Chemistry

XAFS Study on Iron(II) Complexes Encapsulated within the Alkali Metal Cation-Exchanged Zeolite Y

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Introduction

Zeolites are attractive materials for encapsulation of metals, semiconductors, and organometallic complexes because of its ordered microporous structure. It is well known that some characteristics, such as electrostatic potential, electric field, and volume in the micropore, are controlled by exchangeable alkali metal cations that exist on the zeolite extraframework.
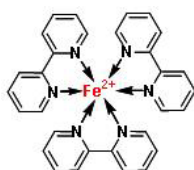

Fig. 1. $[Fe(bpy)_3]^{2+}$

In this study, we encapsulated tris(2, 2'-bipyridine) iron(II) complexes within alkali metal cation-exchanged zeolite Y (Fig. 1). Local structure and electronic state of iron(II) complexes were investigated by XAFS.

Experimental

Alkali metal cation-exchanged zeolite Y (LiY, KY, RbY, CsY) were prepared from NaY (SiO_2/Al_2O_3=5) by ion-exchange at 363 K using aqueous nitrate solutions of alkali metal cations. To prepare iron-exchanged zeolite, alkali metal cation-exchanged zeolites were suspended in an aqueous solution of $FeCl_2 \cdot 4H_2O$ and stirred at r.t. for 20 h. The prepared iron-exchanged zeolites were refluxed in an aqueous solution of 2, 2'-bipyridine (bpy) for 20 h to give iron(II) complexes encapsulated zeolite Y ($[Fe(bpy)_3]^{2+}$@MY, M = Li, Na, K, Rb, Cs). Fe K-edge XAFS spectra were recorded at room temperature in fluorescence mode. EXAFS data were examined using an EXAFS analysis program, Rigaku EXAFS. The pre-edge peaks in the XANES regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region. Fourier transformation (FT) of k^3-weighted normalized EXAFS data was performed over the range $3.5 < k/Å^{-1} < 11$ to obtain the radial structure function. The values of CN (coordination number), R (distance between an absorbing atom and scatterer), and the Debye-Waller factor were estimated by curve-fitting analysis with the inverse FT of the $0.8 < R/Å < 2.8$ range assuming single scattering.

Results and discussions

Fig.2 shows the results of Fe K-edge XAFS analysis of $[Fe(bpy)_3]^{2+}$@MY, with $Fe(bpy)_3(ClO_4)_2$ as a reference. In the XANES spectra, the edge position (measured at the half-height of the edge jump) depends on the electronic charge of the iron ions and the energies increased in the order $Fe(bpy)_3(ClO_4)_2$ (7120.1 eV) < $[Fe(bpy)_3]^{2+}$@LiY (7122.5 eV) < $[Fe(bpy)_3]^{2+}$@NaY (7122.6 eV) = $[Fe(bpy)_3]^{2+}$@KY (7122.6 eV) < $[Fe(bpy)_3]^{2+}$@RbY (7123.2 eV) < $[Fe(bpy)_3]^{2+}$@CsY (7123.2 eV). Thus the encapsulated $[Fe(bpy)_3]^{2+}$ appears to be in an electron-deficient state compared to $Fe(bpy)_3(ClO_4)_2$ and the electron density of the Fe atoms decreased as the ionic radius of the alkali metal cations increased. All FT-EXAFS spectra showed a strong peak at around 1.5 Å due to a Fe-N bonds. Compared to $Fe(bpy)_3(ClO_4)_2$, the first peaks of $[Fe(bpy)_3]^{2+}$@MY are shifted toward shorter interatomic distances. The average Fe-N distances decreased as the size of the alkali metal cations increased, suggesting that the encapsulated iron(II) complexes may undergo distortion within the zeolite cavities due to the steric constraints induced by limited void space. In the photocatalytic styrene oxidation, the turn over number increased as the size of the alkali metal cations increased. This tendency is corroborated with that the electron density of the Fe atoms decreased as the ionic radius of the alkali metal cations increased.
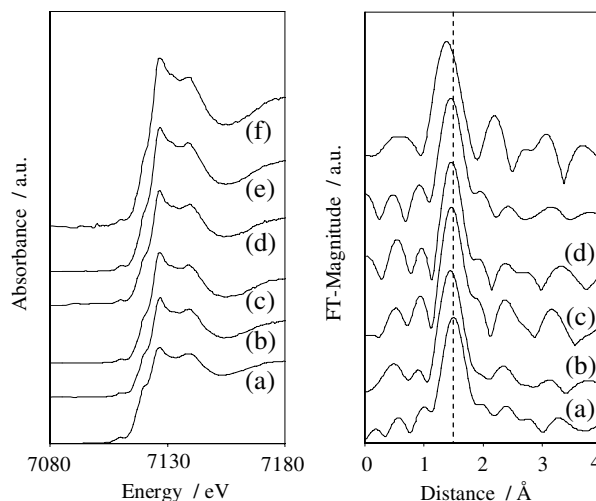

Fig. 2. Fe K-edge XANES and FT-EXAFS spectra of (a) $Fe(bpy)_3(ClO_4)_2$, (b) $[Fe(bpy)_3]^{2+}$@LiY, (c) $[Fe(bpy)_3]^{2+}$@NaY, (d) $[Fe(bpy)_3]^{2+}$@KY, (e) $[Fe(bpy)_3]^{2+}$@RbY, (f) $[Fe(bpy)_3]^{2+}$@CsY

References

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