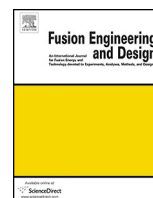




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# Desorption behavior of tritiated water from organic functionalized mesoporous silica

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### HIGHLIGHTS

- $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  and  $-\text{NH}_2$  grafted SBAs were prepared.
- Concentrated tritiated water was obtained by sequential spontaneous and thermal desorption from  $-\text{SO}_3\text{H}$  and  $-\text{NH}_2$  functionalized SBAs.
- The presence of strong interactions between  $-\text{COO}-$  and heavier hydrogen isotopes is expected according to tritium desorption and FT-IR studies.

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### ABSTRACT

The desorption and enrichment of tritiated water from organic functionalized mesoporous SBA-15 were investigated. The desorption behavior of tritiated water was dependent on the nature of the organic functional group present i.e.,  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ , and  $-\text{NH}_2$ . Enriched tritiated water was obtained by thermal desorption from  $-\text{SO}_3\text{H}$  and  $-\text{NH}_2$  grafted SBAs after spontaneous desorption of tritiated water at 25 °C. Although the volumetric amount of concentrated tritiated water was small, the concentration ratios of tritiated water thermally desorbed and at 25 °C were 1.2 and 1.3 for  $-\text{SO}_3\text{H}$  and  $-\text{NH}_2$  grafted SBA, respectively. In contrast,  $-\text{COOH}$  grafted SBA showed a lower T concentration after thermal desorption. Fourier transform infrared spectroscopy studies using deuterated water ( $\text{D}_2\text{O}$ ) indicated the presence of strong interactions between  $-\text{COO}-$  groups and D.

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## 1. Introduction

Porous materials, such as zeolites, silica gels or active carbons, are used in diverse industrial areas of catalysts, adsorbents and ion-exchangers [1–3]. In the tritium (T) science and technology, zeolites are mostly used as HTO sorbents as drying agents and/or for HTO enrichment because of their large adsorptive capacity for water molecules [4–7].

Besides zeolitic microporous materials, mesoporous materials (e.g., MCM-41, SBA-15) having larger pore diameter and pore volume than zeolites are increasingly being applied in the field of environmental remediation and other industry-based areas [8,9]. Mesoporous materials feature interesting properties. For instance, their functionalities can be easily controlled to bestow selectivity and/or stability features in mesoporous material sorbents. For example, in waste management, as part of the nuclear fuel cycle, the

separation or extraction of environmentally hazardous materials including radioisotopes has been investigated [10–13].

Previously, we have reported that mesoporous materials and their organic functionalized analogues show higher tritium adsorption capability from tritiated water than conventional microporous zeolites or amorphous silica [14,15]. Although the adsorption performance is insufficient for practical applications, further studies on the desorption behavior of tritium from these mesoporous materials are interesting from the viewpoint of determining the tritium affinity of the sorbents. Accordingly, in the present study, we investigate the desorption behavior of tritiated water from mesoporous SBA-15 modified with  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ , or  $-\text{NH}_2$  groups. Fourier transform infrared spectroscopy studies using  $\text{D}_2\text{O}$  were also conducted to further understand the desorption behavior.

## 2. Experimental

### 2.1. Synthesis and functionalization

SBA-15 was prepared according to a literature procedure with slight modifications [16]. The raw materials tetraethyl

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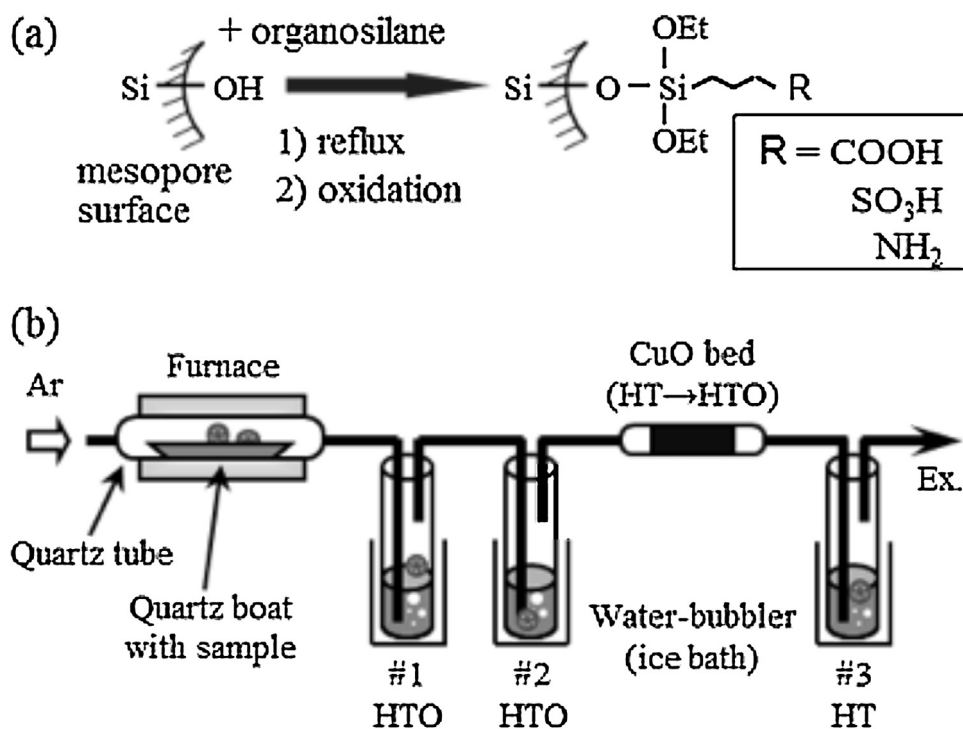


Fig. 1. Schematic representations of (a) grafting of organosilanes on the mesopore surface of SBA and (b) tritium desorption apparatus.

orthosilicate and HCl were purchased from Kanto Chemical and Pluronic P123 was purchased from Sigma-Aldrich. The composition (wt%) of the starting solution of tetraethyl orthosilicate:Pluronic P123:HCl:H<sub>2</sub>O was 6.00:2.80:6.30:84.9. The solution was aged at 40 °C for 4 h and then kept static at 80 °C for 24 h. The resulting white precipitate was filtered, washed with deionized water, and dried at 80 °C for 6 h. Finally, SBA-15 was obtained upon calcination at 550 °C for 10 h, with a ramp rate of 2 °C/min (denoted hereafter as SBA). Subsequently, organic functionalization was conducted using organosilane reagents (2-cyanoethyl) triethoxysilane, (3-mercaptopropyl)triethoxysilane, and (3-aminopropyl)triethoxysilane as precursors for the –COOH, –SO<sub>3</sub>H and –NH<sub>2</sub> groups surface functionalization, respectively [17,18]. The precursors were purchased from Tokyo Kasei. In a typical functionalization procedure, SBA (previously dried at 180 °C under vacuum for more than 18 h) and an appropriate amount of organosilane reagent were refluxed in dry toluene (Kanto Chemical) for 3–24 h (Fig. 1a). For the SBA samples grafted with –COOH and –SO<sub>3</sub>H groups, the samples were treated with H<sub>2</sub>SO<sub>4</sub> (50%) and H<sub>2</sub>O<sub>2</sub> (30%), respectively, to oxidize the cyano and thiol groups. The obtained SBAs grafted with –COOH, –SO<sub>3</sub>H and –NH<sub>2</sub> functional groups are denoted as SBA-COOH, SBA-SO<sub>3</sub>H, and SBA-NH<sub>2</sub>, respectively.

## 2.2. Tritium desorption study

For the T desorption study, the conventional T desorption apparatus, schematically shown in Fig. 1b, was used. Under an Ar flow, T desorbed from the sample (mainly as HTO) was collected in water bubblers #1 and #2 in an ice bath. The gas component, i.e., HT was introduced into a CuO bed heated at 527 °C, where HT oxidized to HTO and was collected in water bubbler #3. More than 98% of T was collected as HTO. The mass balance of T in this experiment was 92 ± 3%.

Prior to the T desorption experiments, the sorbents were dehydrated at 180 °C for more than 2 days, and then cooled to room temperature under vacuum. Tritiated water with a T concentration

of 176.5 kBq/mL was impregnated into the sorbents by the incipient wetness method. The loading amount of tritiated water was 71–80 wt%. The impregnated sample (about 0.1 g as adsorbent), in a quartz boat, was introduced in a desorption apparatus under an Ar flow of 100 mL/min at 25 °C for 23.5 h. The desorbed T was then collected in water bubblers at appropriate times. Subsequently, the temperature of the furnace was increased to 100 °C at a ramp rate of 5 °C/min, and this temperature was maintained for 1 h. After the water bubblers were changed to new ones, the temperature was raised to 150 °C (5 °C/min) and maintained this temperature for 30 min. This stepwise heating, in increments of 50 °C, was repeated up to 250 °C. The amount of T collected was measured using a liquid scintillation counter (LSC-LB5, Hitachi-ALOKA).

## 2.3. Characterization

The prepared materials were characterized by X-ray diffraction (XRD; Philips, PW1825/00), N<sub>2</sub> sorption analysis (Quantachrome Instruments, Autosorb-1MP), thermogravimetric-differential thermal analysis (TG-DTA; Rigaku, ThermoPlus 2), and transmission electron microscopy (TEM; JEOL, JEM-2100). Fourier transform infrared (FT-IR) spectra were recorded on a Spectrum 100 instrument (PerkinElmer). Prior to measurements, the samples were dehydrated at 180 °C for more than 2 days. For the desorption studies using D<sub>2</sub>O (99.9% D, Wako Pure Chemical Industries, Ltd.), a self-supported wafer (diameter: 20 mm) was loaded into an in-house built cell with CaF<sub>2</sub> windows; and a resolution of 4 cm<sup>-1</sup> was used. Deuteration was achieved by treatment of the dehydrated sample at 180 °C with D<sub>2</sub>O vapor (equilibrium pressure: 2 kPa, reaction time: 18 h, temperature: 25 °C), followed by evacuation. The spectra were recorded after thermal desorption of T at 100, 150, or 200 °C under N<sub>2</sub> flow.

## 3. Results and discussion

Fig. 2 shows a TEM image of SBA, which displayed a periodic hexagonal mesostructure. Nitrogen sorption analysis revealed

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