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Hydrogen Isotope (H₂ and D₂) Sorption Study of CHA-type Zeolites

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Abstract

Using either single H₂ and D₂ or H₂-D₂ mixed gases, the sorption abilities of CHA-type zeolites ion-exchanged with K, Na or Ca were studied at 77, 201 and 250 K. The LTA(3A) and FAU zeolites were also examined for comparison. The pore diameters in these materials were found to decrease in the order of FAU > Ca-CHA > (K-CHA, Na-CHA and LTA(3A)). The quantities of D₂ adsorbed on these zeolites were larger than the amounts of H₂. At higher temperatures, the CHA-type zeolites having smaller pores exhibited superior D₂/H₂ selectivity compared with the LTA(3A) and FAU, suggesting that hydrogen isotope separation using zeolites is affected by pore size.

Key words:

Zeolite, Porous materials, Hydrogen isotope separation

Introduction

The separation of hydrogen isotopes, which include hydrogen (H, or protium), deuterium (D), and tritium, is important in fusion engineering, and tritium and D have long been regarded as potential fuels for nuclear fusion reactors [1]. These isotopes also have other potential applications. As an example, the synthesis of D-labeled pharmaceutical compounds that exhibit novel properties have been investigated [2]. The separation of hydrogen isotopes on a large scale is currently possible with limited techniques, including cryogenic distillation or the Girdler-Sulfide process [1]. However, these processes are costly, and thus the development of a simple and versatile separation method is required.

Zeolites and related porous materials have long been studied as adsorbents or desiccants [3,4] because their high surface areas and porous structures (having narrow pore diameter distributions) result in large sorption capacities and/or selective sorption properties. Among the zeolites, FAU (so-called Y or X zeolite) [5,6], MOR (mordenite) [7], LTA (3A, 4A and 5A) [8-10] and CHA (chabazite) [11], having pore sizes of 0.74×0.74 , 0.70×0.65 , 0.41×0.41 and 0.38×0.38 nm [12], respectively, have been studied as candidate materials for isotope separation, and the separation performance and sorption kinetics have been reported. At present, LTA and CHA-type zeolites, which have small pores consisting of 8-membered rings, are the most promising materials. Kotoh et al. studied hydrogen isotope adsorption by molecular sieves (MS)-3A containing an LTA(3A) zeolite [8,9]. Using H_2 -HD- D_2 mixed gas, the HD/ D_2 separation factors were determined to be 3.19, 2.60 and 2.20 at 130, 140 and 160 K, respectively. Xiong et al. also evaluated D_2/H_2 separation by LTA(5A) below 77 K [10]. Their cryogenic adsorption and desorption studies determined the heats of adsorption for H_2 and D_2 and the onset temperatures for desorption at 10 mbar as well as the D_2/H_2 selectivity of 8.83 at 30 K and 50 mbar. Recent research with Cs-CHA by Physic et al. demonstrated H_2/D_2

breakthrough separation at 293 K and 0.17 MPa [11] and proposed a new method for separating the D (0.0156 %) that is present in standard grade H₂.

In the present study, the hydrogen isotope separation abilities of CHA-type zeolites containing 8-membered rings were investigated. The K-CHA, Na-CHA, and Ca-CHA were prepared by the hydrothermal conversion of FAU (HY zeolite) and subsequent ion-exchange treatments. The single H₂ and D₂ gas sorption abilities of the resulting materials were examined. Subsequently, a desorption study using a H₂/D₂ mixture was carried out, and the D₂ selectivities of these CHA-type zeolites were evaluated.

Experimental

Materials

Potassium (K⁺)-type CHA was synthesized by the hydrothermal conversion of commercially available HY zeolite with an aqueous KOH solution according to a procedure in the literature [13,14]. The resulting product is designated herein as K-CHA. Subsequently, this K-CHA was ion-exchanged with Na⁺ or Ca²⁺ using aqueous solutions of NaOH or Ca(OH)₂, respectively [15]. FAU (H-Y, Tosoh Corporation, Japan) and LTA-type zeolites (3A, Tosoh Corporation, Japan) were also assessed in this study for comparison and are denoted herein as FAU and LTA, respectively.

Hydrogen isotope adsorption and desorption studies

Hydrogen isotope adsorption isotherms were obtained using an Autosorb-1MP instrument (Quantachrom, USA). Samples were pre-evacuated at 350 °C for more than 15 h. The temperature of the cooling bath was set at either 77, 201, or 250 K. These baths were prepared using either liquid nitrogen, a dry ice/ethanol bath, or a circulating freezer containing ethylene

glycol, respectively. These same cooling baths were also used in a subsequent desorption study.

The desorption studies were performed using a gas sorption apparatus designed in our own laboratory in conjunction with a quadrupole mass spectrometer (Qulee BGM, ULVAC, Inc. Japan) [8,9]. In each case, a zeolite sample of approximately 1.0 g was loaded into a quartz cell and evacuated at 400 °C for 2 h. After cooling to room temperature under vacuum (below 5.0×10^{-5} Pa), the sample was placed in the cooling bath at 77, 201, or 250 K and held at that temperature for 30 min. Following, H₂ (99.99999%), D₂ (99.9%) or H₂-D₂ mixed (50.7/49.3 *vol./vol.*) gas was introduced into the cell to a pressure of 10 kPa, and the specimen was allowed to adsorb the gas for 30 min. In the case of the experiment conducted at 77 K, after 30 min of adsorption, any non-adsorbed gas was evacuated for 30 min using a turbomolecular pump (TMP). On the other hand, in the case of the experiment at 201 and 250 K, the cell was immersed in liquid nitrogen while simultaneously evacuating the gas phase by the TMP for 30 min. In each study, the pressure in the apparatus was reduced to below 5.0×10^{-5} Pa after the 30 min evacuation. The liquid nitrogen cooling bath was subsequently removed, and the sample was allowed to desorb H₂, D₂ or H₂/D₂ as it warmed to room temperature. The hydrogen isotopes released during this stage were quantitatively analyzed by mass spectroscopy. In this mass spectrometric analysis, the HD was not calibrated. However, the ratio of the HD peak area (at $m/z = 3$) to the H₂ peak area (at $m/z = 2$) was found to be almost constant in all experiments, indicating that H-D exchange did not occur to any significant extent. Therefore, the amount of HD was ignored with regard to the quantification of H₂ and D₂ in this study.

Results and discussion

Materials characterization

Figure 1 shows the X-ray diffraction (XRD) patterns generated by the K-CHA, Na-CHA and Ca-CHA. No obvious diffraction signals due to other zeolites, in particular the FAU used as the starting material, are observed in these patterns. Both the Na-CHA and Ca-CHA showed XRD patterns similar to that of the K-CHA, indicating that the ion-exchange process maintained the original CHA structure. The chemical formulas of the samples as determined by energy dispersive X-ray spectroscopy (EDS; JED-2300, JEOL, Japan) and thermogravimetry-differential thermal analysis (TG-DTA; Thermo Plus 2, Rigaku Co., Japan) are summarized in Table 1. The Si/Al ratios in the K-CHA, Na-CHA, and Ca-CHA were found to be 2.5, 2.4, and 2.5, all of which were close to the ratio of 3.2 in the original FAU. The data also indicate that the K^+ cations in the parent K-CHA were not fully exchanged with Na^+ or Ca^{2+} .

Hydrogen isotope sorption properties

H₂ and D₂ single gas adsorption

The H₂ and D₂ adsorption isotherms of the K-CHA, Na-CHA, Ca-CHA, FAU and LTA at 77 K are shown in Figure 2. The Ca-CHA and FAU exhibited a steep uptake at low pressure followed by slower H₂ adsorption at higher pressures. On the other hand, the sorption behaviors of the Na-CHA, K-CHA and LTA were quite different. The amounts of H₂ adsorbed by these materials were very small compared with the quantities adsorbed by the Ca-CHA and FAU throughout the entire pressure range, suggesting that the diffusion of H₂ molecule into the zeolite micropores was hindered. In the case of LTA-type zeolites, the micropore diameter will be affected by the counter cations in the order of $Ca^{2+}(5A) > Na^+(4A) > K^+(3A)$, resulting in a molecular sieving effect [16]. Thus, the change in the sorption properties of the CHA-type zeolites seen in Figure 2 are associated with H₂ sieving. A similar phenomenon was observed in the D₂ sorption experiments at 77 K, during which the Ca-CHA

and FAU exhibited significant adsorption, whereas the Na-CHA, K-CHA and LTA showed less. Table 2 summarizes the amounts of H₂ and D₂ adsorbed at 10 kPa and 77 K. Figure 2 and Table 2 also show that the amount of D₂ adsorption was larger than that of H₂. This result is in agreement with previous studies, which have determined that CHA [17], LTA [8,10] and FAU [5] all preferentially adsorb D₂. Figure 2 and Table 2 also suggest that the pore diameters decrease in the order of FAU > Ca-CHA > (K-CHA, Na-CHA and LTA).

Table 2 summarizes the amounts of H₂ and D₂ adsorbed at 201 K and 250 K at 10 kPa when introduced as single gas. The adsorption amounts decreased with increases in the adsorption temperature, indicating that temperature has an effect on sorption ability [10]. However, it is worth noting that the amounts of H₂ and D₂ adsorbed by the K-CHA and Na-CHA were comparable to those adsorbed by the Ca-CHA. These data confirm that the K-CHA and Na-CHA, as well as the LTA, could adsorb H₂ and D₂ at around 201 K. Interestingly, the D₂/H₂ adsorption ratios remained above 1.0 even at 250 K, although the values were closer to 1.0 at the higher temperature.

H₂ and D₂ single gas desorption

Based on the above findings, the desorption of H₂ or D₂ single gases were measured using an apparatus of our own design and the procedures described in the Experimental section. The amounts of H₂ and D₂ desorbed from the K-CHA, Na-CHA, Ca-CHA, FAU and LTA are summarized in Table 3 and demonstrate that these uptake amounts were affected by both temperature and pore size. In the case of the K-CHA, Na-CHA and LTA (the small pore samples), the H₂ and D₂ uptake amounts at 77 K were smaller than the values expected on the basis of the adsorption studies (Table 2). It is possible that the relatively short gas exposure time did not allow the samples to reach sorption equilibrium, which was found to require more than 20 h in the adsorption experiments. In addition, in the case of the FAU (which had

large pores) or even the Ca-CHA, the uptake amount was smaller than that expected from the data in Table 2. This discrepancy is attributed to the ready desorption of H₂ or D₂ during TMP evacuation following adsorption.

At the higher gas loading temperature of 201 K, the uptake amount was increased compared to the value at 77 K. This result shows that some amounts of H₂ and D₂ were adsorbed in the K-CHA, Na-CHA and LTA, which had smaller pores. Thus, it appears that the pore sizes were slightly increased by the thermal expansion of the zeolite framework such that H₂ molecules were able to migrate into the zeolite cages [8,9]. Following quenching of the samples by liquid nitrogen, after loading with H₂ and D₂ such that the pore sizes were decreased in size at 77 K, the adsorbed H₂ and D₂ were encapsulated inside the zeolite.

The resultant uptake amounts summarized in Table 3 are similar to the amounts adsorbed under equilibrium conditions (Table 2), except in the case of the FAU. The consistency of these data allows a quantitative evaluation of the amounts of encapsulated H₂ and D₂. These results also indicate that the only a minimal amount of H₂ or D₂ is removed from the samples by TMP evacuation. It should also be noted that the uptake amount exhibited by the FAU, which had large pores, was very small, likely due to continuous desorption during the TMP evacuation as was also observed during the experiment at 77 K. At the relatively high temperature of 250 K, the uptake amounts were decreased compared to those at 201 K. The H₂ or D₂ adsorption amount decreased with an increase of temperature [10] as shown in Table 2. It is also confirmed that the FAU uptake amount was the lowest among the samples. On this basis, the desorption of a H₂-D₂ mixed gas was subsequently examined.

Desorption of H₂-D₂ mixed gas

Employing the same procedure as with the single gases but using a H₂-D₂ mixed gas (50.7/49.3, *vol./vol.*), the desorption properties were further investigated. The amounts of H₂ and D₂ desorbed following loading at 77, 201 and 250 K are summarized in Table 4 and show that the lowest desorption amount was obtained at 77 K loading. This result is ascribed to insufficient gas uptake during the relatively short exposure period, as was discussed in Table 3. In contrast, substantial gas desorption was observed at both 201 K and 250 K. Interestingly, the small pore zeolites (CHA and LTA) showed larger D₂ desorption than H₂ desorption, except for the Na-CHA at 250 K. In addition, the D₂/H₂ ratio was greater than 1.0 for the CHA and LTA zeolites, suggesting a high selectivity for D₂. The D₂ affinities of these materials were evaluated by defining selectivity (S_{D_2/H_2}) as the following equation (1) [8,17]:

$$S_{D_2/H_2} = \frac{(x_{D_2}/x_{H_2})}{(y_{D_2}/y_{H_2})} = \frac{x_{D_2} \cdot y_{H_2}}{x_{H_2} \cdot y_{D_2}}, \quad (1)$$

where x and y are the mole fractions of H₂ or D₂ in the adsorbed and gas phase, respectively.

In Figure 3, the S_{D_2/H_2} values at 77, 201 and 250 K are plotted as a function of the crystallographic pore sizes of the CHA (0.38×0.38 nm), LTA (0.41×0.41 nm), and FAU (0.74×0.74 nm) zeolites. The error bars represent the ranges of three to five replicated measurements. Although the uptake amounts were low at a loading temperature of 77 K (Table 4), the largest S_{D_2/H_2} (1.07) was obtained with the LTA. The S_{D_2/H_2} values of the CHA zeolites were lower than those of the LTA, and thus the plot has a convex shape.

In contrast, at 201 K, the S_{D_2/H_2} values increased as the pore size decreased such that the largest value was obtained for the Na-CHA (1.15) rather than for the LTA. At 250 K, the S_{D_2/H_2} for the Ca-CHA and K-CHA were 1.05 and 1.03, respectively, both of which were larger than that for the LTA (1.01), although this S_{D_2/H_2} value was decreased compared with

that at 201 K. From these data, it is apparent that the pore sizes giving the highest D₂ selectivity became smaller as the loading temperature was increased.

These experiments show that the H₂ and D₂ sorption properties, including D₂ selectivity, depend on both the temperature and the zeolite pore size. Since the gas composition is independent from the release of encapsulated H₂ and D₂, the change in S_{D_2/H_2} evident in Figure 3 mainly result from the different adsorption properties of H₂ and D₂. The Na-CHA, K-CHA and LTA (all having small pores) adsorbed very little H₂ or D₂ at 77 K but were able to adsorb these gases at 201 and 250 K. According to the molecular dynamics (MD) simulation studies by Kumar and Bhatia, obvious differences of diffusivity between H₂ and D₂ were not found at higher temperature (typically above 100 K~) [18-20]. D₂ molecules (0.269 nm) are also smaller than H₂(0.289 nm) [6] and therefore preferentially pass through the zeolite pores. These results suggest that it may be possible to separate hydrogen isotopes by sieving at or above 200 K, where the intrinsic pore size plays a crucial role in determining the onset temperature. At present, however, in Figure 3, the role of cations is not considered, although the cation size ($K^+ > Na^+ > Ca^{2+}$) is known well to affect the pore size in LTA [16]. Both pore size and the specific cations is thought to affect the selectivity of the CHA-type zeolites. Beside, the Si/Al ratio in a zeolite can change and modify the concentrations of cations. The detail of the effects of cations will be intended in future work.

Conclusions

The hydrothermal conversion of FAU and subsequent ion-exchange treatments provided K-, Na- and Ca-CHA. The K⁺ cations were not fully exchanged with Na⁺ or Ca²⁺ and that the CHA zeolite framework was maintained during the ion-exchange treatment.

Both the K-CHA and Na-CHA adsorbed minimal amounts of H₂ and D₂ at 77 K, and single gas adsorption experiments determined that the pore diameters in the specimens

decreased in the order FAU > Ca-CHA > (K-CHA, Na-CHA and LTA). The adsorption capacity of the zeolites decreased with increases in temperature, and higher temperatures allowed the small pore zeolites (K-CHA, Na-CHA and LTA) to adsorb both H₂ and D₂, suggesting that pore sizes were extended due to thermal expansion of the zeolite framework. The H₂ and D₂ uptake amounts evaluated from these sorption studies indicated the preferential adsorption of D₂. A S_{D_2/H_2} value of 1.15 was obtained for the Na-CHA using a H₂-D₂ mixed gas at 201 K, which was larger than the value of 1.08 determined for the LTA. The CHA-type zeolites showed larger S_{D_2/H_2} values than the LTA above 201 K.

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Figure captions

Fig. 1 The XRD patterns of the K-CHA, Na-CHA and Ca-CHA prepared. The triangles mark the peaks assignable to CHA-type zeolite.

Fig. 2 The hydrogen adsorption isotherms obtained by the CHA, LTA and FAU-type zeolites at 77 K.

Fig. 3 Selectivity values (S_{D_2/H_2}) at 77, 201 and 250 K as a function of the crystallographic pore sizes of the CHA, LTA and FAU-type zeolites. The error bars indicate the data ranges obtained from three to five replicated measurements.

Table 1. The composition of zeolites used in this study.

Sample Code	Composition
K-CHA	$K_{10.8}[Si_{25.6}Al_{10.4}O_{72}] \cdot 29.5H_2O$
Na-CHA	$(Na_{3.5}K_{7.2})[Si_{25.3}Al_{10.7}O_{72}] \cdot 28.1H_2O$
Ca-CHA	$(Ca_{3.1}K_{5.8})[Si_{25.8}Al_{10.2}O_{72}] \cdot 30.7H_2O$
FAU	$(Na_{12.9}H_{32.5})[Si_{146.6}Al_{45.4}O_{384}] \cdot 140H_2O$
LTA	$(Na_{5.8}K_{5.9})[Si_{12.1}Al_{11.9}O_{48}] \cdot 17.4H_2O$

Table 2. The amounts of H₂ and D₂ single gas adsorbed under equilibrium conditions at 10 kPa at various temperatures.

Sample Code	77 K		201 K		250 K	
	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹
K-CHA	41.8	54.1	15.9	18.4	5.68	5.97
Na-CHA	158.8	204.6	12.7	14.3	5.51	6.08
Ca-CHA	2034.3	2526.2	16.4	18.8	5.20	5.28
FAU	1032.1	1279.5	9.7	11.5	4.95	5.05
LTA	30.7	30.8	7.3	11.1	n.d.	n.d.

Table 3. The uptake amounts of H₂ and D₂ single gas at 10 kPa and various temperatures.

Sample Code	77 K		201 K		250 K	
	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹
K-CHA	2.04	3.30	15.23	15.49	8.28	8.32
Na-CHA	0.65	1.45	11.11	12.33	7.15	5.90
Ca-CHA	3.36	4.07	15.30	17.91	11.93	11.08
FAU	0.46	0.05	1.93	3.01	2.09	1.57
LTA	0.15	0.84	8.58	9.95	4.19	4.08

Table 4. The H₂ and D₂ uptake amounts from H₂-D₂ mixed gas at 10 kPa and various temperatures.

Sample Code	77 K		201 K		250 K	
	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹	H ₂ / mmol g ⁻¹	D ₂ / mmol g ⁻¹
K-CHA	1.01	0.96	7.09	7.57	1.17	1.17
Na-CHA	0.73	0.68	3.83	4.22	2.06	2.00
Ca-CHA	4.97	4.70	5.91	6.11	5.60	5.70
FAU	n.a.	n.a.	1.01	0.96	n.d.	n.d.
LTA	0.52	0.54	4.00	4.22	1.45	1.41

Figure 1

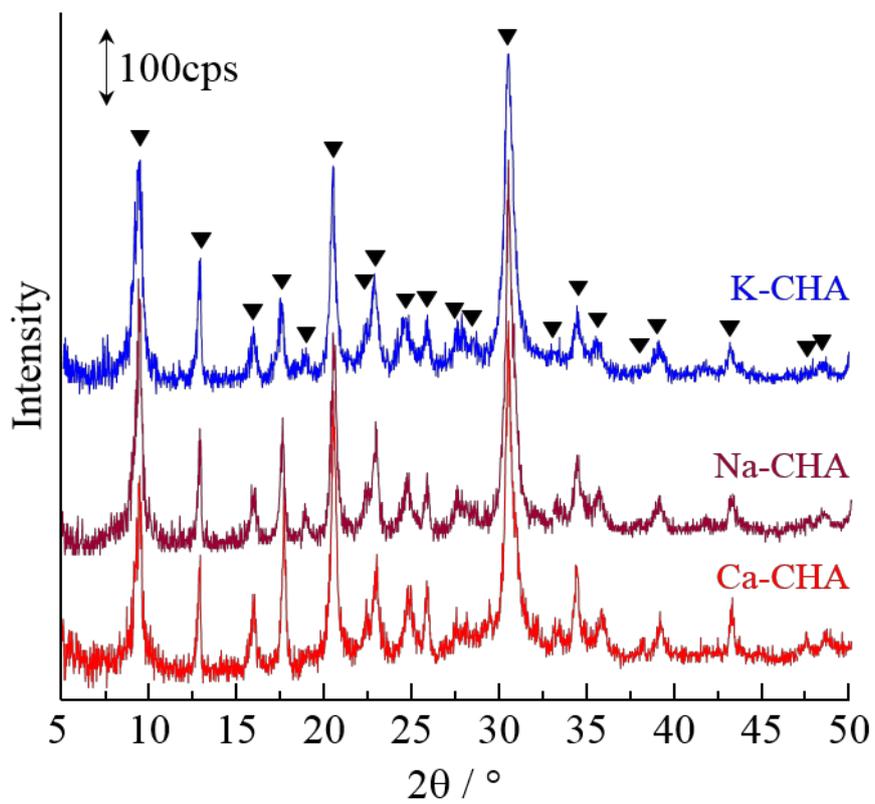


Figure 2

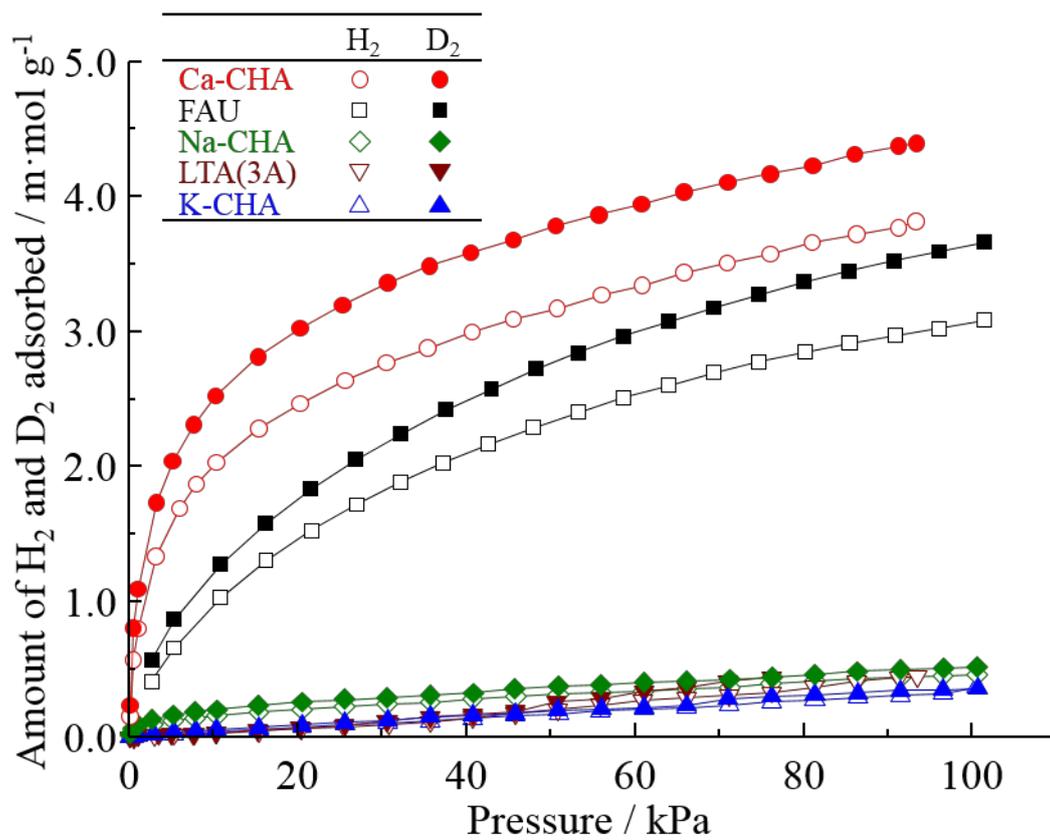


Figure 3

