



# Different modes of adsorptions of arsenate on silica grafted with $\text{Fe}^{3+}$ -coordinated silanes



Ryo Otsuka, Hideaki Yoshitake\*

Division of Materials Science and Chemical Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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## ABSTRACT

In order to optimize the adsorption of arsenate, we prepared silica based adsorbents by grafting  $\text{Fe}^{3+}$ -coordinated N-(2-aminoethyl)-3-aminopropyltriethoxysilanes (aeaptes) in various Fe:aeaptes ratios (mixing ratios). Two kinds of mesoporous silica (MCM-41 and SBA-15) and fumed silica (Cab-O-sil M7D) were used as substrates. The adsorption of arsenate saturated at As/Fe = 1, 2 and 3 on mesoporous silica based adsorbents from with Fe:aeaptes ratios of 1:1, 1:2 and 1:3, respectively. On the other hand, saturation occurred at As/Fe = 1 on Cab-O-sil M7D-based adsorbents for all three Fe:aeaptes ratios. In addition to this dependence of the adsorption on the coordination conditions, two different modes were clearly distinguished in the adsorption isotherm for the MCM-41 based adsorbent prepared with a Fe:aeaptes ratio of 1:1. These two distinct adsorptions are likely to be due to the induction of well-defined coordination structures by this method. This result is significantly different from that found in a previous study where adsorbents were prepared by the grafting of aeaptes followed by the coordination of  $\text{Fe}^{3+}$ , where a single mode of adsorption was observed. The adsorptions were further analyzed using the Langmuir equation and by X-ray adsorption spectroscopy.

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## 1. Introduction

Ordered mesoporous silicas, which have uniform mesopores of several nanometers in size and whose total pore volume often reaches as much as  $1 \text{ cm}^3/\text{g}$ , have attracted considerable attention from researchers working in the materials chemistry, especially in fluorescence and electrochemical sensing [1–5], chromatography [6–9] and biomolecular analysis [10–12]. The unique property required by these applications is the combination of their potential molecular sieving ability due to the uniform mesopores and the high surface area that can enhance the interaction between the solid surface and the guest molecules and ions. As a consequence, the adsorption of various molecules and ions has been extensively studied [13–20]. For physicochemical and biochemical analyses, the selectivity of the target ions and molecules is critically important as well as the strength of the chemical bonds. The interaction with the adsorption sites is one of the most influential factors, which is closely related to the geometric features of the mesoporous silica surface.

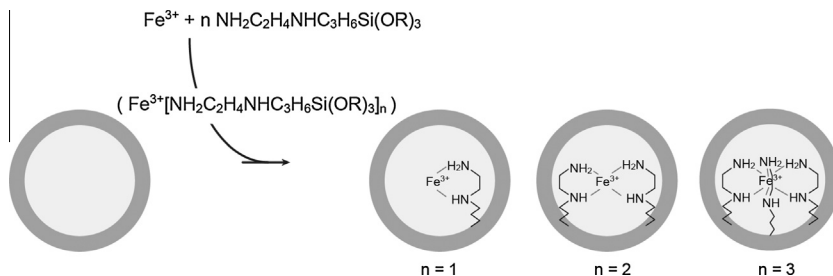
Although inhibiting the diffusion of aqueous ions has been considered as a problematic, there is also a significant problem in grafting to functionalize the surface of mesoporous silica, where the reactive organosilane is coupled with silanol [13,14,21,22].

Large rates of diffusion compared with the surface reactions between silanes and silanols are closely related to the uniform distribution of functional sites [13], though non-uniform functional group distributions have been demonstrated even for small silanes [21,22]. Furthermore, the concentration of functional groups results in interactions between vicinal adsorption sites [14] and the cooperative action of neighboring sites [15]. These properties of functional groups bring about serious problems in selectivity and specificity in the detection of molecules and ions when these materials are used in chemical, physicochemical and biochemical analyses. Although the large surface area potentially provides a large density of adsorption sites and improves the performance of sensing materials and fillers for chromatography, these static and dynamic non-uniformities reduce the specificity in detection.

We have reported that functionalized MCM-41 prepared by the grafting of N-(2-aminoethyl)-3-aminopropyltriethoxysilane (aeaptes) followed by the coordination of  $\text{Fe}^{3+}$  adsorbs more than 2.20 mmol/g of aqueous arsenate. This adsorption capacity is two orders of magnitude higher than conventional adsorbents and a high selectivity from aqueous sulfate has also been found [23]. This functionalized porous solid is potentially an important material for the remediation of groundwater, sensors and separating agents. However, as explained above, the N-(2-aminoethyl)-3-aminopropyl tethers are concentrated and randomly distributed on the surface and  $\text{Fe}^{3+}$  can be coordinated with either one, two or three tethers. Thus it is likely that the structure of the adsorption sites and the

\* Corresponding author. Fax: +81 45 335 4378.

E-mail address: yos@ynu.ac.jp (H. Yoshitake).



**Scheme 1.** Preparation of adsorbents: grafting of cation-precoordinated silane.

mode of adsorption are non-uniform. If we are able to know the structure of adsorption site that forms a strong bond with a large number of adsorbate ions, effective progress in the design of the sensing material can be made.

Considering that the formation of stable coordination bonds for ethylenediamine-type ligands occurs under ambient conditions, it is possible to coordinate the aepptes with  $\text{Fe}^{3+}$  before grafting onto silica. For the present study, we prepared grafts with three different ratios,  $\text{Fe}^{3+}$ :aepptes = 1:1, 1:2 and 1:3, and they were grafted onto mesoporous silicas, MCM-41 and SBA-15, as illustrated in Scheme 1. The adsorption of arsenate was analyzed using these functionalized mesoporous silicas to explore the dependence on the coordination conditions. The results are compared with functionalized Cab-O-sil M7D prepared by the same procedure to demonstrate the structural uniqueness of mesoporous silica as a substrate.

## 2. Materials and methods

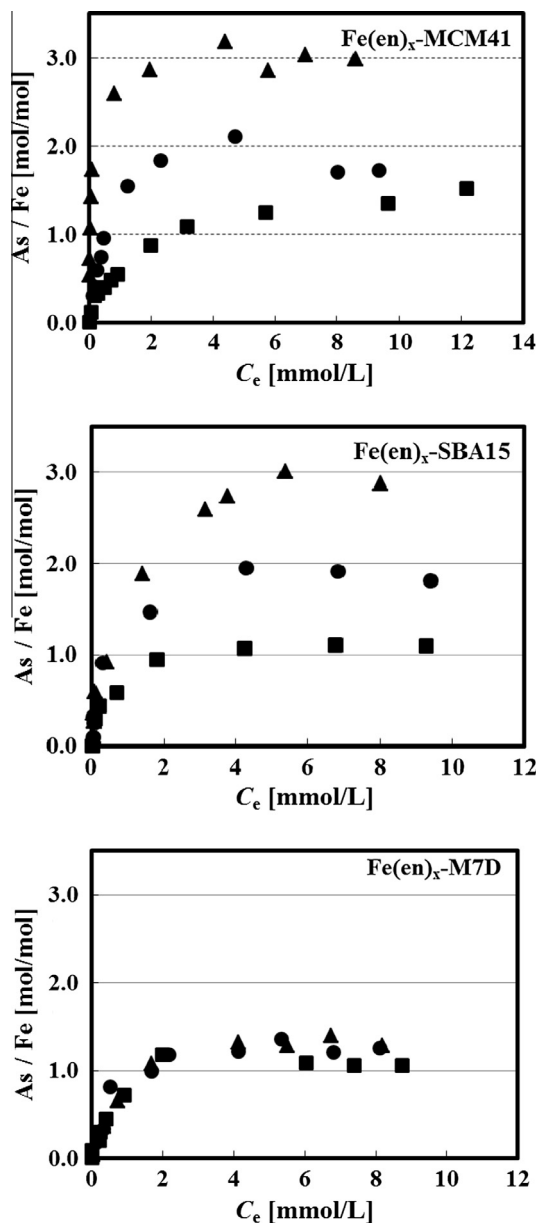
**Materials:** All reagents were purchased from Wako Pure Chemical Industries, Ltd. except N-(2-aminoethyl)-3-aminopropyltriethoxysilane, aepptes, which was supplied by Tokyo Chemical Industries Co. Ltd. These reagent grade chemicals were used without further purification. The aqueous solutions were prepared with Milli-Q water.

**Grafting of  $\text{Fe}^{3+}$ -coordinated aepptes on silicas:** The mesoporous silicas, MCM-41 and SBA-15, were synthesized by a standard method described in the literature [18,22,23]. 0.150 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was mixed with 0.146 g, 0.292 g or 0.438 g of aepptes (to give Fe:aepptes molar ratios of 1:1, 1:2 or 1:3, respectively,) in 50 mL of toluene. The mixture was then stirred for 30 min at room temperature before the addition of MCM-41. After stirring for 24 h, the temperature was raised to 393 K and it was left to stand for a further 24 h. The above described procedure was carried out under an argon atmosphere. The solid was collected by filtration, and then washed with water and ethanol. These solids are referred to as  $\text{Fe}(\text{en})$ -MCM-41,  $\text{Fe}(\text{en})_2$ -MCM-41 and  $\text{Fe}(\text{en})_3$ -MCM-41 for Fe:aepptes molar ratios of 1:1, 1:2 and 1:3, respectively.  $\text{Fe}(\text{en})_x$ -SBA-15 and  $\text{Fe}(\text{en})_x$ -M7D ( $x = 1, 2, 3$ ) were prepared by the same procedure using SBA-15 and Cab-O-sil M7D (Cabot Corporation), respectively, instead of MCM-41.

**Adsorption of arsenate:** 0.03 g of the adsorbents described above was added to 10 mL of aqueous potassium arsenate monobasic ( $\text{KH}_2\text{AsO}_4$ ) solution at room temperature. The concentration of arsenate was varied from 0.1 to 1000 ppm. The solution was stirred for 24 h before separating the solid by suction filtration. Analysis of the filtrate was carried out by ICP-AES (SPS 300 Rigaku Co.)

**Structural analysis:** The Fe in the  $\text{Fe}(\text{en})_x$ -silicas was dissolved using 1M HCl and the ferric ions in the solution were quantified using a Rigaku SPS 300 ICP-AES apparatus. The X-ray absorption spectra of the Fe and As K-edges were measured in the BL-7C beamline at the Photon Factory, High Energy Accelerator Research

Organization (Proposal No. 2011G093). A Si(111) double crystal was used as a monochromator for the X-ray beam after removal



**Fig. 1.** Adsorption isotherms of arsenate on  $\text{Fe}(\text{en})$ -MCM41 (square, upper),  $\text{Fe}(\text{en})_2$ -MCM41 (circle, upper),  $\text{Fe}(\text{en})_3$ -MCM41 (triangle, upper),  $\text{Fe}(\text{en})$ -SBA15 (square, middle),  $\text{Fe}(\text{en})_2$ -SBA15 (circle, middle),  $\text{Fe}(\text{en})_3$ -SBA15 (triangle, middle),  $\text{Fe}(\text{en})$ -M7D (square, lower),  $\text{Fe}(\text{en})_2$ -M7D (circle, lower) and  $\text{Fe}(\text{en})_3$ -M7D (triangle, lower).

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