

Arsenate-iron complex in the pore of functionalized MCM-41

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Introduction

Grafting technique of silanes introduces functional groups into the pores of MCM-41, which anchor ions strongly in a proper pH condition. The high surface area, large pores and strong adsorbing properties imply the environmental applicability of functionalized MCM-41. Amino groups in the pores works as adsorbent of oxyanions such as AsO_4^{3-} , CrO_4^{2-} , SeO_4^{2-} and MoO_4^{2-} in $\text{pH} < 8$ [1]. And, in addition, these organic groups anchor certain transition metal cations such as Fe^{3+} , Co^{2+} and Cu^{2+} , which bind the toxic oxyanions selectively. These adsorption centres have a molecular nature and this mode of interaction cannot realize in the adsorption on the minerals. However, the humic materials likely binds both cations and anions though amino group. The clarification of the interactions between cations, anions and organic groups in functionalized MCM-41 will be helpful for understanding the behaviour of these toxic anions in nature and developing effective adsorbents for the area suffering from the pollutions. In this study we analysed the structure of oxyanion- Fe^{3+} complexes anchored by amino groups in the pores of MCM-41 by EXAFS.

Method

MCM-41 prepared by the method in ref. [2] was stirred in toluene containing [1-(2-aminoethyl)-3-aminopropyl]trimethoxysilane and heated to 383 K in dry nitrogen for 6 h. The powder was washed and dried. We denote this diamino-functionalized silica as en-MCM-41. The en-MCM-41 was stirred in 0.1 M 2-propanol solution of FeCl_3 for 2 h, washed and dried. The Fe^{3+} -anchored en-MCM-41 is denoted as Fe/en-MCM-41.

50 mg of Fe/en-MCM-41 was stirred for 10 h in 100 ml of aqueous solution of KH_2AsO_4 . The concentrations of the oxyanion in the solution were determined by ICP-AES. The detection limit was 1×10^{-6} g/L (= 1 ppb). Typical pH value of the solution at the beginning was 2 where the dominant species is H_2AsO_4 .

X-ray absorption experiments were carried out in a transmission mode at BL-9A and BL-10B. The data were processed by EXAFS analysis program REX 2000 (Rigaku). After normalised with using the McMaster tables, k^3 -weighted EXAFS oscillation, $k^3\chi(k)$, in $30 - 135 \text{ nm}^{-1}$ region was Fourier transformed into a radial distribution function. The amplitude and phase-shift functions were calculated by using the parameter set by Mckale et. al.

Results and Discussion

Figures 1 and 2 shows the Fourier transforms of Fe K-edge and As K-edge in Fe/en-MCM-41 and arsenate adsorbed Fe/en-MCM-41. The unresolved peak at 0.1-0.22 nm in Fe/en-MCM-41 is well fitted with two shells, Fe-N ($N = 3.3$, $r = 0.192 \text{ nm}$) and Fe-Cl ($N = 2.1$, $r = 0.224 \text{ nm}$). No other characteristics are observed in this FT. After adsorption of arsenate, two peaks appear in

0.1- 0.24 and 0.24 – 0.36 nm. These are fitted with four shells; Fe-N ($N = 2.9$, $r = 0.194 \text{ nm}$), Fe-Cl ($N = 0.5$, $r = 0.228 \text{ nm}$) and two Fe-As ($N = 1.5$, $r = 0.327 \text{ nm}$ and $N = 1.4$, $r = 0.359 \text{ nm}$). Two kinds of arsenates bound to Fe are distinguished. This is confirmed by the structural parameters obtained in the peaks in Figure 2, where three shells are necessary for a good fitting; As-O ($N = 3.9$, $r = 0.168 \text{ nm}$) and two As-Fe ($N = 0.93$, $r = 0.327 \text{ nm}$ and $N = 0.40$, $r = 0.351 \text{ nm}$). At the adsorption saturation, Fe/en-MCM-41 releases a part of Cl but retaining the chelate coordination by en.

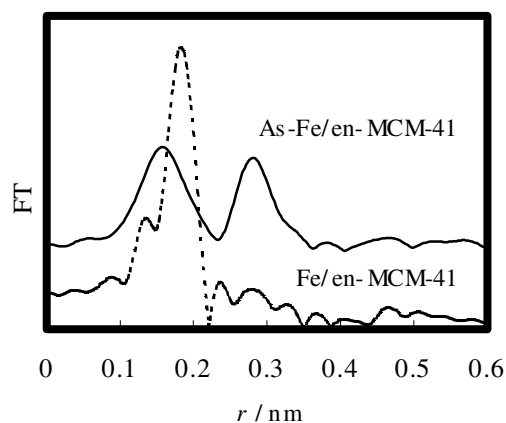


Figure 1. Fourier Transform of Fe K-edge in Fe/en-MCM-41 and arsenate adsorbed Fe/en-MCM-41.

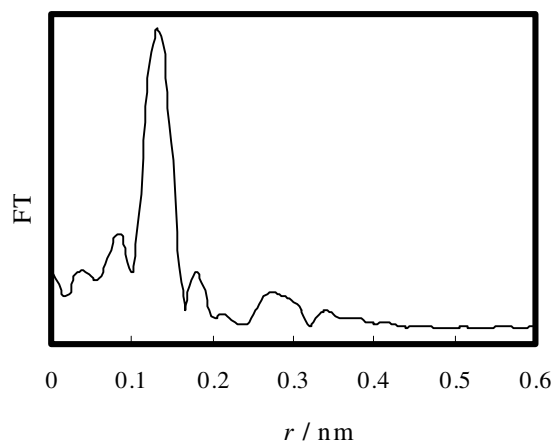


Figure 2. Fourier Transform of As K-edge in arsenate adsorbed Fe/en-MCM-41.

References

- [1] H. Yoshitake et al., *Chem. Lett.* **2002**, 586.
- [2] H. Yoshitake, et. al. *Stud. Surf. Sci. Catal. in press.*

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