Adsorption of Hydrogen Isotopes on Micro- and Mesoporous Adsorbents with Orderly Structure

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The equilibrium and dynamic adsorption data of H_2 and D_2 on different micro- and mesoporous adsorbents with orderly structure including 3A, 4A, 5A, Y, and 10X zeolites; carbon CMK-3; silica SBA-15; and so forth were collected. Critical effect of the nanodimension of adsorbents on the adsorption behavior of hydrogen and its isotopes is shown. The highest adsorption capacity was observed at pore size 0.7 nm, but equal or even larger isotope difference in the equilibrium adsorption was observed at larger pore sizes, whereas the largest isotope difference in the dynamic adsorption was observed at 0.5 nm. The adsorption rate of D_2 is larger than that of H_2 in microporous adsorbents, but the sequence could be switched over in mesoporous materials. Linear relationship was observed between the adsorption capacity for hydrogen and the specific surface area of adsorbents although the adsorbents are made of different material, which provides a convincing proof of the monolayer mechanism of hydrogen adsorption. The linear plot for microporous adsorbents has a larger slope than that for mesoporous adsorbents, which is attributed to the stronger adsorption potential in micropores.

1. Introduction

The heavy isotope of hydrogen, deuterium, is an important material in nuclear industry. It also has important application in medical cure and as a tracer. The natural abundance of deuterium is very small, only about 0.015 mol %. Therefore, searching for a low-cost separation method is critical for the industrial application of deuterium. However, the separation between hydrogen isotopes is difficult because of the similarity of isotope properties. This problem receives research interest again following the increasing attention paid to nuclear energy recently. The industrialized methods, such as cryogenic distillation, electrolysis, dual temperature chemical exchange, and thermal diffusion, are highly energy consumptive.[1−3] The separation cost is usually low if the separation is based on the difference of components in adsorption;[4−6] however, adsorbent is the decisive factor of feasibility and separation cost. Physical adsorption is reversible, but the selectivity of adsorption depends on the difference of components either in equilibrium or in dynamic adsorption. Physical adsorption relies on the van der Waals force, which is sensitive to the dimension of the nanospaces accessible to hydrogen molecules in adsorbents. The steric barrier effect also functions in small nanospaces. To study the dependence of hydrogen isotope adsorption on the nanodimension of adsorbents, molecular sieves that have orderly nanostructure and narrow pore size distribution were used as adsorbents in the present study. The adsorbents used in experiments include microporous 3A, 4A, 5A, Y, and 10X zeolites and mesoporous carbon molecular sieve CMK-3 and silica molecular sieve SBA-15 and so forth. The nominal pore size of the tested adsorbents ranges in 0.3−5.1 nm. Since the

difference between H_2 and D_2 in adsorption increases as temperature and pressure decreases,[7] adsorption isotherms were collected at 77 K with a volumetric method for low pressures. The ratio of the adsorbed amounts of D_2 over H_2 at pressure 0.1 MPa was used as an index of isotope difference in equilibrium adsorption. Dynamic adsorption curves of H_2 and D_2 were collected at different initial pressures, and the rate constant of adsorption was determined. The ratio of the rate constants of isotopes was used as an index of isotope difference in dynamic adsorption. Dependence of H_2 and D_2 adsorption and the difference therein on the dimension of nanospaces was observed.

2. Experimental Section

The zeolite 3A was provided by the Heng-Ye Molecular Sieves, Ltd, Shanghai; 4A, 5A, and 10X zeolites were provided by the Jing-Zhong Molecular Sieves, Ltd, Shanghai; Y zeolite was provided by the Molecular Sieve Factory, Nankai University, Tianjin. The mesoporous molecular sieves SBA-15 and CMK-3 were synthesized in the authors' lab. Details of the synthesis were reported previously.[8,9] All adsorbents were grinded and sifted to particle sizes of 0.4−0.5 mm and were dried in a vacuum at 150 °C for 24 h before adsorption measurements. The nominal pore size and other major structural parameters of adsorbents are given in Table 1. Hydrogen of purity above 99.999% was provided by Liu-Fang High-Tech Co., Tianjin. Deuterium of purity above 99.9% was provided by Hai-Pu Gas Industry Co., Beijing.

It is impossible to use microbalance at 77 K; therefore, adsorption isotherms and the dynamic curves of adsorption were collected with a volumetric setup that was commonly used for the adsorption of nitrogen at 77 K to evaluate the BET surface area of adsorbents. The adsorption cell is initially in a vacuum (0.01 Pa) for both equilibrium and dynamic adsorption measure-

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TABLE 1: Adsorbents Used in the Present Study

no.	molecular sieve name[a]	type	nominal pore size (nm)	S_{BET} (m^2 g^{-1})
1	3A	micropore	0.3	33.00
2	4A	micropore	0.4	168.58
3	Pd-4A	micropore	0.28	27.87
4	5A	micropore	0.5	312.95
5	ZSM-5	micropore	0.5	272.30
6	VP800-5	micropore	0.5	360.34
7	VP800-5(a)	micropore	0.44	256.21
8	VP800-5(b)	micropore	0.38	204.28
9	VP800-5(c)	micropore	0.35	171.89
10	VP800-5(d)	micropore	0.32	142.68
11	VP800-5(e)	micropore	0.25	81.57
12	CMS	micropore	0.4−1.0	340.35
13	Y	micropore	0.6−0.7	367.04
14	10X	micropore	0.8	473.56
15	13X	micropore	1.0	97.93
16	CMK-3	mesopore	3.5	972.10
17	SBA-15	mesopore	5.1	653.29
18	SBA-15(a)	mesopore	4.2	507.04
19	SBA-15(b)	mesopore	3.7	489.38
20	SBA-15(c)	mesopore	3.3	443.78
21	SBA-15(d)	mesopore	3.1	431.36

[a] Adsorbents marked with a, b, c, d, or e are modified with loading different amounts of CuCl.
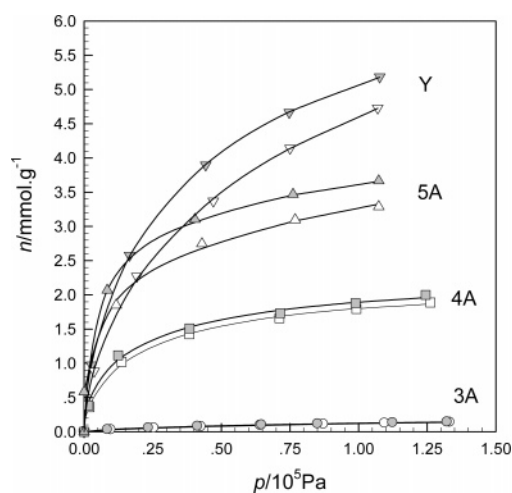

Figure 1. Adsorption isotherms of H_2 and D_2 on 3A, 4A, 5A, and Y-zeolite at 77 K. Symbols: white for H_2; gray for D_2.

Figure 2. Adsorption isotherms of H_2 and D_2 at 77 K. ○, 10X; □, CMK-3; △, SBA-15. Symbols: white for H_2, gray for D_2.

Figure 3. Dependence of the adsorbed amount of H_2 and D_2 on pore size.

Figure 4. Dependence of the equilibrium adsorption ratio on pore size.

ments. However, the pressure in the adsorption cell was increased stepwise until 0.14 MPa was reached in 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.

3. Results and Discussion

3.1. Isotope Difference in Equilibrium Adsorption. The obtained adsorption isotherms of H_2 and D_2 at 77 K are shown in Figure 1 for microporous 3A, 4A, 5A, and Y zeolites and in Figure 2 for 10X zeolite and mesoporous CMK-3 and SBA-15. It seems that the adsorption of H_2 and D_2 is quite sensitive to pore size, and the dependence is clearly shown in Figure 3, where the amount adsorbed at pressure 0.1 MPa is drawn against the nominal pore size of adsorbents with orderly structure. It seems 0.7 nm is the optimal pore size for the highest adsorption capacity of hydrogen as was indicated previously by several simulation studies.[10−13] However, it might not be the optimal pore size for the separation of hydrogen isotopes as shown in Figure 4, where R_A is the ratio of the adsorbed amounts of the
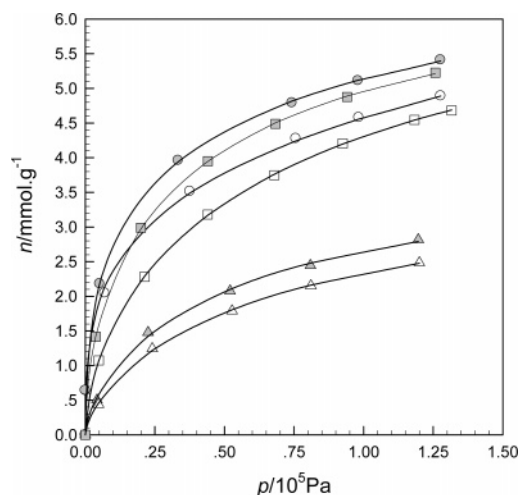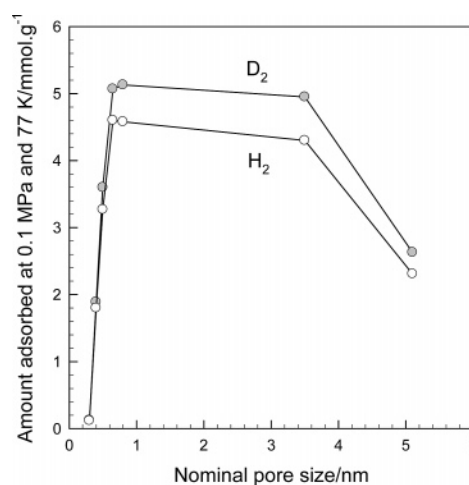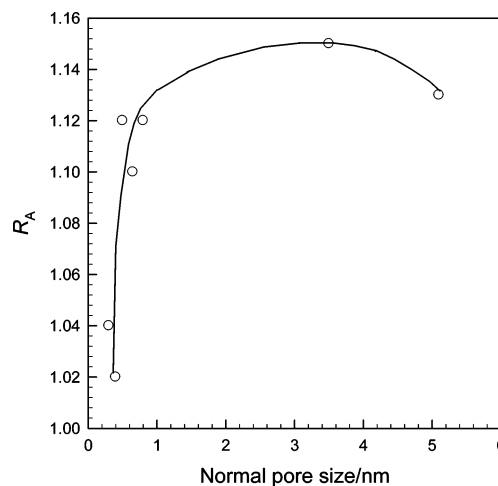
two isotopes at pressure 0.1 MPa. Mesoporous carbon molecular sieve CMK-3 yields the largest difference in equilibrium adsorption between H_2 and D_2, although it does not yield the highest adsorption capacity. Detailed information of the isotope difference in equilibrium adsorption is given in Table 2.

3.2. Isotope Difference in Dynamic Adsorption. Another adsorption difference that can be used for separation is the

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TABLE 2: Effect of Pore Size on the Equilibrium Adsorption of Hydrogen Isotopes

adsorbent	norminal pore size, nm	adsorbate	adsorbed amount at 0.1 MPa/mmol g	ratio of adsorption
3A-zeolite	0.3	D_2	0.125	1.04
		H_2	0.120	
4A-zeolite	0.4	D_2	1.84	1.02
		H_2	1.80	
5 A-zeolite	0.5	D_2	3.62	1.12
		H_2	3.24	
Y-zeolite	0.6−0.7	D_2	5.07	1.10
		H_2	4.60	
10X-zeolite	0.8	D_2	5.12	1.12
		H_2	4.59	
CMK-3	3.5	D_2	4.95	1.15
		H_2	4.31	
SBA-15	5.1	D_2	2.63	1.13
		H_2	2.33	

TABLE 3: Rate Constants of Adsorption at Different Initial Pressures

adsorbent	$k_a/$ $MPa^{-1} S^{-1}$	0.0093 MPa	0.015 MPa	0.022 MPa	0.031 MPa	0.064 MPa
4A	k_{H_2}	15.89	3.24	3.06	1.79	0.59
	k_{D_2}	25.32	6.76	4.17	2.24	0.53
	k_{D_2}/k_{H_2}	1.59	2.09	1.36	1.25	1.11
5A	k_{H_2}	76.62	9.02	8.53	5.41	1.02
	k_{D_2}	141.11	22.36	14.55	5.92	0.94
	k_{D_2}/k_{H_2}	1.84	2.48	1.71	1.09	0.92
Y	k_{H_2}	8.23	5.29	3.57	2.37	0.89
	k_{D_2}	10.60	6.96	4.56	2.55	0.87
	k_{D_2}/k_{H_2}	1.29	1.32	1.28	1.05	0.98
10X	k_{H_2}	115.16	9.58	5.04	2.73	0.92
	k_{D_2}	143.48	12.45	6.15	3.11	0.85
	k_{D_2}/k_{H_2}	1.25	1.30	1.22	1.14	0.93
CMK-3	k_{H_2}	9.34	5.40	3.36	2.19	0.92
	k_{D_2}	9.44	5.15	3.25	2.07	0.76
	k_{D_2}/k_{H_2}	1.01	0.95	0.97	0.95	0.83
SBA-15	k_{H_2}	5.23	3.50	2.42	1.46	0.62
	k_{D_2}	6.06	3.81	2.38	1.45	0.61
	k_{D_2}/k_{H_2}	1.16	1.09	0.98	1.00	0.98

difference of components in the adsorption rate, therefore, the dynamic adsorption curves of H_2 and D_2 were measured for different initial pressures on adsorbents with characteristic dimension, and the results are given in Table 3. Since the adsorbed amount of H_2 and D_2 on 3A zeolite was very low, the adsorbent was not used in the dynamic adsorption tests. The result obtained for the initial pressure 0.022 MPa is shown in Figures 5 and 6 for H_2 and D_2, respectively. According to the mathematical model shown in the Supporting Information, the dynamic adsorption data were plotted in $\ln[(1 − \theta)/(1/c − \theta)]$ versus t and are shown in Figures 7 and 8 for the initial pressure 0.022 MPa as an example, from which the rate constants of adsorption were evaluated and are listed in Table 3 for different adsorbents and the five levels of initial pressure. The isotope difference in the dynamic adsorption is expressed in the ratio of rate constants of D_2 over H_2, $R_k = k_{D_2}/k_{H_2}$. The dependence of the isotope difference in dynamic adsorption is clearly shown in Figure 9 for the initial pressure 0.022 MPa as an example. Two important facts were observed. First, nanodimension of 0.5 nm yields the largest isotope difference in the rates of adsorption; second, D_2 has a higher rate of adsorption than H_2 on adsorbents with smaller pore sizes, say, less than 2 nm, which was explained with the difference in the zero energy of them.[14−16] However, this sequence could be switched over on adsorbents with larger pore sizes, say, in the mesopore range, at higher pressures as shown in Table 3. The second fact is
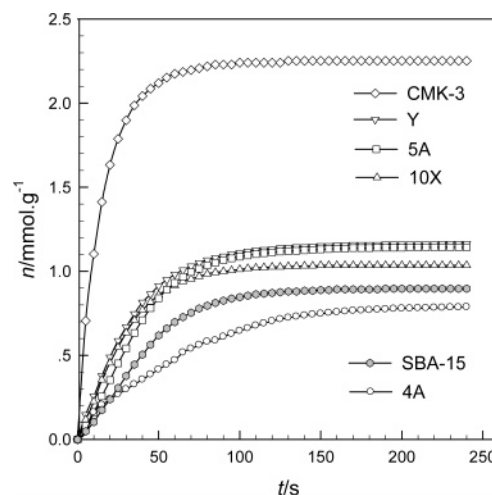
Figure 5. Increasing curves of the adsorbed H_2 for initial pressure 0.022 MPa.
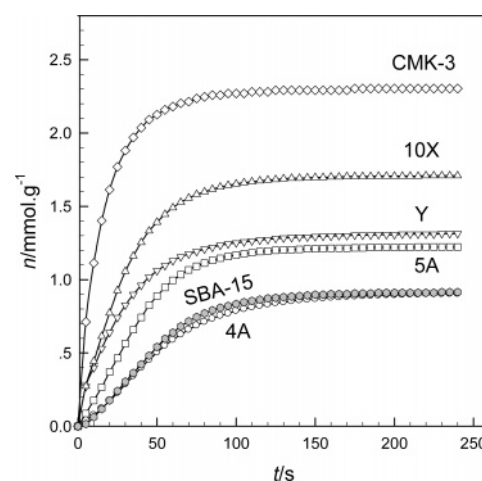
Figure 6. Increasing curves of the adsorbed D_2 for initial pressure 0.022 MPa.
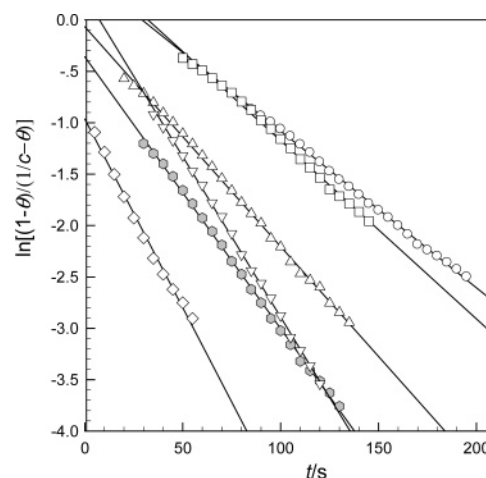
Figure 7. The plot for evaluating rate constants at initial H_2 pressure 0.022 MPa.

important for the PSA technology because it determines which isotope is the column top product.

3.3. Dependence of Adsorption Capacity on Specific Surface Area. Ströbel et al.[17] and Nijkamp et al.[18] reported the linear dependence between the adsorption capacity of carbon materials for hydrogen and the specific surface area of materials. The amount adsorbed at 77 K and 0.1 MPa was plotted against
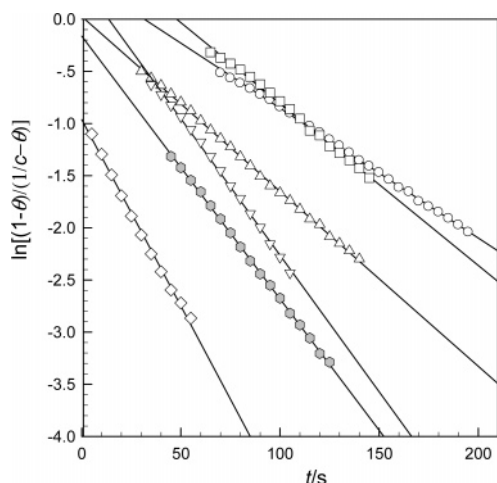
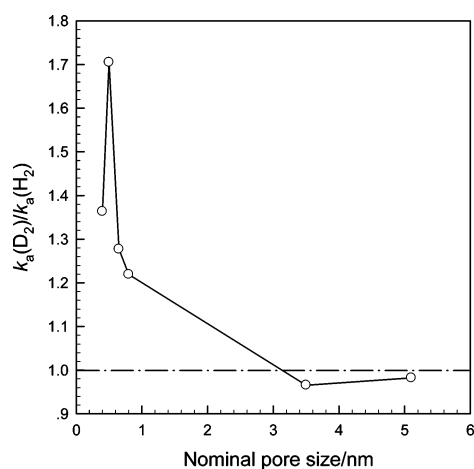**Figure 8.** The plot for evaluating rate constants at initial D_2 pressure 0.022 MPa.

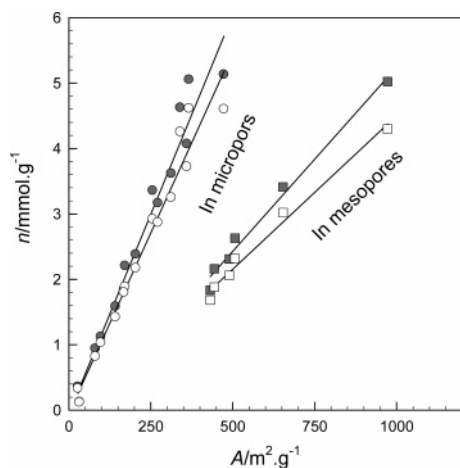**Figure 9.** Dependence of adsorption rate ratio on pore size.

Figure 10. Dependence of adsorption amount on specific surface area. Light marks: H_2; dark marks: D_2.

the specific surface area of adsorbents as shown for H_2 and D_2 in Figure 10. Linearity of the dependence is clearly shown for all adsorbents tested no matter carbonaceous or not. Furthermore, the slopes of the linearity are remarkably different in the microporous section (including 15 adsorbents) and the mesoporous section (including 6 adsorbents), and a little difference between H_2 and D_2 is observed in each section also. The adsorption capacities of adsorbents that made of different material locate on unique linear plot indicate a fact that the

hydrogen adsorption can only be monolayer coverage on adsorbent surface, and the difference in the interactions between hydrogen molecules and the solid surface is not important for the adsorption capacity. However, pore size is more important than the surface property for the adsorption capacity of hydrogen, which explains the two sections for the two classes of adsorbents. It is well-known that adsorption potential of the opposite walls is overlapped and the adsorption of hydrogen in micropores is thus enhanced. However, such overlap of adsorption potential does not occur in mesopores and, therefore, yields smaller adsorption capacity for hydrogen. These observations should be kept in mind in searching for hydrogen carriers.

4. Conclusion

On the basis of the static and dynamic adsorption data of H_2 and D_2 at 77 K on micro- and mesoporous adsorbents with orderly nanostructure, it is concluded that the adsorption behavior of hydrogen isotopes depends strongly on the dimension of the characteristic nanospaces of adsorbents. The highest adsorption capacity was observed at 0.7 nm for both H_2 and D_2, but the largest isotope difference in equilibrium adsorption was observed at larger pore size and the largest isotope difference in dynamic adsorption was observed at 0.5 nm. The adsorption rate of D_2 is higher than that of H_2 if the pore size is small and the pressure is low; however, the sequence can be switched over for the condition of higher pressure and larger nanodimension. The adsorption capacity is proportional to the specific surface area of adsorbents no matter what kind of material the adsorbent is made of. However, the linearity is affected by the nanodimension of adsorbents. The slope of the linear relationship is larger for microporous adsorbents than for mesoporous ones.

Supporting Information Available: The adsorption measurement apparatus and the mathematical treatment of the dynamic adsorption curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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