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Adsorption capacity of hydrogen isotopes on mordenite

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ABSTRACT

In a fusion reactor system, a monitoring of hydrogen isotopes including tritium is necessary for the safety of system control and operation. A gas chromatography using a cryogenic separation column is one of the methods for hydrogen isotope analysis. Synthesis zeolite such as molecular sieve 5A (CaA) is a candidate material of the separation column, and its property varies by the ratio of silica to alumina, the kinds of cation and so on. If the factor affected the hydrogen adsorption property of the synthesis zeolite is clarified, it may lead to the development of the new zeolite optimized to the separation column. So, in this work, adsorption capacity of hydrogen (H_2) and deuterium (D_2) for mordenite (MOR) and NaY type zeolite (NaY) were investigated at various temperatures, and were compared with CaA. The amount of adsorption per unit weight of MOR was larger than that of CaA, and that of NaY was smaller than that of CaA. The adsorption isotherms were expressed by sum of two Langmuir equations, and the Langmuir coefficients of H_2 and D_2 were proposed. Furthermore, the Langmuir coefficients of HD, HT, DT and T_2 were estimated by the reduced mass. The correlation between the adsorption properties and the physical parameters of the zeolite were not confirmed.

1. Introduction

In a nuclear fusion reactor system, measurement and analysis of hydrogen isotopes including tritium are necessary from the viewpoint of safety of system control and operation. A gas chromatograph (GC) with a cryogenic separation column is one of the methods for hydrogen isotope analysis. Alumina is a typical packed material of the cryogenic separation column, and it is used at liquid nitrogen temperature (77 K). However, use of liquid nitrogen is a cause of long analysis time (tens of minutes). The long analysis time becomes a weak point when a GC with a cryogenic separation column is used as process monitor. The present author has proposed to use a micro gas chromatograph (micro GC) for hydrogen isotope analysis and has developed the cryogenic separation column for micro GC, and has reduced the analysis time to less than a few minutes successfully [1–3]. However, liquid nitrogen is still used to cool the separation column, and it is an obstruction to good sensitivity and easy installation of micro GC. The development of the column material having separation capability at the temperature, which can be reached by an electric device, is one of the solutions for this weak point. Synthesis zeolite is a probable candidate of the column material. Its structure varies by the ratio of silica (SiO_2) to alumina (Al_2O_3), the kinds of cation and so on, and it gives the unique function to each zeolite. If the factor effected to the hydrogen adsorption property of the synthesis zeolite is clarified, it may lead to the development of the new zeolite optimized to the hydrogen isotope separation column. Therefore, investigation of the hydrogen adsorption properties about various synthesis zeolite is necessary. Molecular sieve 5A (CaA) is a typical packed material of separation column, and its hydrogen adsorption capacity at various temperatures has been already investigated [4]. Mordenite (MOR) is also a kind of a synthesis zeolite, and it has been reported that the separation column with it can separate hydrogen isotope mixture at fairly high temperature [5,6]. However, its specific data have been not clearly indicated. The investigation of sorption rate and its isotope effect is necessary to evaluate a material that is suitable for GC separation column or not. And, to evaluate the sorption rate and its isotope effect, the investigation of the adsorption capacity (adsorption isotherm) of hydrogen isotopes on the material is needed. This is also necessary to investigate the factor that affects the isotope effect of hydrogen adsorption on the material. So, in this work, as a first step of the evaluation as a GC separation column and of the investigation of the factor effected to the isotope effect on hydrogen adsorption, hydrogen (H_2) and deuterium (D_2) adsorption capacities of MOR are investigated. And then, that of Y type zeolite (NaY) is also investigated to compare with CaA and MOR.

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2. Experimental

MOR and NaY used in this work were the high silica zeolite (HSZ-642NAA and HSZ-320NAA) purchased from TOSOH Co. The cation in common with these zeolites is sodium ion (CaA includes not only sodium ion but also calcium ion). The ratio of silica/alumina of MOR and NaY are about 20 and 5, respectively, and are larger than CaA (Si/Al = 2). It is necessary to notice that MOR used in this work does not include calcium ion and is not same one in Refs. [5,6]. Sample specifications are listed in Table 1.

Fig. 1 shows the schematic diagram of the experimental apparatus. A volumetric method was applied to the measurement of adsorption isotherm. The measurements of the system volume (the sample container, piping and the sample) were carried out using helium gas, and were based on the reference volume whose volume was known. The experimental procedures were as follows:

(1) The sample was charged into the sample container, and was kept at 473 K under the vacuum condition for 12 h or more to eliminate the residual water.
(2) The sample container was immersed into the refrigerant to cool down the sample to the experimental temperature.
(3) The experimental apparatus was isolated from the vacuum system by closing the isolation valve, and the system pressure was recorded, and then, the sample container was isolated by closing the sample isolation valve.
(4) The sample gas (H_2 or D_2) was introduced to the reference volume including the piping, and the system pressure was recorded.
(5) The sample isolation valve was opened to start adsorption. The system pressure change was recorded until the equilibrium state was attained.
(6) The amount of the sample gas residual in gas phase of the experimental apparatus was calculated from the system pressure, the system volume and temperature, and then, the amount of adsorption was obtained by subtracting it from the amount of the sample gas introduced at procedure (4).
(7) The sample container was isolated again, and the procedure was returned to (4). Then, the procedures (4–7) were repeated until the system pressure was attained to the certain pressure.

Table 1
Sample specification

Brand name	HSZ-642NAA	HSZ-320NAA	MS-5A
Type	MOR	NaY	CaA
Cation	Na^+	Na^+	Na^+, Ca^{2+}
Pore size (Å)	7	8	5
BET surface area (m^2/g)	360	700	650
SiO_2/Al_2O_3	17.8	5.5	2
Na (Ca)/Al_2O_3	1.05	1	0.38 (0.42)

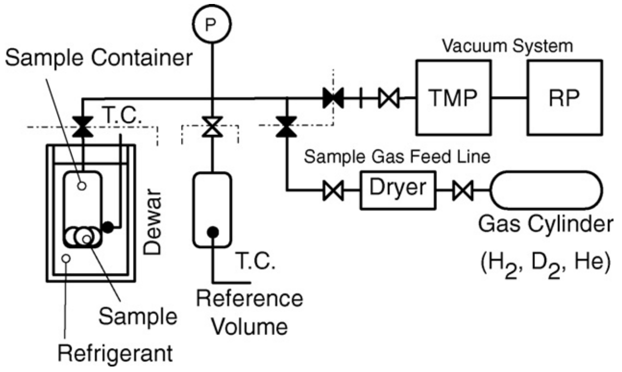

Fig. 1. A schematic diagram of the experimental apparatus.

Table 2
An experimental condition

	Sample	
	MOR	NaY
Charged weight [g]	17.02	15.03
Adsorbate	H_2, D_2	
Temperature [K]		
N_2 (boling point)	77	
Ar (bp)	87	
Isopentane (melting point)	113	
n-Pentane (mp)	143	
Dry ice in ethanol	195	
System volume [cm^3]		
Reference volume	104.3	
Sample container	186.7	
Piping	35.6	

The experimental temperature was changed from 77 K to 195 K by using various refrigerants. When the sample container was immersed into the refrigerant, temperature gradient was on the sample container. So, the net volume of the sample container was not able to use for the calculation of adsorbed amount. Therefore, the apparent volume of the sample container was measured at each experimental temperature, and was used for the calculation. The experimental conditions were listed in Table 2.

3. Results and discussions

Fig. 2 shows the adsorption capacity of H_2 (top) and D_2 (bottom) on MOR at various experimental temperatures. The adsorption capacity decreased with increase of temperature. The amount of

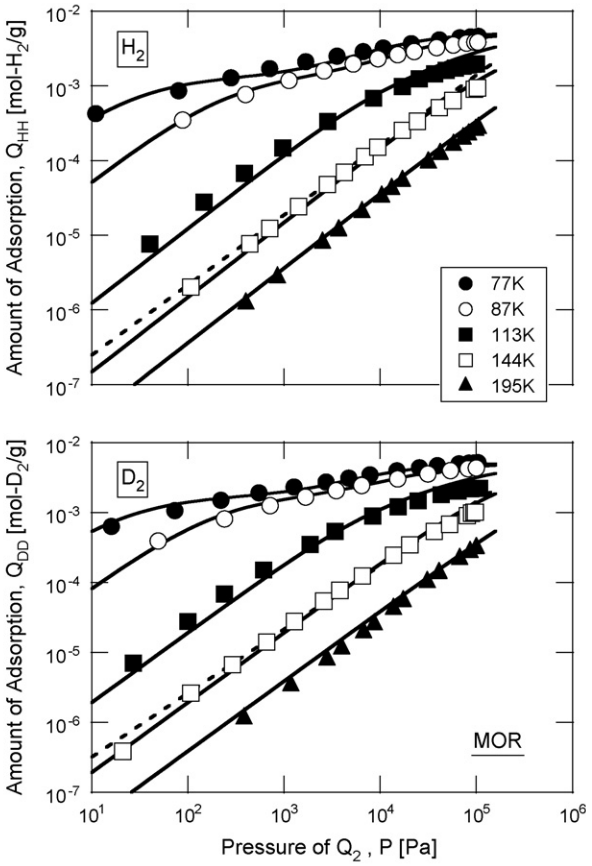

Fig. 2. Adsorption capacity of H_2 (top) and D_2 (bottom) on MOR at various temperatures.