

Structural determination of metal cations in interlayer space of inorganic clay materials by K-edge XAFS

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Introduction

Montmorillonites of smectite clays are composed of negatively charged two-dimensional silicate layer and an interlayer with cationic species[1]. Based on their large cation-exchange ability, various polyvalent metal species could be introduced into the interlayer. We have already explored a unique structure of the metal species within the interlayer that acted as highly efficient solid catalysts for a variety of environmentally friendly organic synthesis[2]. We also found an outstanding catalysis of scandium cations immobilized in the montmorillonite interlayer (Sc^{3+} -mont) for the Michael reaction under solvent-free conditions[3]. In this report, the local structure of the Sc^{3+} -mont catalyst was determined by Sc K-edge XAFS.

Experimentals

The Sc^{3+} -mont was prepared by stirring the Na^+ -mont in an aqueous solution of $\text{Sc}(\text{OTf})_3$ (OTf: trifluoromethanesulfonate). The obtained solid was washed with deionized water, and then dried at 110 °C. X-ray absorption spectra were measured in a transmission mode at the EXAFS facilities of KEK-PF, Tsukuba. Details of data analysis are referred to the reported procedure[4].

Results and Discussion

The elemental analysis showed that any OTf groups did not exist in the Sc^{3+} -mont. Retention of the layered structure, with a basal spacing of 3.6 Å, was verified by XRD measurements, and its XPS spectra revealed a formation of trivalent Sc species.

As depicted in Figure-a, in Fourier-transform (FT) of k^3 -weighted Sc K-edge EXAFS of the Sc_2O_3 , the broad peak due to Sc-Sc and Sc-O shells in the second coordination sphere was observed at around 2.8 Å. On the other hand, for the Sc^{3+} -mont samples, the lack of this peak showed monomeric Sc species in the interlayer of mont. This situation of Sc^{3+} species is sharply contrast to the Fe^{3+} cations in the interlayer where the Fe ions are linked by a M-O-M moiety to form a one-dimensional structure[2].

The peak at 1.7 Å was assignable to an Sc-O shell and the results of curve-fitting analysis for the Sc^{3+} -mont were listed in Table; the interatomic distance (R) and the coordination number ($C.N.$) were 2.13 Å and 6.0, respectively. The distance between Sc and oxygen atoms is close to that found in hexa-coordinated scandium aqua complexes. Conclusively, a monomeric aqua Sc ion is generated with the interlayer of the montmorillonite.

The Sc^{3+} -mont acted as heterogeneous and recyclable catalyst in the Michael reaction of various 1,3-dicarbonyl compounds with enones[3]. Correspondingly, stability of the $\text{Sc}(\text{H}_2\text{O})_6$ species in the recovered Sc^{3+} -mont catalyst was straightforwardly established by XAFS measurement, as described in Figure-c and Table.

The present preparation method using the cation-exchange ability of mont can provide a powerful protocol to stabilize an catalytically active metal species unwrapped within the interlayer as a macrocounteranion.

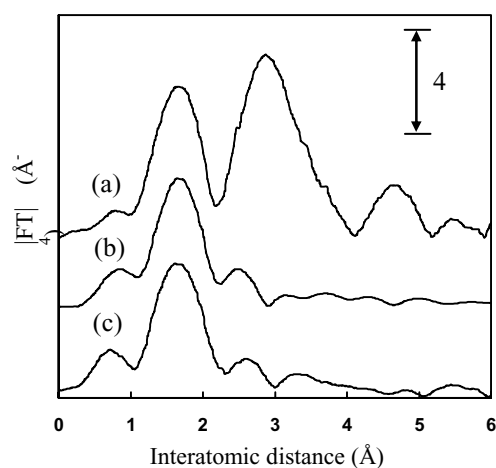


Figure: Fourier-transforms of k^3 -weighted Sc K-edge EXAFS of (a) Sc_2O_3 , (b) fresh Sc^{3+} -mont, and (c) recovered Sc^{3+} -mont catalyst. Phase shift was not corrected.

Table: Curve-fitting analysis of Sc-O shell for Sc^{3+} -mont catalysts

Sample	R (Å) ^a	$C.N.$ ^b	$\Delta\sigma$ (Å ²) ^c
Fresh	2.13	6.0	0.0019
Recovered	2.13	6.1	0.0014

^aInteratomic distance. ^bCoordination number. ^cDifference between Debye-Waller factor of the Sc^{3+} -mont and that of the reference sample.

References

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