

Selenate-iron complex in functionalized MCM-41

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Introduction

The environmentally toxic oxyanions are negatively charged and the central atoms are surrounded by T_d oxygen. Among the oxyanions in T_d structure, selenate draws attention in the environmental science because of its toxicity to animals and mobility in the soil environment. The structural characteristics of well-ordered hexagonal mesoporous silica are attractive in developing adsorbents of toxic ions in the environment [1]. The Fe-anchored functionalized mesoporous silica is effective on one of the most difficult separations in relation to the toxic oxyanions, SeO₄²⁻ / SO₄²⁻ [2]. In the present study, we have investigated the structure of the adsorption site by EXAFS spectroscopy.

Method

MCM-41 was prepared by a conventional method using tetraethyl orthosilicate, cetyltrimethylammonium bromide and trimethylammonium hydroxide. The calcined powder was reacted with 3-aminopropyltrimethoxysilane at 383 K. This amino-functionalized MCM-41 was treated with 0.1 M 2-propanol solution of FeCl₃. The adsorption capacity of selenate was 117 mg (g-adsorbent)⁻¹, when the ratios of N/Fe and Se/Fe were 3.8 and 1.5, respectively. EXAFS spectra of the Fe and Se K edges were measured on a BL-10 B in a transmission mode. The EXAFS spectra were acquired five times under the same measuring conditions and from the extracted spectra, the average $\chi(k)$ was calculated. The data were processed by a REX2000 program (Rigaku Co.) The EXAFS oscillation is extracted by fitting a cubic spline function through the post edge region. After normalization using the McMaster tables, the k^3 -weighted EXAFS, $k^3\chi(k)$, in the 3 - 13 Å⁻¹ region was Fourier transformed into a radial distribution function. The amplitude and phase functions for Fe-N, Fe-Cl, Fe-Se and Se-O were calculated by FEFF 7.02 code. The curve fitting analysis was carried out between 4 and 12 Å⁻¹ in the k -space of inversely Fourier transformed spectra (from FT filtered at 0.77 < r < 3.65 Å and 0.89 < r < 3.34 Å for Fe K and Se K-edges, respectively.)

Results and Discussion

Figure 1 shows the EXAFS oscillations of Fe and Se K-edges before and after the adsorption of selenate. A large difference was found between Fe spectra while the profile was almost unchanged in Se spectra, suggesting that the coordination environment of Fe was considerably

disturbed by selenate adsorption while T_d structure of selenate was not much influenced by anchoring on Fe site.

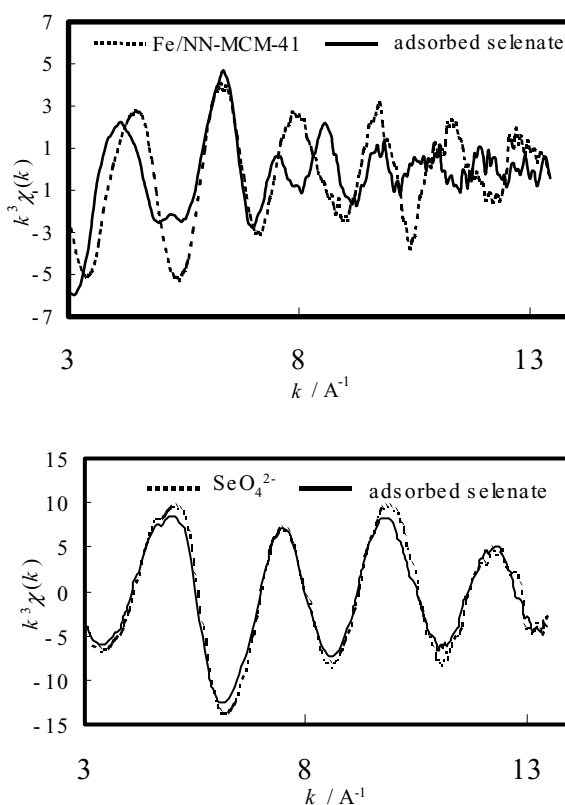


Figure 1 EXAFS oscillation of Fe and Se K edges before and after adsorption.

The structural parameters (after adsorption) calculated by curve fitting analysis of Fe K edge are $N(\text{Fe-N}) = 3.8 \pm 0.7$, $N(\text{Fe-Cl}) = 0.41 \pm 0.2$, $N(\text{Fe-Se}) = 0.93 \pm 0.2$ with $r(\text{Fe-N}) = 2.00 \pm 0.03$ Å, $r(\text{Fe-Cl}) = 2.26 \pm 0.03$ Å and $r(\text{Fe-Se}) = 3.27 \pm 0.04$ Å. On the other hand, from the Se K edge spectrum, $N(\text{Se-O}) = 3.7 \pm 0.7$ and $N(\text{Se-Fe}) = 0.43 \pm 0.2$ with $r(\text{Se-O}) = 1.65 \pm 0.02$ Å and $r(\text{Se-Fe}) = 3.28 \pm 0.04$ Å are deduced.

References

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