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Research Note

繰り返し使用したMCM-41からのトリチウム水の脱着

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Desorption of tritiated water from reused MCM-41

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Abstract

The mesostructure and tritium desorption properties of as-synthesized MCM-41 and that after 5 cycles of sequential H_2O impregnation/desorption have been compared. The XRD and tritium desorption experiments showed good reusability and reproducibility in the enrichment of tritiated water.

Research note

The enrichment of tritiated water is an important and indispensable task in tritium (T) recycling and environmental protection. Although there are several methods for deuterium enrichment that are practically available and used in operations, these methods, such as gas diffusion, distillation, and electrolysis [1], are not applicable to T enrichment because of their high cost and low efficiency. The development of a novel method for the enrichment of T from tritiated water has long been required. Selective sorption and separation of T with certain adsorbents is an attractive method. Zeolites, a family of microporous aluminosilicates, are one of the candidates for adsorbents, and much effort has been devoted in optimizing the operation conditions [2].

Mesoporous silicas, such as MCM-41 [3,4] and SBA-15 [5], which possess large surface areas (up to ca. 1200 m^2/g) and pore volumes (larger than ca. 0.8 cm^3/g) with uniform mesopores (larger than ca. 2.0 nm), are interesting adsorbents since they have large water adsorption capacities [6]. We have investigated the desorption of T from several porous materials including MCM-41, SBA-15, LTA(5A) zeolite, and amorphous SiO_2 [7]. Among them, MCM-41 was found to have a superior intrinsic T desorption property as compared with LTA(5A). It was also found that such T enrichment could be reproduced after 5 cycles of water impregnation and desorption [7]. In this research note, we report the details of T desorption behavior of MCM-41 after 5 cycles of water impregnation/desorption treatments.

MCM-41 was prepared by the procedure given in the literature with slight modifications [8]. The starting materials were colloidal silica (Snowtex-20, Nissan Chemical Industries, Ltd.) as the silica source, dodecyltrimethylammonium bromide (Tokyo Kasei) as the template, NaOH (Kanto Chemical), and distilled water. The mixed solution with the molar composition of 1.00 SiO_2 : 0.50 DTAB : 0.28 NaOH : 54.5 H_2O was hydrothermally treated at 130°C for 48 h in a stainless-steel autoclave. The white precipitate was post-treated by dispersion in distilled water (solid/water = 1:10 by weight) at 130°C for 24 h. Calcination in order to burn-off the template was done under an air flow at 550°C for 10 h with a ramp rate of 2°C/min. The as-synthesized material was denoted as MCM(1).

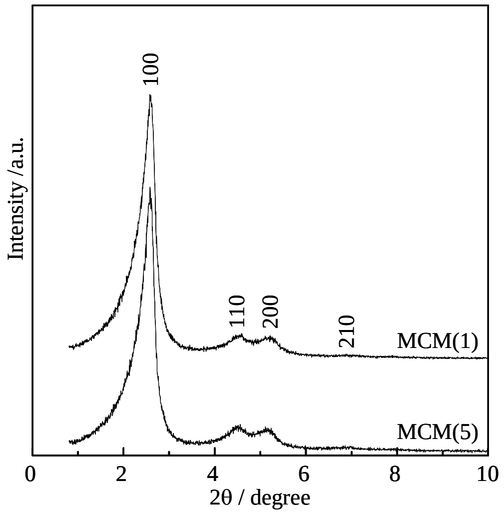

Fig. 1 XRD patterns of MCM-41. MCM(1): as-synthesized, MCM(5): after 5 cycles of water impregnation/desorption.

The obtained MCM(1) was dehydrated at 180 °C for more than two days, and then cooled to room temperature under a vacuum. Then, distilled water impregnation was performed by the incipient wetness method. The sample in a quartz boat was placed in the desorption apparatus equipped with an oven under an Ar flow of 50 cm^3/min at 25°C for 24 h. Subsequently, the sample was placed in a quartz tube in a furnace. The temperature of the furnace was increased to 100°C at a ramp rate of 5°C/min, and this temperature was maintained for 60 min. Then, the temperature was raised to 150°C for 30 min. By repeating this stepwise heating, temperature was raised in increments of 50°C up to 550°C. The impregnation and desorption cycles were repeated 5 times, and the resulting material was denoted as MCM(5).

The periodic mesostructure of MCM(1) and MCM(5) was confirmed by X-ray diffraction (Philips, PW1825/00). Figure 1 shows the XRD patterns of MCM(1) and MCM(5). The XRD patterns of both samples exhibited well-resolved diffraction signals assignable to the 100, 110, 200, and 210 reflections of hexagonal symmetry (*p*6mm). This indicates that the structural collapse is not critical in MCM(5). The unit cell parameter ($a_0 = 2d_{100}/\sqrt{3}$) was estimated to be

3.88 and 3.89 nm for MCM(1) and MCM(5), respectively. Nitrogen sorption isotherms (Autosorb-1MP, Quantachrome Instruments) showed type-IV curves with a steep H1 hysteresis loop in the relative pressure range of 0.2-0.3 in both MCM(1) and MCM(5), indicating uniform tubular pore channels [9]. The Brunauer-Emmett-Teller (BET) surface area, pore diameter by Non-Local Density Functional Theory (NLDFT [9]), and pore volume were estimated, respectively, to be 1109 m^2/g, 3.13 nm, and 0.79 cm^3/g for MCM(1), and 1114 m^2/g, 3.18 nm, and 0.78 cm^3/g for MCM(5). These results indicate that mesostructure is more stable under the present experimental conditions than that in previous studies, which were carried out under steam [10], hydrothermal [11,12], and high temperature conditions [13].

T desorption was studied using the apparatus [14] in the radioisotope laboratory of Hydrogen Isotope Research Center, University of Toyama. Experimental procedures were the same as those mentioned above, except that tritiated water was used instead of distilled water. Briefly, a dried (180 °C and evacuation) sample was impregnated with tritiated water (231.1 kBq/mL) by the incipient wetness method. The total amount of T impregnated was 462 and 410 kBq/g for MCM(1) and MCM(5), respectively (Table 1). The sample (0.1–0.3 g as adsorbent) in a quartz boat was placed in the T desorption apparatus equipped with an oven under an Ar flow of 50 cm^3/min at 25 °C. Here, under an Ar flow, T was allowed to desorb spontaneously from the sample (mainly as HTO) and was collected in water bubblers in an ice bath. Then, water-insoluble species such as HT were led into a CuO bed heated at 527°C, where HT was oxidized to HTO and collected in a separate water bubbler. The amount of T

Table 1 Summary of T impregnation and desorption for MCM(1) and MCM(5)

	T impregnated		Spontaneous desorption			Thermal desorption		
			Weight loss	T desorbed		Weight loss	T desorbed	
	wt%	kBq/g	wt%	kBq/g	kBq/mL	wt%	kBq/g	kBq/mL
MCM(1)	66	449	65.5	424.6	216.5	1.10	9.57	290.0
MCM(5)	65	410	62.8	382.2	219.3	1.18	9.27	282.4

collected was measured by using a liquid scintillation counter (Tri-Carb 2100TR, Packard) with a liquid scintillator (Ecoscint XR, National Diagnostic). It should be noted that more than 98% of T was collected as HTO in the desorption experiments.

Spontaneous desorption of T from MCM-41 was observed under Ar flow at 25°C. The desorbed T was collected over an adequate period up to 24 h. Figure 2 shows the T desorption profiles of MCM(1) and MCM(5). Here, the amount of T desorbed is normalized with respect to the weight of the adsorbent and time (kBq/g·h). It was revealed that a large amount of T was desorbed in the early stages up to 5 h. The desorption rate decreased after 5 h, and became about 0.2 kBq/g·h after 24 h. As listed in Table 1, the cumulative amount of T desorbed during the first 24 h was estimated to be 424.6 and 382.2 kBq/g for MCM(1) and MCM(5), respectively, which were almost 90 % of the quantities impregnated. A significant weight loss was also observed as shown in Table 1; more than 95 % of the tritiated water was released. On the basis of the amount of T desorbed and the weight loss, the concentration of the tritiated water released was calculated to be 216.5 and 219.3 kBq/mL, respectively. These values were clearly lower

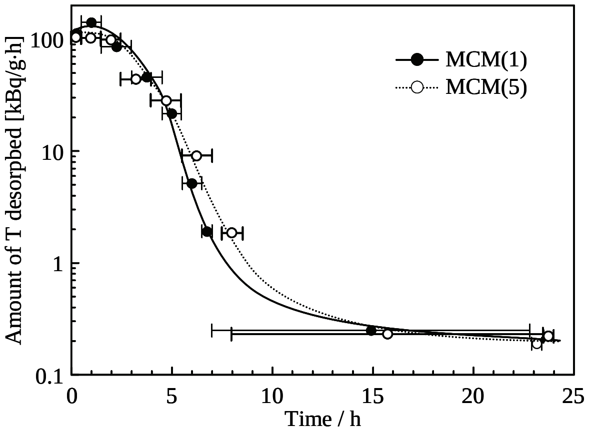

Fig. 2 Change in the amount of T desorbed from MCM(1) and MCM(5) at 25 ºC. Bars along the x-axis represent the periods of T collection.

than those of the tritiated water used for impregnation, suggesting that a certain amount of T remained in the samples.

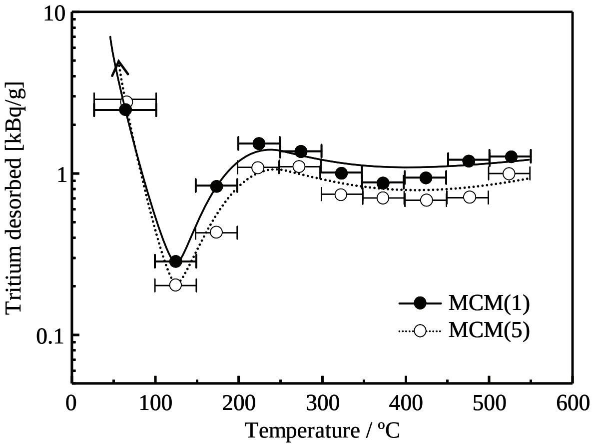

Fig. 3 Tritium desorption profile from MCM(1) and MCM(5) at 25 – 550 ºC. Error bars represents the period of T collected.

Subsequently, the T remaining in the samples were thermally desorbed. The sample was placed in a quartz tube in a furnace under an Ar flow (100 cm^3/min). Then, the temperature of the furnace was increased to 100°C at a ramp rate of 5°C/min, and this temperature was maintained for 60 min. After the water bubblers were changed, the temperature was raised to 150°C for 30 min. By repeating this stepwise heating, temperature was raised in increments of 50°C up to 550°C.

Figure 3 shows the change in the amount of T desorbed depending on temperature. The amount of T desorbed was normalized to the weight of the adsorbent as unity. The T desorption profiles of MCM(1) and MCM(5) were very similar to each other, as seen in Figure 3. Both in MCM(1) and MCM(5), T desorption decreased when temperature rose from 25 to 150 °C, and showed a minimum of about 0.2–0.3 kBq/g at 100–150 °C. Then, the desorption amount increased again above 150 °C. An almost constant amount of T of 0.8–1.1 kBq/g was observed at temperatures from 200 to 550 °C. Such desorption profile can be explained by the state of adsorbed HTO molecule [7]. Namely, a large number of physisorbed HTO molecules desorbed below 100°C. Thereafter, desorption of HTO via condensation of surface silanol groups dominated above 100°C [7].

The cumulative amount of T desorbed from 25 to 550 °C was estimated to be 9.57 and 9.27 kBq/g for MCM(1) and MCM(5), respectively. The sum of the T desorbed at 25 °C and under thermal conditions corresponded to 434.2 and 391.5 kBq/g for MCM(1) and MCM(5), respectively, showing more than 95 % of mass balance (Table 1). Besides, after thermal desorption, a weight loss of 1.10 wt% for MCM(1) and 1.18 wt% for MCM(5) were observed. On the basis of the amount of T desorbed and the weight loss, the concentration of tritiated water was calculated to be 290.0 and 282.4 kBq/mL, respectively. It is obvious that the concentration of tritiated water increased as compared with that used for impregnation. The concentration ratio, defined as the ratio of the concentration of T desorbed under thermal conditions to that derived from spontaneous desorption, was 1.34 and 1.29, respectively. These indicate good reproducibility and reusability of MCM41 in the enrichment of tritiated water. Although the volume of tritiated water obtained under thermal conditions was small, the optimization of desorption and especially adsorption conditions might improve the effective enrichment of tritiated water.

In conclusion, the structural stability and T desorption behavior of MCM-41 was investigated. The mesostructure of MCM-41 was found to be maintained up to 5 cycles of sequential impregnation and spontaneous and thermal desorption. The T desorption behavior of reused MCM-41 was very similar to that of as-synthesized one, showing a good reusability and reproducibility. The results suggest that MCM-41 is one of the attractive adsorbents for the enrichment of tritiated water.

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