Low Temperature Adsorption of Hydrogen on Nanoporous Materials

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Hydrogen adsorption on various porous materials have been studied with a volumetric method at low temperature in the pressure of 0-760 torr. Their hydrogen uptakes depend at least partly on microporosity rather than total porosity. However, it is also necessary to consider other parameters such as pore size and pore architecture to explain the adsorption capacity. The heat of adsorption and adsorption-desorption-readsorption experiments show that the hydrogen adsorption over the porous materials are composed of physisorption with negligible contribution of chemisorption. Among the porous materials studied in this work, SAPO-34 has the highest adsorption capacity of 160 mL/g at 77 K and 1 atm probably due to high micropore surface area, micropore volume and narrow pore diameter.

Key Words : Hydrogen adsorption, Molecular sieve, Aluminophosphate, Metal-organic framework

Introduction

Recently, hydrogen storage is a topic of intensive research since hydrogen is regarded as a renewable energy carrier. Effective means of hydrogen storage is one of the prerequisite for the utilization of the sustainable energy source, hydrogen. Hydrogen is also considered as an alternative fuel because of non-polluting nature and abundance.[1,2] The hydrogen can be stored by several states or means including compressed gas, liquefaction, adsorption, hydrides and chemical reactions etc.[3] The storage via adsorption, mainly physisorption, has advantages of fully reversible adsorption-desorption and high energy effiency.[4] However, hydrogen adsorption on porous materials such as zeolites[4-8] and metal-organic frameworks (MOF)[9-14] has not been studied well compared with the adsorption on carbon materials[15,16] such as carbon nanotubes and carbon nanofibers. Moreover, the hydrogen adsorption results reported so far in the literature sometimes do not coincide[6,7,10,17] with one another like the inconsistency of the results measured for carbon materials.[4] Therefore, the reproducible and precise measurement of hydrogen adsorption is very important for the development of hydrogen storage materials.

Several parameters have been regarded as dominant factors to affect the adsorption capacity on porous materials. The adsorption capacity on zeolites correlates quite well with the BET surface area.[6] The adsorption capacity over various carbon, silica, alumina and zeolites shows linear dependence with the micropore volume.[4] Kazansky et al. have shown that the electrostatic field (according to Si/Al ratio of framework and content and type of cations) and basicity of the faujasite zeolites affect the adsorption strongly.[7] However, it has also been reported that the surface area or pore volume cannot explain the adsorption capacity of porous materials, especially the capacity of MOFs.[14,17] Therefore, it is necessary to clarify what are the main parameters to control the hydrogen uptake on various porous materials.

So far, the adsorption capacities on aluminphosphate (AlPO) or silicoaluminphosphate (SAPO) molecular sieves including AFI-type structure[18] such as AlPO-5, SAPO-5 and CoAPO-5 etc. have not been reported in detail[5] even though the AlPO families are versatile in structure and easy to synthesize. In this article, the adsorption capacities of various porous materials including aliminosilicate zeolites, AlPO-5, SAPO-5, SAPO-34, and MOFs have been determined at low temperature in the pressure of 0-760 torr. The results are compared with previous literature data to confirm the accuracy of the measurement. The main parameters to determine the hydrogen uptake are estimated.

Experimental Section

Commercially available HZSM-5 (PQ, $SiO_2/Al_2O_3 = 50$) and HY (Zeolyst, USY, CBV760, $SiO_2/Al_2O_3 = 60$) were used without modification. AlPO-5,[19] SAPO-5,[19,20] SAPO-34,[20] CoAPO-5, and VAPO-5[21] molecular sieves were synthesized as reported previously. MOFs such as MOF-5,[22] MIL-53,[23] MIL-77,[24] MIL-100[25] and manganese formate[26] were prepared as described.

The hydrogen uptake was measured volumetrically after degassing under vacuum (~10^{-5} torr) at 373-676 K. The adsorption capacity was calculated by utilizing the ideal gas law. The adsorption on glass sample holder without any sample was calibrated for the calculation of adsorption capacity. After the adsorption of hydrogen up to about 1 atm, the physisorbed hydrogen was evacuated for 10 min at 77 K and hydrogen was re-adsorbed to estimate the amount of chemisorption by the difference of the two adsorption capacities. The heat of adsorption (ΔH_{ads}) was calculated with the Clausius-Clapeyron equation[27] using the adsorption isotherms at liquid nitrogen (77 K) and liquid argon (87 K) temperatures. The nitrogen adsorption-desorption experiments to measure the surface area and pore volume were carried out using Micromeritics ASAP2400 at 77 K.
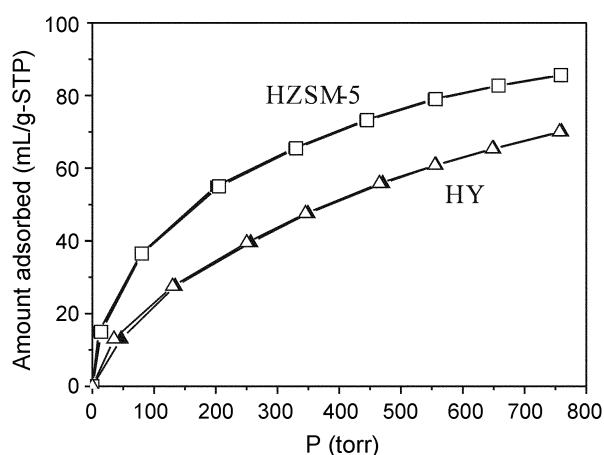
Figure 1. Hydrogen adsorption isotherms on HZSM-5 and HY zeolites at 77 K. The filled symbols and empty symbols represent the adsorption on fresh zeolites and on evacuated zeolites (after desorption of pre-adsorbed hydrogen for 10 min at 77 K under vacuum), respectively.

Results and Discussion

Figure 1 shows the hydrogen adsorption isotherms on HZSM-5 and HY at 77 K. The adsorption isotherms are very similar to those reported by Makarova et al.[28] The adsorption capacity on HZSM-5 is also very similar to that of a previous literature data.[4] Moreover, the adsorption isotherms after the desorption of the pre-adsorbed hydrogen at 77 K are practically same as the isotherms measured on fresh HZSM-5 and HY, representing the negligible contribution of chemisorption on HZSM-5 or HY at 77 K.

Table 1 represents the hydrogen adsorption capacities ($V_{ads}(H_2)$) and sorption properties of various porous materials such as zeolites, AlPO, SAPOs and MOFs. HY zeolite has a smaller amount of hydrogen adsorption compared with

HZSM-5 even though the BET surface area is larger than that of HZSM-5. Similar to the results of HZSM-5 and HY, the $V_{ads}(H_2)$ values of MOF-5 and manganese formate are very similar to those reported in literature,[4,17,26] confirming the accuracy of the adsorption apparatus used in this work.

The adsorption capacities of AlPO-5s and SAPO-5s were measured to understand the effect of silica and cation (mainly proton) of the AFI molecular sieves on the adsorption of hydrogen. As shown in Table 1 (Entry 5-7), the adsorption capacities do not depend noticeably on the content of silica and cation of the AFI molecular sieves including AlPO-5 and SAPO-5. Similarly, the adsorption capacities on vanadium-incorporated AlPO-5 (VAPO-5) and cobalt-incorporated AlPO-5 (CoAPO-5) are nearly same as those on AlPO-5 and SAPO-5s.[29] Moreover, their ΔH_{ads} values do not depend on the silicon contents of the AFI molecular sieves (Table 1). Therefore, the hydrogen adsorption does not depend remarkably on the content of silica and cation, representing that the electrostatic field is not a major factor to control the hydrogen adsorption. More detailed work is necessary to support this preliminary conclusion.

The effect of crystal morphology on the adsorption has been evaluated using spherical SAPO-5 and plate-like SAPO-5 molecular sieves[19] (Entry 6 and 8). The adsorption capacities do not rely on the aspect ratios of the SAPO-5 crystals. The very long AlPO-5 crystal (Entry 9) shows negligible adsorption because of the very low surface area or pore volume (due to pore blocking[19]) rather than the effect of crystal morphology.

The adsorption capacities on various MOFs are also summarized in Table 1 (Entry 11-13). The amount of hydrogen adsorption increases with the following order: MIL-100 > MIL-53 > MIL-77; however, the $V_{ads}(H_2)$ of MIL-77 is not so low considering that the BET surface area of MIL-77 ($S_{BET} = 313$ m^2/g) is only 18-28% of those of MIL-53 ($S_{BET} = 1100$ m^2/g) and MIL-100 ($S_{BET} = 1706$ m^2/g).

Table 1. Hydrogen uptakes on various porous materials measured at 77 K and at 1 atm. The sorption characteristics of the porous materials are also summarized[a]

Entry	Category	Sample	Remark	Evacuation Temp. (°C)	S$_{BET}$ (m^2/g)	S$_\mu$ (m^2/g)	PV$_{total}$ (mL/g)	PV$_\mu$ (mL/g)	$V_{ads}(H_2)$ (mL/g)	Heat of Ads. (kJ/mol)
1	Zeolite	HZSM-5	PQ, Si/Al$_2$ = 50	300	448	394	0.25	0.22	86	ND
2	Zeolite	HY	Zeolyst, USY, Si/Al$_2$ = 60	300	743	533	0.46	0.21	70	ND
3	MOF	MOF-5		100	1603	ND^c	ND	ND	135	ND
4	MOF	Mn-formate		150	280^b	ND	ND	ND	110	ND
5	AlPO	AlPO-5	0 Si/UC	300	319	255	0.25	0.10	59	−5.8
6	SAPO	SAPO-5	1 Si/UC	300	327	271	0.17	0.12	66	−5.5
7	SAPO	SAPO-5	2 Si/UC	300	322	270	0.17	0.11	49	−6.1
8	SAPO	SAPO-5	1 Si/UC, aspect ratio: 0.3	300	268	229	0.14	0.11	60	ND
9	AlPO	AlPO-5	0 Si/UC, aspect ratio: 30	300	3	3	0.0	0.0	4	ND
10	SAPO	SAPO-34		300	633	630	0.29	0.29	160	ND
11	MOF	MIL-53		200	1100	730	0.50	0.23	120	ND
12	MOF	MIL-77		200	313	197	0.14	0.08	85	ND
13	MOF	MIL-100		150	1706	766	0.97	0.32	150	ND

^{a}S$_{BET}$: BET surface area; S$_\mu$: micropore area; PV$_{total}$: total pore volume; PV$_\mu$: micropore volume. ^{b}Determined with CO$_2$ adsorption because nitrogen is not adsorbed due to small pore size. ^{c}ND: not determined.
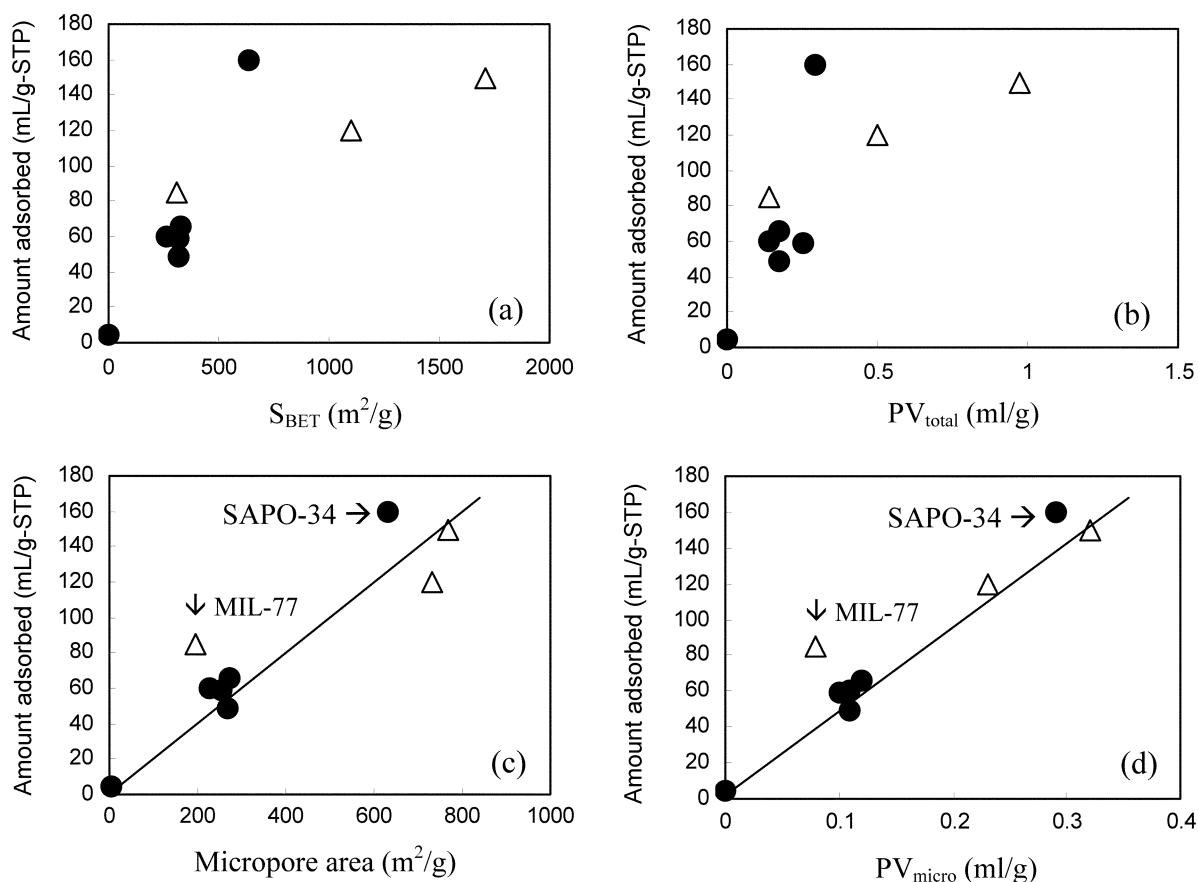
Figure 2. Dependences of hydrogen adsorption capacities on the (a) BET surface area, (b) total pore volume, (c) micropore surface area and (d) micropore volume of the AlPOs and MOFs. The filled circles and empty triangles represent AlPOs and MOFs, respectively.

SAPO-34 has the highest adsorption capacity of 160 mL/g among various zeolites, AlPOs and MOFs even though the BET surface area and pore volume are not so high, illustrating that the porosity is not a major factor to determine the adsorption capacity. The high adsorption capacity on SAPO-34 might be related with the narrow pore size and microporosity (see below).

Figure 2 displays the dependence of hydrogen uptake on textual properties of AlPO and MOFs such as MIL-53, MIL-77 and MIL-100. Even though the linearity is not so high in every case, the adsorption capacity depends fairly well on the micropore volume or micropore surface area, representing that the microporosity is more important for hydrogen adsorption than total porosity as suggested by Nijkamp *et al.*[4] This conclusion can be supported by the adsorption capacity on a mesoporous silica SBA-15 to has $V_{ads}(H_2)$ of 40 mL/g even though its total pore volume is very high (0.85 mL/g).[29] However, SBA-15 has a low micropore volume (0.06 mL/g) and micropore surface area (149 m^2/g). The SAPO-34 and MIL-77 have higher adsorption capacities than the capacities that are expected by the general trends in Figure 2(c) and (d). Similarly, porous manganese formate has comparable adsorption capacity to that on MOF-5 even though the micropore volume of the former adsorbent is very small.[30] This might be related with the narrow pore sizes (and/or

complicated pore architectures) of SAPO-34, manganese formate and MIL-77 compared with those of SAPO-5, MOF-5 and MIL-100, respectively. Further work is necessary to understand the effect of pore size and pore architecture on the hydrogen adsorption.

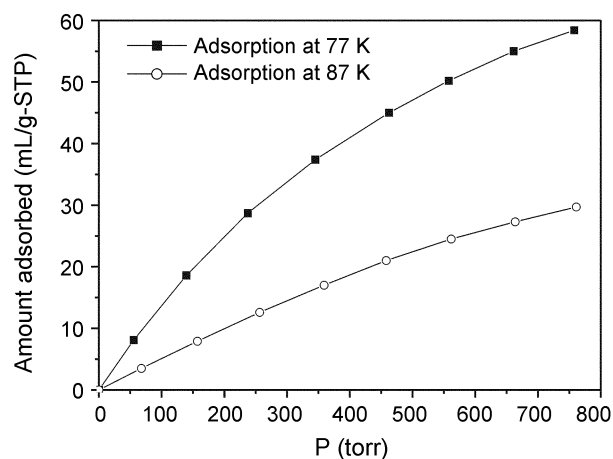Similar to the results of HZSM-5 and HY in Figure 1, all

Figure 3. Hydrogen adsorption isotherms on AlPO-5 at 77 K and 87 K to calculate the heat of adsorption. In this study, the data points of 20 mL/g were used for the calculation.

of the porous materials investigated in this study do not show any difference in the adsorption isotherms on fresh samples and the second re-adsorption after the desorption of the pre-adsorbed hydrogen at 77 K, representing the negligible contribution of chemisorption. The heat of adsorption (ΔH_{ads}) was measured by using the Clausius-Clapeyron equation[27] for AlPO-5 and SAPO-5 to calculate the strength of the hydrogen adsorption. The adsorption isotherms at 77 K and 87 K on AlPO-5 are displayed in Figure 3. As shown in Table 1, the heat of adsorption is about $-5.5 \sim -6.1$ kJ/mol irrespective of the chemical composition of the AFI-type molecular sieves. Moreover, these values are close to the ΔH_{ads} on graphite (4 kJ/mol),[2] meaning that their adsorption behaviors are mainly based on physisorption in nature. Moreover, the ΔH_{ads} values in this study are very similar to that of Li-ZSM-5 ($\Delta H_{ads} = -6.5$ kJ/mol).[31]

Conclusions

The hydrogen adsorption capacities on various porous materials have been volumetrically measured at low temperature in the pressure of 0-760 torr. The adsorption capacities of AFI molecular sieves including AlPO-5 and SAPO-5 do not depend on their silica concentrations, which may show that the electrostatic field is not a major factor for the adsorption capacity. The heat of adsorption and adsorption-desorption-readsorption experiments show that the adsorption is mainly composed of physisorption. Compared with total surface area or total pore volume, the micropore surface area or micropore volume probably has a dominant role in the hydrogen adsorption on the porous adsorbents investigated in this study. Among the porous materials studied, SAPO-34 has the highest adsorption capacity of 160 mL/g due to high microsurface area, micropore volume and narrow pore diameter.

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