower PSD curve than 3KT-172 with a mean pore size located at around 0.46 and 0.49 nm, respectively. Moreover, the diffusion rate of CO₂ adsorption in 3KT-172 is slightly faster than the corresponding profile in 1.5GN-H under the same conditions (**Fig. S1**, ESI†). Comparatively, the calculated PSD curve for the PC determined from N₂ adsorption data is located in the range of less than 1.5 nm, and ultramicropores size for the PC is located at around 0.57 nm which is also determined from CO₂ adsorption data at 273 K and 1 bar (**Fig. S2**, ESI†). Taking into accounts that both the molecular diameters of H₂ and D₂ are around 0.3 nm and their de Broglie wavelengths are about 0.176 and 0.124 nm at 77

K, respectively, we can expect that adsorption of H₂/D₂ in these nanopores with diameters up to 0.5 nm probably involve quantum effects.^{8a} However, the equilibrium adsorption isotherms in **Fig. 1** suggested that D₂ isotherms had slightly larger adsorbed amounts than H₂ on a mole basis, and the ratio between D₂ and H₂ did not vary significantly as pressure increment (**Fig. S3**, ESI†). The significant difference of D₂/H₂ in equilibrium adsorption uptakes observed in several MOFs^{2b, 7d, 10} was absent from the present carbon-based materials. In addition, the exclusion of H₂ from the ultrasmall pores due to strong quantum effects predicted by some simulation studies^{6c, 15} was also not experimentally observed in this work. The calculated molar ratios at 1 bar for 3KT-172, 1.5GN-H and PC were up to 1.038, 1.006 and 1.194, respectively. It is very interesting to find that all these mole ratios are almost identical to our previous works on other types of adsorbents in which a zeolite-templated carbon with ratio of 1.05, a zinc/copper mixed MOF of 1.02, and an activated carbon of 1.16.^{1c, 9b, c, 9g} All these results indicate that the fundamental correlation has been experimentally established between D₂/H₂ molar ratios and pore structures of framework materials. The subtle difference for the adsorbed amounts in various adsorbents implied that the effective separation of H₂/D₂ can not be achieved at 77 K only based on equilibrium thermodynamic adsorption in microporous carbons with different pore sizes even if samples have strong confinement effects. That is, the equilibrium quantum sieving separation effect is probably not a fundamental force during separation process for the hydrogen isotopes.

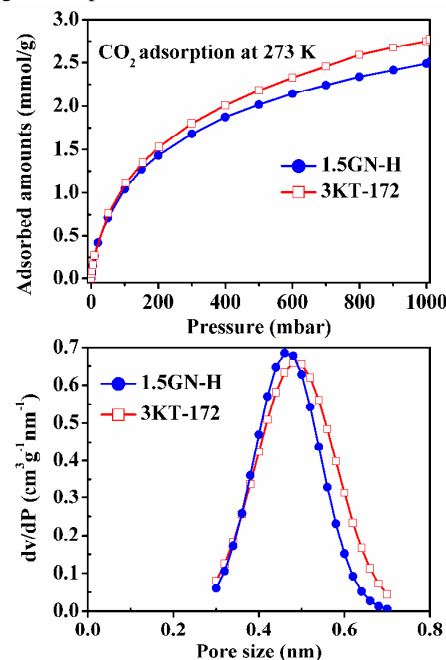


Fig. 2, CO₂ adsorption isotherms for 3KT-172 and 1.5GN-H at 273 K and 1 bar, and the corresponding pore size distributions determined from CO₂ adsorption data based on the Dubinin-Radushkevich-Stoeckli model.

On the other hand, the separation of D₂/H₂ is probably derived through kinetic quantum sieving effect. The faster diffusion of D₂ than H₂ at 77 K has been largely demonstrated in our previous works with the difference up to 1.9 times.^{9a} The kinetic profiles for typical pressure increments of H₂/D₂ adsorption on the present three kinds of materials at 77 K are illustrated in **Fig. 3**. Although the porous structures of 1.5GN-H and 3KT-172 only have subtle

differences (Fig. 2, and Fig. S1, ESI†), it was very evident that the diffusion rates for D₂ were significant faster than H₂ on 1.5GN-H (Fig. 3a) and 3KT-172 (Fig. 3b), providing the direct evidence of kinetic quantum sieving effect for the samples, in agreement with previous data collected from thermal desorption spectroscopy (TPD)^{2b, 7d, 8a} and QNS^{7a, b} techniques. Furthermore, the diffusion of D₂ also reached the equilibrium state more quickly than H₂. As shown in Fig. 3a, the diffusion of D₂ on 1.5GN-H is close to an equilibrium state at 3000 s whereas H₂ is not fully equilibrated even up to 8000 s, indicating that the kinetic quantum sieving effect of H₂ isotopes is indeed existed in the sample. Significantly, the quantum effect in 1.5GN-H is largely more than our previous observation in another CMS Takeda 3Å.^{9a} Usually, quantum effects in these confined small pores decrease as an increase of pressure and temperature,^{8c, 16} and the kinetic quantum sieving effect in 1.5GN-H at 77 K is still rather evident as the pressure up to 800 mbar (Fig. S4, ESI†). We believe that if we continue to reduce the temperatures in these confined materials, the larger kinetic diffusion difference between D₂ and H₂ will be observed, resulting in an effective separation of hydrogen

isotopes. In addition, the kinetic quantum sieving effect for H₂/D₂ in 3KT-172 is also existed until the pressures up to 400 mbar (Fig. S5, ESI†). However, adsorption kinetics of H₂/D₂ in the PC shown in Fig. 3c were wholly reverse compared with 3KT-172 and 1.5GN-H. The adsorption rate at different pressure increments for D₂ was slightly slower than the corresponding profile for H₂ in PC, which is in excellent agreement with the classical rate diffusion theory that H₂ diffuses faster than D₂. We attributed the classical normal order in diffusion rates for H₂/D₂ to the larger average pore size of PC, and then the disappearance of kinetic quantum sieving. Both D₂ and H₂ diffusions in the PC sample were fully equilibrated within 400s which is also much faster than the corresponding profiles in 3KT-172 and 1.5GN-H. However, the diffusion rates of D₂/H₂ in PC are still much slower than typical carbons with an equilibrium time less than 180 s.^{9c} Overall, the diffusion of H₂/D₂ in these three samples indicates that quantum sieving effect is very sensitive to the pore apertures of materials and a small increase in pore size will greatly decrease the quantum sieving effect.

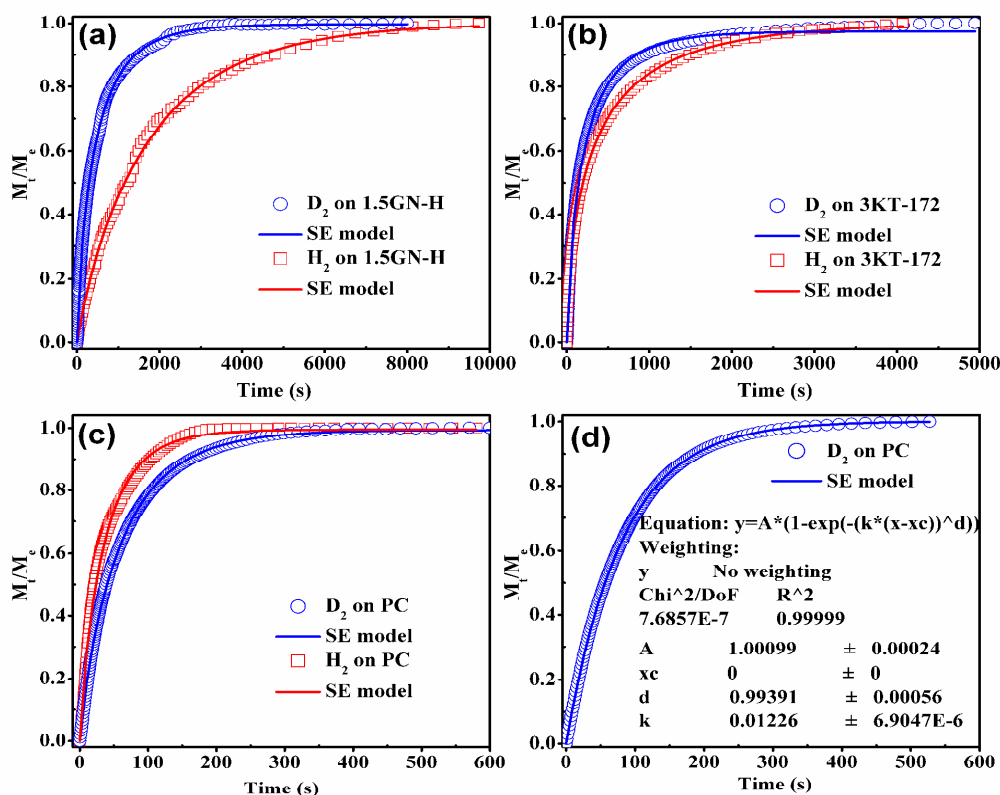


Fig. 3. Typical H₂/D₂ kinetic profiles at 77 K with pressure increment, and fitted lines with stretched exponential (SE) model: (a) 5-20 mbar on 1.5GN-H, (b) 5-20 mbar on 3KT-172, and (c) 10-50 mbar on PC. (d) An illustration of SE model fitting for D₂ adsorption on PC with pressure increment of 100-200 mbar.

Usually, the adsorption kinetics profiles of molecules can be described using a stretched exponential (SE) model:¹⁷

$$\frac{M_t}{M_e} = 1 - e^{-(kt)^\beta} \quad (1)$$

In equation (1), k is the rate constant, t is the equilibrium time, and β is the exponential parameter for adsorption process. As illustrated in Fig. 3, the kinetics profiles of H₂/D₂ adsorption on the three materials can be well described using the SE model.

A representative SE model fitting for D₂ adsorption on the PC with pressure increments of 100-200 mbar was shown in Fig. 3d to describe the comparison of SE model fitting and experimental data. It should be mentioned that β is a very important parameter in determining the kinetic diffusion mechanisms, usually covering the range from 0 to 1. Moreover, the β value can provide an indication of the dimension for adsorption.^{9a} Adsorption process is a one-dimensional as the value of β is 0.5, while it suggests a three-dimensional process as β is 1. Moreover, the

equation (1) will transform into a linear driving force (LDF) mass transfer model as the value of β is 1, which is a nested kinetic model of SE model and usually used to describe the kinetic process of N_2/O_2 in the applications of air separation.¹⁸ Therefore, intermediate values of β maybe corresponded to transitional state and suggest a two-dimensional process. All the β values of H_2/D_2 adsorption on 3KT-172, 1.5GN-H, and PC vary a little as pressure increment, locating in the range of 0.73-0.85, 0.77-0.98, and 0.88-0.98, respectively (Fig. S6, ESI[†]). Therefore, the main factor in SE model can be largely predominated by the difference of different rate constants.

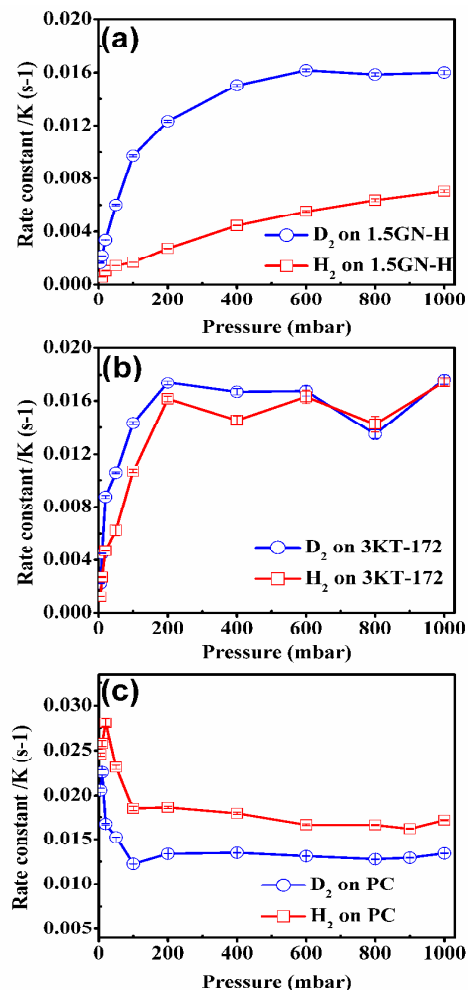


Fig. 4, Variation of SE model rate constant parameters with the increment of pressures for H₂ and D₂ adsorption on: (a) 1.5GN-H, (b) 3KT-172, and (c) PC at 77 K.

In order to understand the kinetic quantum sieving effect on the relationship of diffusion rate, Fig. 4 exhibits the rate constants k of H_2/D_2 in the three materials at 77 K determined from the SE model. Both k values for H_2/D_2 adsorption on 1.5GN-H (Fig. 4a) increase gradually as an increase of pressure in good accordance with gas diffusion theory. However, it should be noted that the difference of diffusion rates between H_2 and D_2 is still very significant even as the pressures up to 800 mbar which was never observed in any other kinds of porous adsorbents. The ratios of rate constants (k_{D_2}/k_{H_2}) for D_2 and H_2 adsorption in 1.5GN-H at 77 K initially increase as an increase of pressure and the ratios will then descend at higher pressure (Fig. S7, ESI[†]). Significantly,

the kinetic rate constant of D_2 in 1.5GN-H at 77 K is highly up to 5.83 times faster than the corresponding rate constant of H_2 , which is the highest determined experimentally to date, to the best of our knowledge. As for H_2/D_2 adsorption in 3KT-172 (Fig. 4b), both the rate constants varied with pressure. The diffusion of D_2 is slightly faster than H_2 as the pressure lower than 600 mbar, and the kinetic parameters for H_2/D_2 adsorption seem to be equal at higher pressure. The kinetic rate constant of D_2 adsorption in 3KT-172 at 77 K is up to 1.86 times faster than H_2 (Fig. S7, ESI[†]), very close to our previous observations on CMS Takeda 3Å.^{9a} Comparing with the 1.5GN-H, the smaller kinetic quantum sieving in 3KT-172 is probably due to the existence of slightly larger micropores, generating small quantum effects in the diffusion and rotation of H_2/D_2 in the pores. Taking into accounts that H_2 isotopes have the equal diameters and shapes, the slower adsorption kinetics of H_2 compared with D_2 in the two CMS samples are wholly due to the presence of kinetic quantum sieving effect during the diffusion through constricted nanopores, which was due to the lower zero-point energy and smaller de Broglie wavelength for D_2 than the corresponding ones for H_2 , generating lower barrier to diffusion into pore structure and faster adsorption kinetics for D_2 . Here, we would like to emphasize that the slight difference in pore width of carbon materials will result in dramatic change for the quantum sieving effect in view that the aperture difference between the two CMS 1.5GN-H and 3KT-172 is only about 0.03 nm (see Fig. 2). Comparing with 3KT-172 and 1.5GN-H, on the other hand, the rate constants of H_2/D_2 in the PC sample listed in Fig. 4c showed a reverse trend with D_2 diffusing slightly slower than H_2 , indicating the absence of kinetic quantum effect. Therefore, we can conclude that when the pore diameter of carbon-based materials is larger than 0.57 nm there would be no observation of kinetic quantum sieving effect, and the quantum sieving effect is enhanced in the limited pore space available for hydrogen molecule motion where the difference (c.a. ~ 0.20 nm) of the accessible pore width and the hydrogen molecule hard core diameter is comparable to the de Broglie wavelength of hydrogen isotopes.^{8a, 19} Moreover, both the rate constants of H_2 and D_2 in PC seem to gradually decrease at low pressure and then change a little as an increase of pressure. As the kinetics diffusion for H_2/D_2 adsorption on most of adsorbents are too fast to analyze, the present investigations showed significant difference in the kinetic diffusion of H_2 and D_2 adsorption on two commercially available CMS materials and a polymer-based activated carbon. These observations illustrated in Fig. 4 brought us a new concept to effectively separate hydrogen isotopes using the kinetic quantum sieving effect.

In summary, we have successfully used adsorption method to demonstrate the existence of kinetic quantum sieving effect of hydrogen isotopes on CMS materials. The difference between D_2 and H_2 kinetic diffusions is still significant in 1.5GN-H, even at a high pressure of 800 mbar at 77 K. This observation is a huge breakthrough for our previous studies and indicates the promising potential of special CMS materials in separation of light isotopes. The kinetic quantum sieving effect of hydrogen and deuterium on 1.5GN-H at 77 K with the ratios up to 5.83 is the highest value experimentally collected to date. However, a small change in the pore size will arouse significant effects on the quantum sieving. More research work is needed to be further explored the influence

of pore structures of CMS materials on kinetic quantum sieving. Considering the complexity of pore apertures in CMS materials, on the other hand, special MOFs with uniform pores may be more promising potential in the aspect of exploring the quantum sieving effect.

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Notes

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 †Electronic supplementary information (ESI) available: The detailed experimental procedures and other characterization information. See DOI: 10.1039/c4cp00179f

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