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The State of Europium Complexes on Alumina Surface

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Abstract. Amide complexes of europium prepared by dissolving Eu in a liquid ammonia were fixed on alumina and heated at various temperatures in vacuo. The activity of the samples for the isomerization of 2,3-dimethylbut-1-ene changed remarkably with the evacuation temperature and the loading amount of Eu. XANES analysis of the samples showed that the Eu species are a mixture of divalent- and trivalent-ion complexes and the samples exhibiting high activity include only divalent Eu species. EXAFS analysis demonstrated that there are two kinds of divalent Eu species in the samples, i. e., the Eu species fixed by OH group on the alumina and the species consisting of Eu ions bridged by nitrogen. EXAFS analysis also revealed that the former is the inactive Eu species, while the latter is the active species for isomerization of 2,3-dimethylbut-1-ene. The catalytic activity closely related to the degree of the aggregation of the latter Eu active species.

1. INTRODUCTION

Amide complexes of europium prepared by dissolving Eu in a liquid ammonia were fixed on alumina ($\text{Eu}/\text{Al}_2\text{O}_3$) and heated at various temperatures in vacuo. The activity of the samples for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene was much influenced by the loading amount of Eu. The $\text{Eu}/\text{Al}_2\text{O}_3$ loading Eu less than 5 wt% was inactive, while above 5 wt%, the catalytic activity increased with the Eu loading until 8 wt% and then the activity fell off. In addition, the catalytic activity changed remarkably with the evacuation temperature, and it reached a maximum when the sample was evacuated at around 480 K. These results suggest that the valence and the structure of Eu species are different by the loading amount of Eu and the evacuation temperature. In the present work, XANES and EXAFS have been applied to clarify the electronic state and the local structure of Eu species supported on alumina.

2. EXPERIMENTAL

$\text{Eu}/\text{Al}_2\text{O}_3$ were prepared by an impregnation method.[1] The Al_2O_3 was impregnated with an Eu metal solution of liquid ammonia under an inert condition, followed by evacuation at various temperatures for 1 h. The $\text{Eu}/\text{Al}_2\text{O}_3$ evacuated at T (T: 353 - 973 K) are referred to as $\text{Eu}/\text{Al}_2\text{O}_3(\text{T})$ hereinafter.

X-ray absorption (XA) experiments were carried out at beam line 7C station at Photon Factory in National Laboratory for High Energy Physics (KEK-PF) with a ring energy, 2.5 GeV and stored current, 250 - 350 mA (Proposal no. 91-175 and 93G168). XA data of $\text{Eu}/\text{Al}_2\text{O}_3$ were collected in a fluorescence mode at room temperature with an Si(111) two-crystal monochromator. Each XA spectrum of an $\text{Eu}/\text{Al}_2\text{O}_3$ was recorded using an in situ cell made of Pyrex glass with a Kapton window. The non-linear curve-fitting analysis was performed for the Fourier-filtered EXAFS by using empirical parameters extracted from EXAFS of reference compounds and those compiled in FEFF package.[2] The parameters for Eu-O or Eu-N (Eu-O,N) were extracted from the EXAFS of cubic C-type Eu_2O_3 . For the Eu-Eu shells, we used those compiled in FEFF package. For Eu-Al shell, we adopted the phase shift for an Eu-Mg shell obtained by calculating from those of Eu-O, Ni-O and Ni-Mg shells. The phase shifts for Ni-O and Ni-Mg shells were extracted from the EXAFS of a NiO and $\text{Ni}_{0.02}\text{Mg}_{0.98}\text{O}$ solid solution,[3] respectively. For the backscattering amplitude of Al, we also adopted the parameter for Ni-Mg shell.

3. RESULTS AND DISCUSSION

Fig. 1 shows Eu L₃-edge XANES spectra of 8 wt% and 4 wt% $\text{Eu}/\text{Al}_2\text{O}_3$ evacuated at various temperatures. The spectra exhibit two absorption maxima at 6972 and 6980 eV, so-called white lines, indicating that $\text{Eu}/\text{Al}_2\text{O}_3$ samples consist of at least two kinds of Eu species. From the peak positions, these peaks are assignable to $2p_{3/2} - 5d$ transition in Eu^{2+} and Eu^{3+} ions, respectively.[4] To estimate the fraction of Eu^{2+} and Eu^{3+} species, we carried out deconvolution[5, 6] of each XANES spectrum with two sets of a Lorentzian for a white line and an arctangent function for a continuum absorption. In the present case, the sums of the areas of two white lines were found to be constant for all samples (ca. 16.5 eV unit), suggesting that the ratio of areas indicates directly the ratio of Eu^{2+} and Eu^{3+} species. The fraction of Eu^{2+} species closed to 100 % in

Eu/Al₂O₃ samples evacuated around 500 K, which samples exhibited high activity for the isomerization reaction. This result clearly indicates that Eu²⁺ species is the active species for the isomerization of 2,3-dimethylbut-1-ene. However, the change of the catalytic activity did not correlate to the valence variation of Eu species. For example, the fractions of Eu²⁺ species in Eu/Al₂O₃ samples evacuated at 473 K and 573 K are almost the same (93 % and 85 %, respectively), but the catalytic activity of Eu/Al₂O₃(473 K) is much higher by a factor of ten than that of Eu/Al₂O₃(573 K). In addition, the dominant valence state of Eu is divalent in 4 wt% Eu/Al₂O₃(423 K), but the activity of this sample was inactive for the reaction.

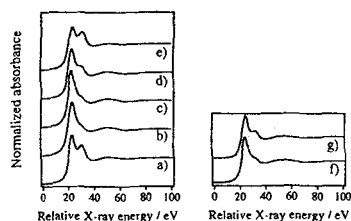


Figure 1: Eu L₃-edge normalized XANES spectra of 8 wt% Eu/Al₂O₃ evacuated at a) 353, b) 423, c) 473, d) 573 and e) 973 K and those of 4 wt% Eu/Al₂O₃ evacuated at f) 423 and g) 523 K. Energy offset is taken to be 6950.0 eV.

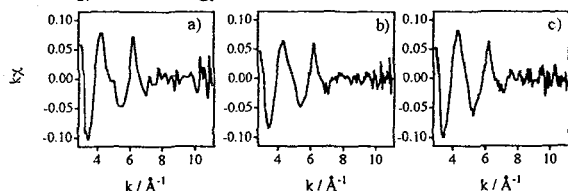


Figure 2: k-weighted EXAFS spectra of 8 wt% Eu/Al₂O₃ evacuated at a) 473 K and b) 573 K and that of c) 4 wt% Eu/Al₂O₃ evacuated at 423 K.

Table 1: The curve-fitting results. N; coordination number, R; interatomic distances.

Samples	shell	N	R / Å	$\sigma^2 / \text{Å}^2$
4 wt% Eu / Al ₂ O ₃ (423 K)	Eu-O,N	2.2	2.13	-0.0012 ^{a)}
	Eu-O,N	2.6	2.32	-0.0023 ^{a)}
	Eu-Al	1.4	3.28	0.0072 ^{a)}
8 wt% Eu / Al ₂ O ₃ (473 K)	Eu-O,N	2.2	2.17	-0.0010 ^{a)}
	Eu-O,N	2.1	2.35	0.0018 ^{a)}
	Eu-Al	1.3	3.29	0.0050 ^{a)}
8 wt% Eu / Al ₂ O ₃ (573 K)	Eu-Eu	1.5	3.48	0.0082 ^{b)}
	Eu-O,N	1.6	2.14	-0.0010 ^{a)}
	Eu-O,N	1.6	2.33	-0.0033 ^{a)}
	Eu-Al	0.9	3.29	0.0067 ^{a)}
	Eu-Eu	0.7	3.49	0.0075 ^{b)}

a) Relative Debye-Waller factors against those of reference samples. b) Debye-Waller factors. The estimated errors in N and R are $\pm 10\%$ and ± 0.02 Å, respectively.

Fig. 2 shows k-weighted Eu L₃-edge EXAFS spectra of 8 wt% Eu/Al₂O₃(473 and 573 K) and 4 wt% Eu/Al₂O₃(423 K). As for all Eu/Al₂O₃ samples, EXAFS spectra show fundamentally the same patterns. However, the shoulder around 5 Å⁻¹ seen in the EXAFS of 8 wt% Eu/Al₂O₃(473 K) can not be observed in the EXAFS spectrum of 4 wt% Eu/Al₂O₃(423 K). We also carried out curve-fitting analysis against the Fourier-filtered EXAFS spectra of these samples. The results are summarized in Table 1. It is revealed that there are short and long Eu-O or Eu-N bonds in all the samples. On the other hand, the curve-fitting analysis also shows that both neighboring Eu and Al atoms exist in 8 wt% Eu/Al₂O₃ samples, whereas only neighboring Al atom exists in 4 wt% Eu/Al₂O₃ sample. One of the two kinds of Eu-O,N bonds is assigned to the nitrogen atoms of amide or imide groups bonded to Al atoms on the basis of the results of IR measurements.[1, 7] The other Eu-O,N bond and the neighboring Al atom would indicate the formation of Eu-O-Al bond, because IR study showed that Eu atoms react with OH groups on the alumina surface.[8] As for the neighboring Eu atom, the curve-fitting analysis indicates that the number of the Eu atom in 8 wt% Eu/Al₂O₃ decreases from 1.5 to 0.7 as the evacuation temperature rises from 473 K to 573 K. In the temperature region of 473 - 573 K, we detected the desorption of NH₃ gas from the Eu/Al₂O₃ sample by the TPD measurement.[8] Therefore, the neighboring Eu atom is assignable to the Eu atoms bridged by nitrogen atoms. The decrease of the coordination number of Eu-Eu shell in 8 wt% Eu/Al₂O₃(573 K) probably results from the desorption of the bridging nitrogen atoms as NH₃. These curve-fitting results strongly demonstrate that divalent Eu ions preferentially react with OH group on Al₂O₃ surface to form the isolated Eu species in 4 wt% Eu/Al₂O₃ while the additional Eu species consisting of the Eu atoms bridged by the nitrogen atom are formed in 8 wt% Eu/Al₂O₃. Therefore, we conclude that the former Eu species is inactive for the isomerization of 2,3-dimethylbut-1-ene, but the latter Eu species is active, by comparison with the catalytic activity of 4 wt% Eu/Al₂O₃(423 K) and 8 wt% Eu/Al₂O₃(473 and 573 K). In addition, the coordination number of the neighboring Eu atom in 8 wt% Eu/Al₂O₃(473 K) would indicate that the highest activity for the isomerization of 2,3-dimethylbut-1-ene is obtained when Eu dimer or trimer is formed. One of the important factors controlling the catalytic activity of Eu/Al₂O₃ should be the degree of the aggregation of the active Eu species.

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