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XAFS study of ytterbium complexes as new-type Lewis acid catalysts

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Local structures around Yb atoms in chiral ytterbium(III) trifluoromethanesulfonates ($Yb(OTf)_3$) catalysts prepared by a choice of two types of achiral ligands were studied by Yb L_3-edge XAFS spectroscopy to explain the difference of the catalytic performance of the two catalysts. Both the catalysts were found to be present as trivalent ytterbium oligomer. Curve-fitting analysis of EXAFS showed that Yb-Yb distance of two catalyst complexes is fairly different from each other, i.e., one is 3.68 Å and the other 4.04 Å.

Keywords: Lewis acid catalyst; Yb L_3-edge.XAFS.

1. Introduction

Lewis acid-catalyzed reactions are very important in organic syntheses. In general, this type of reaction should be performed under the strict anhydrous condition, because Lewis acid catalysts are often hydrolyzed easily. On the other hand, ytterbium(III) trifluoromethanesulfonates (ytterbium(III) triflate, $Yb(OTf)_3$) is stable in an aqueous solution and thus is a good Lewis acid catalyst in the Diels-Alder reaction of some dienophiles with cyclopentadiene.(Kobayashi *et al.*, 1992) Moreover, recently, Kobayashi *et al.*, found out that chiral catalysts prepared from $Yb(OTf)_3$ catalyze Diels-Alder reactions of some dienophiles with cyclopentadiene and afford both enantiomer of the corresponding cyclic compounds in high enantiometric excesses by using a single chiral source and a choice of achiral ligands.(Kobayashi *et al.*, 1994) These unique properties are supposed to be related to the specific coordination number of Yb and the configuration of $Yb(OTf)_3$ in the chiral catalysts. In the present work, we performed structural analysis of these chiral catalysts by XAFS spectroscopy to clarify the effect of a choice of achiral ligands on the structure around ytterbium.

2. Experimental

The standard chiral Yb catalyst was prepared in situ from $Yb(OTf)_3$, (R)-(+)-binaphthol, MS4A and cis-1,2,6-trimethylpiperodine, followed by addition of 3-acetyl-1,3-oxazolidin-2-one or 3-phenylacetylacetoneton in dichloromethane.(Kobayashi *et al.*, 1994) We refer to the samples naming the former and latter additives as chiral catalyst A and chiral catalyst B, respectively, hereinafter. The Yb content in each catalyst was ca. 20 mmol/l. For measurement of X-ray absorption spectrum, each catalyst was sealed in polyethylene bags under N_2 atmosphere.

X-ray absorption experiments were carried out at BL-7C station at Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF) with a ring energy of 2.5 GeV and stored current of 250 - 350 mA. XA data of samples were collected by the EXAFS facilities installed at BL7C at room temperature with an Si(111) two-crystal monochromator. Yb L_3-edge spectra of catalyst samples and solid reference samples were measured in fluorescence by a Lytle detector and in transmission modes by ion chambers, respectively. Sampling steps were ca. 0.6 eV for XANES and ca. 2 eV for EXAFS and an integration time for one spectrum was ca. one hour. The curve-fitting analysis was performed for the Fourier-filtered EXAFS with the empirical parameters extracted from EXAFS of c-type Yb_2O_3.

3. Results and discussion

Fig. 1 shows Yb L_3-edge XANES spectra of $Yb(OTf)_3{\cdot}xH_2O$ solid sample, chiral catalyst A and chiral catalyst B. Each XANES spectrum showed a single sharp white line at ca. 8946 eV and the energy position is characteristic for Yb^{3+}, reported by some authors.(Prabhawalkar & Padalia, 1983, Rao *et al.*, 1980, Tanaka *et al.*, 1993) Thus, we can attribute the white line to 2p - 5d electron transitions of Yb^{3+}. This result indicates that Yb ions in both chiral catalysts are in a trivalent state in a similar manner as $Yb(OTf)_3{\cdot}xH_2O$ solid sample. However, a detailed comparison of XANES spectra lead us to notice that white lines for chiral catalysts appear at slightly lower energy position than that of $Yb(OTf)_3{\cdot}xH_2O$ solid sample. Chaturvedi et al.(Chaturvedi *et al.*, 1995) investigated Dy L_3-edge XANES spectra of various Dy complexes and showed the relationship between the position of Dy L_3-edge absorption and the

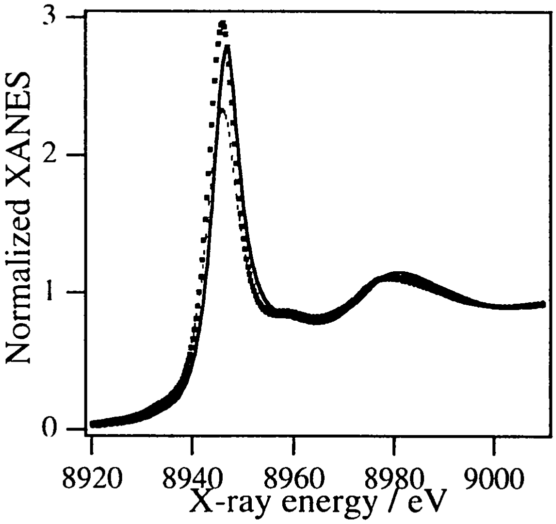

Figure 1
Yb L_3-edge normalized XANES spectra of $Yb(OTf)_3{\cdot}xH_2O$ (solid curve), chiral cat. A (dashed curve) and chiral cat. B (dotted curve).

electronegativity of ligands consisting of Dy complexes. Therefore, XANES spectra in Fig. 1 would indicate that the configuration of $Yb(OTf)_3$ in the chiral catalysts changed from that of $Yb(OTf)_3 \cdot xH_2O$ precursor. In addition, as the intensity of white line for chiral catalyst A is reduced compared with that for chiral catalyst B, the surroundings around Yb atoms in these two chiral catalysts are expected to be different.

To elucidate the difference in local structure around Yb atoms, Yb L_3-edge EXAFS spectra of these samples were measured and shown in Fig. 2. The characteristics of the EXAFS spectra in Fig. 2 became clearer when Fourier-transformation was performed on the EXAFS in $3.0 - 13.0$ Å^{-1} region to obtain their radial structure functions (RSFs). Fig. 3 shows RSFs of the samples mentioned above. In the RSF of

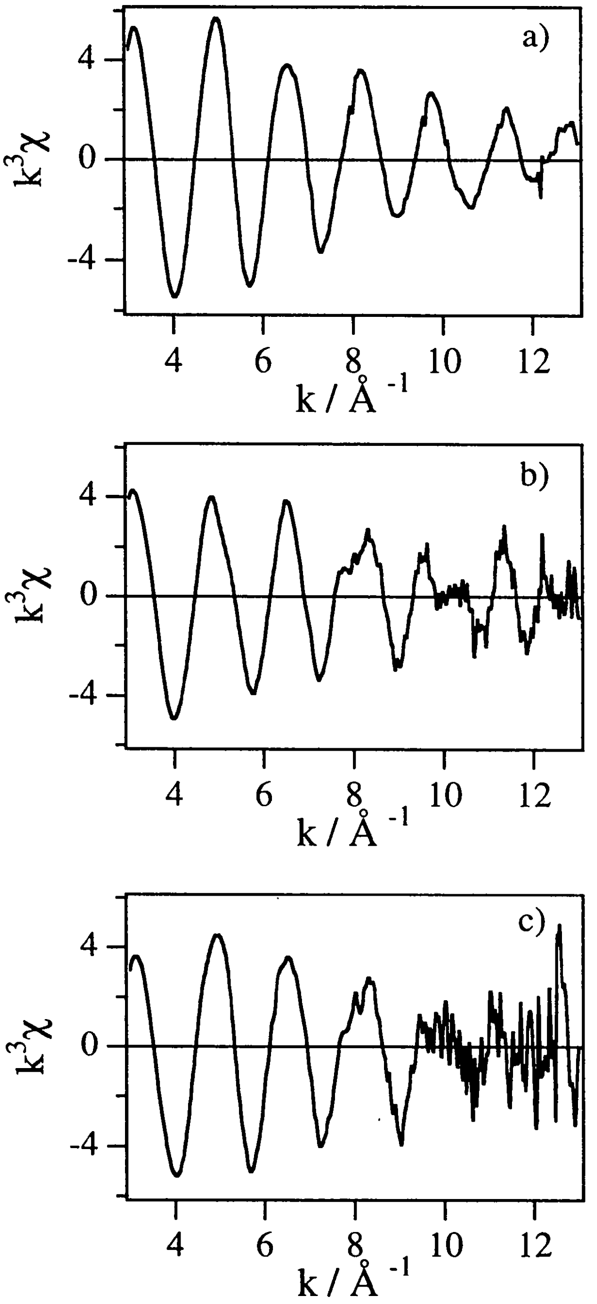

Figure 2
k^3-weighted Yb L_3-edge EXAFS spectra of a) $Yb(OTf)_3 \cdot xH_2O$, b) chiral cat. A and c) chiral cat. B.

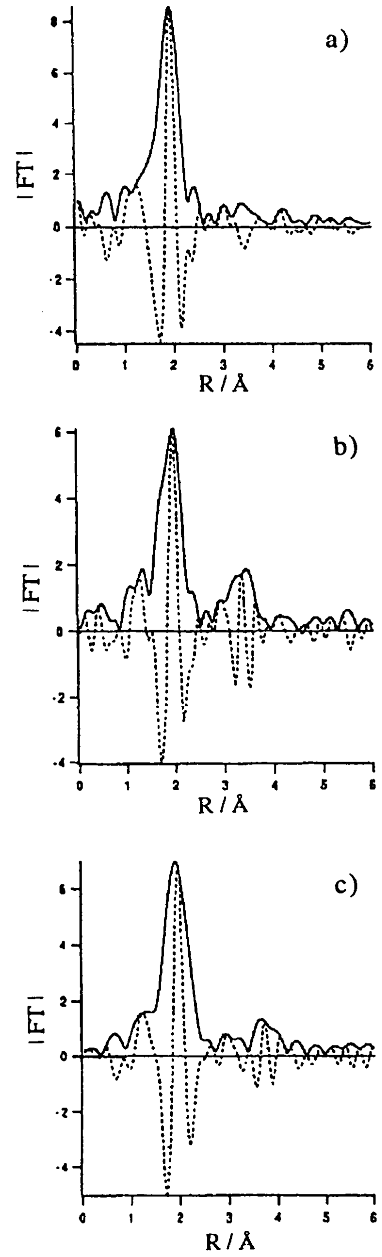

Figure 3
Fourier transforms of k^3-weighted Yb L_3-edge EXAFS spectra of a) $Yb(OTf)_3 \cdot xH_2O$, b) chiral cat. A and c) chiral cat. B.

Table 1

Results of curve-fitting analysis.

	shell	CN	R / Å	$\Delta\sigma^2$ / Å^2
Yb(OTf)$_3$	Yb-O	8.7	2.33	0.00079
chiral cat. A	Yb-Yb	2.4	3.68	0.00011
	Yb-O	7.6	2.33	0.00147
chiral cat. B	Yb-Yb	3.3	4.04	0.00289
	Yb-O	9.5	2.32	0.00213

The region of 1.3-4.0 Å in Fig. 3 were inversely Fourier transformed. The errors in CN and R are ± 10% and ± 0.02 Å, respectively.

Yb(OTf)$_3$·xH$_2$O solid sample, a sharp peak assigned to the Yb-O bond can be seen at around 2 Å while at higher distance range, no pronounced peak appears. This probably results from that Yb-Yb distances spread on a wide interval. Such disordering should induce a great damping of the amplitude of the EXAFS and the corresponding RSF. On the other hand, in RSFs of both chiral catalysts, small but distinct peaks at around 3 - 4 Å can be seen. The peaks were attributed to the presence of neighboring Yb atoms and their coordination numbers were evaluated ca. 2 - 3 by curve-fitting analyses (Table 1), that is, these results should reflect that both Yb chiral catalysts exist as dimer or trimer complexes in dichloromethane solution. As for the difference in the local structure of these chiral catalysts, coordination numbers of neighboring oxygen (Yb-O) and ytterbium (Yb-Yb) for chiral catalyst A are estimated at lower compared with those for chiral catalyst B. However, the difference in coordination number may not be discussed due to the accuracy of the curve-fitting analysis (within ±10 %). On the other hand, the estimated error in the interatomic distance (R) is within ± 0.02 Å, therefore, the difference in the interatomic distance of Yb-Yb, i. e., 3.68 Å for chiral catalyst A and 4.04 Å for chiral catalyst B is obvious. A choice of achiral ligands should mainly affect the distance of Yb-Yb in a chiral catalyst and control the selectivity of enantiomer of the corresponding cyclic compounds in Diels-Alder reactions.

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