Adsorption Characteristics of Water Vapor on Zeolitic Materials for Honeycomb-Type Adsorbent*)

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Tritium release in nuclear fusion power plants must be recovered as efficiently as possible in air cleanup system (ACS). In conventional ACS, the tritium gas is oxidized by catalysts, and then tritiated water vapor is collected by adsorbents, whereas which has a problem related to large ventilation force required to overcome high pressure drop in catalyst and adsorbent beds. Honeycomb-type catalyst and adsorbent offer a useful advantage in terms of their low-pressure drop, and honeycomb-type adsorbent using sepiolite-binder is feasible ability for application of ACS. In this study, we examined adsorption characteristics of water vapor on the building material, zeolitic materials using sepiolite-binder, for honeycomb-type adsorbent by changing temperature and concentration of water vapor, in comparison with those for conventional pebble-type adsorbent, and the experimental data were evaluated using Langmuir and Freundlich isotherm models. Each type of adsorbent includes mainly zeolite-4A. Adsorption capacity of zeolitic materials for both adsorbents gradually decreased with decreasing partial pressure of water or increasing temperature, and experimental data are found to fit Langmuir than Freundlich. The maximum adsorption capacity of water vapor on zeolitic material for honeycomb-type adsorbent, which was calculated by Langmuir isotherm model, is comparable to that for pebble-type adsorbent, and heat of water adsorption on zeolitic material for honeycomb-type adsorbent was higher than that for pebble-type adsorbent. These results indicate that honeycomb-type adsorbent using sepiolite-binder is applicable to ACS.

Keywords: tritium safety, air cleanup system, honeycomb-type adsorbent, pebble-type adsorbent, water vapor, nuclear fusion plant

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1. Introduction

Multiple confinement systems comprise components designed on the principal safety to confine tritium in nuclear fusion plants. Tritium in such nuclear fusion power plants must be safely confined in processing systems and tritium release should be recovered as efficiently as possible in an air cleanup system (ACS). In conventional ACS, the tritium gas, which leaks to rooms by an accident, is oxidized by catalysts, and then tritiated water vapor is collected by adsorbents [1]. This method is expected to enable a recovery ratio more than 99% for hydrogen isotopes. If an accident occurs in an experimental fusion facility, tritium gas could leak into experimental rooms, which requires processing of large volumes of air with the ACS. Also, in large magnetic fusion plasma experimental facility, workers will enter the vacuum vessel should be first clean up after experiments [2]. Hence, the ACS should be designed to process gases under He condition of high volumetric rates.

The high throughput of air causes substantial pressure drop in the catalyst and adsorbent beds, which results in high load on the pumping system and compressors. In the previous study, we examined the applicability of honeycomb catalysts, which are generally used in the automotive industry, to a tritium recovery system. The honeycomb catalyst has an advantage in terms of pressure drop, which is far lower than that in conventional packed particulate catalyst beds, because the open area of the honeycomb catalyst is comparatively large. The pressure drops across catalyst beds were compared by calculation elsewhere and it was shown that the pressure drop in a honeycomb catalyst was smaller than that in a packed bed catalyst by one or two orders of magnitude [1]. A comparison of the two types of bed revealed that the honeycomb catalyst was clearly expected to be suitable for a high throughput of air [3, 4]. Also, the applicability of honeycomb-type adsorbents to water adsorption in an ACS was examined and the pres-

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sure drop in a honeycomb-type adsorbent was found to be smaller by one or two orders of magnitude than in a pebble-type adsorbent, and the adsorption rate in a honeycomb-type adsorbent was higher than that in a pebble-type adsorbent [5]. In addition, adsorption capacity of honeycomb-type adsorbent using sepiolite binder was almost same as that of pebble-type adsorbent, while the adsorption rate in a honeycomb-type adsorbent was higher than that in a pebble-type adsorbent [6]. Therefore, honeycomb-type adsorbent using sepiolite-binder is one of the strong candidates for the application of ACS.

Adsorption characteristics of honeycomb-type adsorbent depend on the chemical characteristics of adsorbent, such as zeolite type and binder-type, and the physical characteristics, such as structure of adsorbent. In this study, we investigated the chemical characteristics of the building material, zeolitic material using sepiolite-binder, for honeycomb-type adsorbents to an ACS. The water vapor adsorption capacity of the materials for adsorbent was examined by changing temperature and concentration of water vapor, and the experimental data were evaluated using isotherm models, in comparison with the zeolitic material for conventional pebble-type adsorbents.

2. Experimental

2.1 Sample

Experiments were performed using the zeolitic materials for honeycomb-type adsorbent and pebble-type adsorbent, which were used in previous papers [5, 6]. For comparison of water adsorption capacity, the zeolitic materials were obtained after the adsorbents were grounded by mill under 500 µm (physical effect of the adsorbent was diminished). Both adsorbent mainly composed of zeolite-4A, determined by X-ray diffraction (XRD) (Figure 1). It is noted that the XRD patterns of binder, such as sepiolite, are undetectable due to the much smaller amount than zeolite 4A.

2.2 Water vapor adsorption

The experiments were conducted by the breakthrough method. Figure 2 shows a flow diagram of the experimental apparatus used in this study. Sample adsorbents were packed in a tubular reactor made of quartz. 0.1-0.2 g of each adsorbent was charged in a reaction tube with 0.6 cm of the inner diameter. The reactor was heated up to 673 K, and kept for 8 h under dried Ar-gas flow to desorb remaining water before each experiment. The water concentration in H_2O/Ar mixed gas at the inlet of sample bed was controlled by the hydrogen oxidizing method. That is to say, H_2/Ar mixed gas was passed through the cold trap (28 mm in diameter, and 200 mm in length) that was a packed column of molecular sieves 3A held at 273 K using ice in dewar flask to remove residual water in the mixed gas, and was introduced into a granular CuO bed (20 mm in diameter, and 225 mm in length) which was heated to 673 K to change H_2 to H_2O completely. Ar gas containing water vapor of a certain partial pressure was passed through the sample bed after setting it to an experimental temperature (303-323 K) with a constant temperature water bath, and the change of water vapor concentration in the outlet gas of sample bed was traced with time by a hygrometer (Transmet IS, Michell Instruments Ltd.). Ar gas containing water vapor was passed through the sample bed until an equilibrium state was attained.

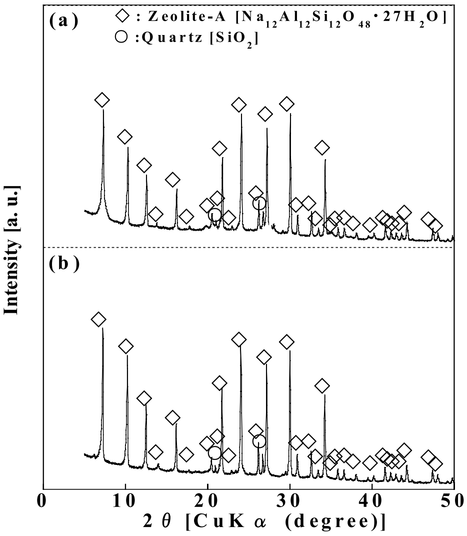

Fig. 1 XRD patterns of (a) honeycomb-type adsorbent and (b) pebble-type adsorbent.

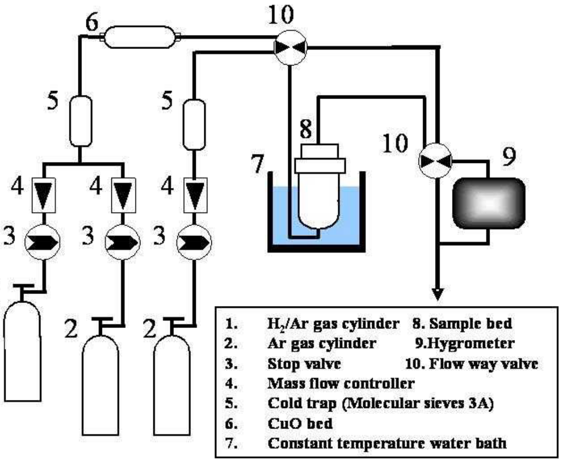

Fig. 2 Experimental apparatus of water vapor adsorption.

3. Results and Discussion

Figure 3 shows the amounts of water adsorbed on both zeolitic materials using adsorbents at various temperatures, as the function of partial pressure of water. The adsorption amounts of water on the materials were investigated in the partial pressure range of 30-2000 Pa. The experimental results indicate that the adsorption capacities of water vapor on both the materials increased with increasing par-

Table 1 Parameters and correlation regression using Langmuir and Freundlich models.

Adsorbent	Temperature [K]	Langmuir model			Freundlich model		
		q_{max}[mmol/g]	$K_L \times 10^3$[1/Pa]	R^2	n	K_F [mmol/(g·Pa)]	R^2
Pebble-type	393	6.82	6.77	0.994	2.85	0.52	0.985
	353	8.42	9.98	0.999	3.37	0.98	0.972
	323	10.03	13.88	0.999	3.39	1.25	0.988
	303	10.00	15.47	1.000	12.82	5.41	0.981
Honeycomb-type	323	9.28	23.10	0.998	4.86	2.28	0.904
	313	9.52	32.13	0.999	6.63	3.37	0.960
	273	9.68	85.24	0.999	6.09	4.07	0.992

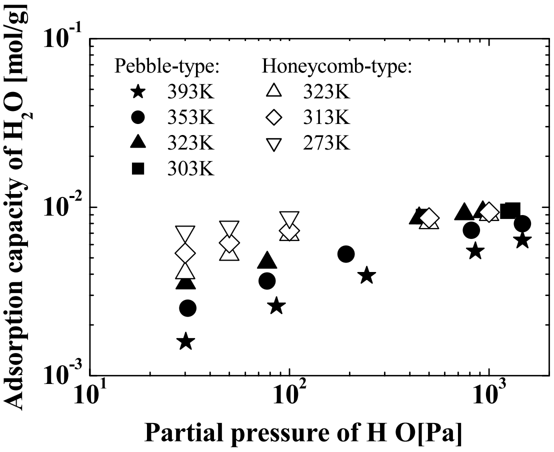

Fig. 3 Amount of water adsorbed on honeycomb-type and pebble-type adsorbents at various temperatures.

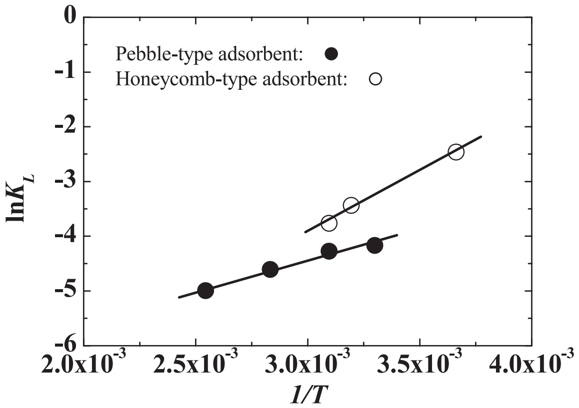

Fig. 4 Plot of lnK_L vs 1/T for pebble-type and honeycomb-type adsorbents.

tial pressure of water, while they increased with decreasing temperature. The adsorption capacity of water vapor on the materials became almost saturated in the temperature range of 273-323 K at higher than 400 Pa, and the adsorption capacity of water vapor on the zeolitic materials for honeycomb-type adsorbent is comparable to that for a conventional pebble-type adsorbent. Thus, the adsorption capacities of water vapor on the zeolitic material using sepiolite-binder are almost same as that using different binder for pebble-type adsorbent.

The equilibrium distribution of water vapor between the solid adsorbent phase and the gas phase is important in determining the maximum sorption capacity. Several isotherm models are available to describe the equilibrium sorption distribution in which two models are used to fit the experimental data: Langmuir and Freundlich models.

The liner form of Langmuir model is given by

$$\frac{p}{q_e} = \frac{1}{q_{max} \cdot K_L} + \frac{p}{q_{max}}, \tag{1}$$

where p is partial pressure of water vapor; q_e is adsorbed amount of water vapor on the adsorbent at equilibrium (mmol of water vapor / g of the adsorbent); q_{max} mmol/g and K_L 1/Pa are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites and a measure of adsorption energy (equilibrium adsorption constant), respectively.

The liner form of the Freundlich model is also given by:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(p), \tag{2}$$

where K_F mmol/(g · Pa) and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich isotherm models were applied to the experimental data as present in Fig. 3, and parameters calculated by each isotherm models were shown in Table 1. Our experimental results give correlation regression coefficient (R^2) for the measure of goodness-of-fit. It can be seen that the Langmuir model has better fitting than the Freundlich one as the former has a higher correlation regression coefficient than the latter. The maximum adsorption capacity (q_{max}), which was calculated by Langmuir isotherm model, increased with decreasing temperature, and that on the zeolitic materials for honeycomb-type adsorbent is comparable to that for pebble-type adsorbent in the temperature range of 273-323 K.

The heat of adsorption (E_{ad}), which is one of the key thermodynamic variables for the design of adsorption system, can be calculated using following the liner equation:

$$\ln K_L = \ln K_0 + \frac{E_{ad}}{RT}, \tag{3}$$

where T is the absolute temperature (K), K_0 is the characteristic constant (1/Pa), E_{ad} is the heat of adsorption

(J/mol), and R is the gas constant (8.314 J/(mol · K)). The equation (3) was applied to the data of Table 1 as presented in Fig. 4. The heats of adsorption for pebble-type and honeycomb-type adsorbents, which were calculated by Fig. 4, are 9.88 and 18.57 kJ/mol, respectively, and the positive sign for E_{ad} indicates that the adsorption reactions of both adsorbents are exothermic reaction. Heat of adsorption for honeycomb-type adsorbent is higher than that for pebble-type adsorbent, which indicates that water adsorption on honeycomb-type adsorbent including sepiolite is more effective than that on pebble-type adsorbent. Also, in previous papers for water adsorption of zeolite 4A, heat of adsorption of the zeolite 4A adsorbents was 50-70 kJ/mol [7–10]. It could be considered that the honeycomb-type adsorbent including zeolite 4A has a potential to improve adsorption performance of water vapor.

Thus, honeycomb-type adsorbent using sepiolite binder could be used to adsorb water vapor as well as pebble-type adsorbent, and has a great potential as effective adsorbent for the removal of tritiated water by improving chemical characteristics and physical factor in the future.

4. Conclusion

In order to develop a high performance adsorbent for tritiated water vapor, the properties of the zeolitic materials using sepiolite-binder for honeycomb-type adsorbent were experimentally studied with the following results:

(1) The adsorption capacities of water vapor on each adsorbent are almost same in the range of temperature between 273 K and 323 K. The adsorption capacity of water vapor on the zeolitic materials for honeycomb-type adsorbent is comparable to that for conventional pebble-type adsorbent.

(2) The adsorption behavior of water vapor on the materials for honeycomb-type and pebble-type adsorbent found to fit the Langmuir isotherm model than Freundlich model. The maximum adsorption capacity of water vapor, which was calculated by Langmuir isotherm model, on the zeolitic materials for honeycomb-type adsorbent is comparable to that for pebble-type adsorbent, while heat of adsorption of the materials for honeycomb-type adsorbent is higher than that for pebble-type adsorbent.

(3) The honeycomb-type adsorbent using sepiolite binder is a viable alternative to conventional pebble-type adsorbent for use in a high-performance ACS by improving the chemical and physical characteristics in the future.

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[1] T. Uda *et al.*, Fusion Sci. Technol. **48**, 480 (2005).
[2] Y. Asakura *et al.*, Fusion Sci. Technol. **48**, 401 (2005).
[3] T. Uda, M. Tanaka and M. Munakata, Fusion Eng. Des. **83**, 1715 (2008).
[4] M. Tanaka *et al.*, Fusion Eng. Des. **84**, 1818 (2009).
[5] T. Wajima *et al.*, J. Nucl. Mater. (In Press).
[6] T. Wajima *et al.*, Fusion Eng. Des. **85**, 1064 (2010).
[7] T. Mizota *et al.*, Thermochim. Acta **266**, 331 (1995).
[8] J.C.M. Muller *et al.*, J. Therm. Anal. **53**, 449 (1998).
[9] W. Zhu *et al.*, J. Membr. Sci. **253**, 57 (2005).
[10] K. Hashiguchi *et al.*, J. MMIJ **117**, 875 (2001).