Catalytic properties of low-valent europium introduced into Y-zeolite

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Abstract

Europium was introduced into K^+-exchanged Y-zeolite (K–Y) by impregnation from an ammoniacal solution of the metal. The catalytic properties of the zeolite were examined by the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene and the Michael reaction of cyclopent-2-enone with dimethyl malonate. The change in the chemical state of the Eu was investigated by IR and X-ray adsorption fine structure. IR spectrum showed the presence of Eu amide by evacuating the zeolite around 350 K. The amide decomposed successively to Eu imide around 420 K and to Eu nitride around 610 K. The Eu L_3-edge X-ray absorption near-edge structure (XANES) spectrum showed that the oxidation states of Eu species are Eu^{2+} (Eu(II)) and Eu^{3+} (Eu(III)). The change of IR and XANES spectra, and that of the catalytic activity of Eu introduced into K–Y with the evacuation temperature suggest that the Eu(II) imide is the catalytically active species for the isomerization of 2,3-dimethylbut-1-ene and the Michael reaction of cyclopent-2-enone with dimethyl malonate, while the Eu(II) nitride is active species for the hydrogenation of ethene.

Keywords: Europium; Isomerization; Michael reaction; Y-zeolite

1. Introduction

Europium and ytterbium dissolve in liquid ammonia to yield a blue solution containing solvated electrons [1]. Imamura et al., reported that the impregnation of Yb and Eu metal on SiO_2 from their ammoniacal solutions of the metals results in the formation of $Si–O–Ln–NH_2$ (Ln: Yb, Eu) and highly dispersed lanthanide metal, and that the metallic lanthanides have the catalytic activity for the hydrogenation and isomerizations of alkynes such as but-2-yne and dienes such as but-1,3-diene, respectively [2,3].

We have reported that the catalytic properties of the low-valent Eu or Yb introduced into Y-zeolites by impregnation from an ammoniacal solution of the metal, followed by heating under vacuum [4]. These metals impregnated on Y-zeolites are hereinafter denoted as Ln/Y-zeolite (Ln:Eu, Yb). The nature of Ln/Y-zeolite can be summarized as follows.

1) Ln/Y-zeolite heated under vacuum at ca. 500 K was active for the isomerization of but-1-ene, while the Ln/Y-zeolite evacuated at a tem-

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perature higher than ca. 600 K was inactive for the isomerization.

2) The isomerization of but-1-ene proceeds via a π-allyl anion intermediate.

3) Ln/Y-zeolite heated under vacuum at ca. 900 K, was an active catalyst for the hydrogenations of ethene and but-1,3-diene, while the Ln/Y-zeolite evacuated at a temperature lower than ca. 500 K was inactive for the hydrogenations.

4) The catalytic activities of the Eu and Yb are strongly influenced by the alkali metal cations present in the zeolites. Eu introduced into K–Y (Eu/K–Y) has the highest catalytic activity for the isomerization of but-1-ene.

Properties 1) and 3) suggest that the states of Eu and Yb species on the zeolite vary by changing the evacuation temperature. This was supported by the measurements of temperature programmed desorption (TPD) spectra [4]. However, the profiles of TPD spectra attributed to H_2 and N_2 desorption from Eu/K–Y are different from those of Yb/K–Y. This result suggests that the change of Eu species is different from that of Yb species.

In this work, the chemical state of eu species impregnated on K–Y was investigated by IR and EXAFS as a function of the evacuation temperature. The nature of the active species of Eu/K–Y for the alkene isomerizations, the Michael reaction and the hydrogenation of ethene [4] will be discussed.

2. Experimental

2.1. Materials

An ingot of Eu (99.9% purity) was obtained from Soekawa Rigaku Inc. Na-exchanged Y-zeolite (Si/Al = 2.88) from Toso Co. Ltd., was used in all experiments. K–Y was prepared by ion exchange with a KCl solution of 0.1 mol dm^{-3} at 353 K, followed by washing with water and drying at 393 K overnight. The degree of K$^+$ ion-exchange was determined to be 99% by atomic absorption analysis.

2.2. Catalyst preparation

Eu/K–Y was prepared by an impregnation method as follows. K–Y was calcined under air at 773 K for 10 h. The K–Y was placed in a quartz tube, and heated under vacuum to 10^{-3} Pa at 773 K for 3 h. After cooling the sample, a piece of Eu metal was put into the quartz tube under nitrogen. After evacuating the system to 10^{-3} Pa at room temperature, ammonia was liquefied into the quartz tube cooled with a mixture of dry-ice and ethanol to dissolve the Eu metal. The ammoniacal solution was kept in contact with K–Y for 1 h. The zeolite was then warmed up to room temperature to remove most of the ammonia, and then heated under vacuum at a given temperature for 1 h. The amount of Eu loaded on K–Y was 8 wt%, the atomic ratio of Eu to K being 1/8.

2.3. Reaction procedures

The isomerization of 2,3-dimethylbut-1-ene was performed in a conventional gas-circulating system, the volume being 422 cm^3. The amount of catalyst was 0.10 g. The reaction temperature was 314 K and the initial pressure of 2,3-dimethylbut-1-ene was 10.5 kPa.

The reactants used for the Michael reaction, cyclopent-2-enone and dimethyl malonate, were distilled under vacuum. The reaction was started by transferring 15 mmol of cyclopent-2-enone and 15 mmol of dimethyl malonate from a side-arm into the reactor containing the catalyst. The amount of catalyst was 0.25 g. The reactants and the suspended catalyst were stirred at 323 K for 20 h. The product was identified by ^{1}H NMR measurements. The yield of products analyzed by a gas chromatograph equipped with a OV-101 column by using propylbenzene as an internal standard.

2.4. IR measurements

IR spectra were recorded on a JASCO FTIR 7000 spectrometer at room temperature by using a home-made IR cell [5]. The most important

characteristic of the IR cell is that a self-supported disk placed on the holder can be impregnated in a metal–ammonia solution and then heat-treated in situ. The samples were then pulled up into the IR beam for IR measurements.

K–Y was pressed into a thin (10 mg cm^{-2}) self-supported pellet. A sample for IR measurement was prepared by the impregnation method as follows: After a disk of K–Y was heated under vacuum at 773 K for 3 h, a 0.03 g piece of the ingot of Eu metal was placed in the bottom of the cell under nitrogen. The IR cell was evacuated to 10^{-3} Pa at room temperature, and 4 ca. cm^3 of ammonia was then liquefied into the bottom of the cell cooled with a mixture of dry-ice and ethanol to dissolve Eu metal. The disk of K–Y was immersed into the ammoniacal solution of Eu for 1 h. The disk placed on the holder was then withdrawn from the ammoniacal solution and ammonia remaining in the bottom was removed by evacuation at room temperature. Here, the amount of Eu supported on K–Y zeolite was not quantified. Finally, the disk was again moved down to be heat-treated under vacuum at a prescribed temperature.

2.5. Measurements of X-ray absorption spectra

A sample for the measurement of X-ray absorption spectrum was prepared by an impregnation method as in the case of the catalyst preparation. The sample was transferred to an X-ray absorption cell without exposing it to air. The neck of the cell was then sealed. The cell was made of Pyrex glass with Kapton windows (i.d. 5 mm).

X-ray absorption experiments were carried out at Photon Factory in National Laboratory for High Energy Physics with a ring energy of 2.5 GeV and a stored current of 300–350 mA. The X-ray absorption spectra were recorded at room temperature in the transmission mode with a Si(311) two-crystal monochromator. X-ray absorption spectra were recorded every 0.3 eV in the XANES region. XANES spectra were normalized as described elsewhere [6,7].

3. Results and discussion

3.1. Influence of evacuation temperature on the catalytic activity

The effect of the heating temperature of Eu/K–Y under vacuum on the catalytic activity for the Michael reaction of cyclopent-2-enone 1 with dimethyl malonate 2 was examined. It is well known that the Michael reactions involve carbanion intermediates and are catalyzed by various bases. The reaction of 1 (15 mmol) with 2 (15 mmol) was carried out at 303 K for 20 h (Scheme 1). The yield of 3-(1,1-bismethoxycarbonyl)cyclopent-1-one 3, increased with increasing evacuation temperature and reached a maximum (81%) around 420 K (Fig. 1). The yield of 3 sharply decreased at higher evacuation temperatures. The selectivity to 3 was 100%.

The catalytic activity of Eu/K–Y for the isomerization of 2,3-dimethylbut-1-ene (DB-1) to 2,3-dimethylbut-2-ene (DB-2) was also examined as
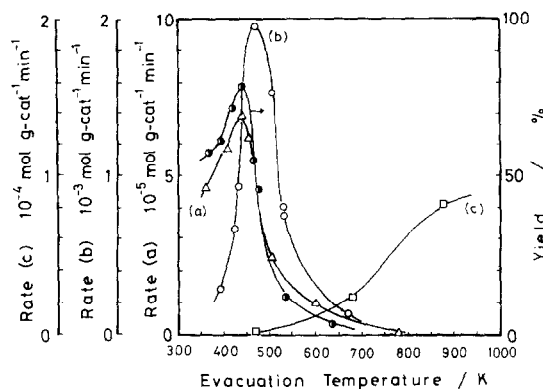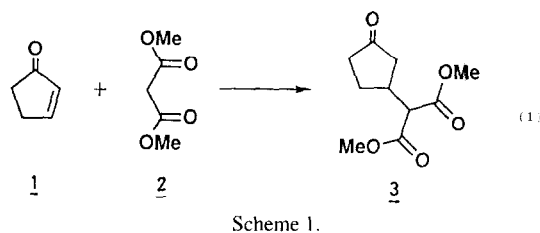
Scheme 1.

Fig. 1. The catalytic activity of Eu (8 wt%)/K–Y plotted against evacuation temperature. (△) Isomerization of 2,3-dimethylbut-1-ene (13.3 kPa) to 2,3-dimethylbut-2-ene at 314 K, (○) isomerization of but-1-ene (20.5 kPa) to but-2-enes at 273 K, (□) hydrogenation of ethene, (●) Michael reaction of cyclopent-2-enone (15 mmol) with dimethyl malonate (15 mmol) at 323 K for 20 h.

a function of evacuation temperature. The initial rates of the isomerization of DB-1 were measured at 314 K. This result is also shown in Fig. 1. The rate of the isomerization varies with the evacuation temperature in the same manner as that for the Michael reaction. As shown in Fig. 1, the highest activity was attained over Eu/K–Y evacuated around 420 K.

We have reported that the catalytic activity of Eu/K–Y for the isomerization of but-1-ene to but-2-enes increased sharply with increasing evacuation temperature and reached a maximum activity around 470 K [4]. At a higher evacuation temperature, the catalytic activity declined, while a catalytic activity for the hydrogenation of ethene was generated [4]. The results are reproduced in Fig. 1.

Although the temperature of the maximum activity for the isomerization of but-1-ene is ca. 50 K higher than that of DB-1, and the Michael reaction, the dependence of the evacuation temperature on the catalytic activity for these reactions is similar. This result indicates that the active species on Eu/K–Y for these reactions may be similar.

Eu/K–Y evacuated around 420 K, has little catalytic activity for ethene hydrogenation. The activity for this reaction increased by increasing evacuation temperature to 973 K. These results suggest that the active species for hydrogenation is different from that for the isomerization of alkenes and the Michael reaction.

3.2. Eu species as determined by IR measurements

The IR spectrum was measured after the sample was evacuated at 353 K for 30 min. The IR spectrum showed three bands at 3367, 3272 and 1526 cm^{-1} as shown in Fig. 2a. The bands at 3367 and 3272 cm^{-1} are attributed to asymmetrical and symmetrical stretch vibrations of N–H, respectively, and the band at 1526 cm^{-1} is attributed to the bending vibration of H–N–H.

Juza et al. [8], maintained that Eu amide was prepared in an ammoniacal solution of Eu metal
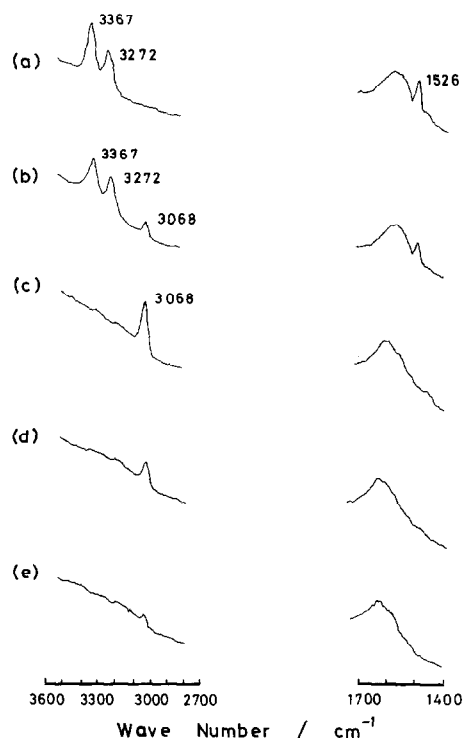

Fig. 2. IR spectra of Eu/K–Y after evacuation at (a) 353 K for 30 min, (b) 353 K for 1 h, (c) 423 K for 1 h, (d) 473 K for 1 h, (e) 523 K for 1 h.

at 232 K for 3 days. On the basis of the gravimetric analysis of Eu amide, they assigned Eu amide as $Eu(NH_2)_2$, although the detail of analytical method was not given. They also reported IR bands due to the $Eu(NH_2)_2$ were observed at 3263, 3200 and 1503 cm^{-1} [9]. Three IR bands as shown in Fig. 2a, agree reasonably well with those of europium amide, indicating that Eu supported on K–Y exists as the amide upon evacuating Eu/K–Y at 353 K for 30 min. However, IR bands cannot distinguish $Eu(NH_2)_2$ from $Eu(NH_2)_3$.

A new small band was observed at 3068 cm^{-1} upon heating the sample under vacuum at 353 K for 1 h (Fig. 2b), while the intensities of the three bands at 3367, 3272 and 1526 cm^{-1} slightly decreased by prolonging the evacuation period from 30 min to 1 h, as compared with those in the spectrum Fig. 2a. The intensity of the band at 3068 cm^{-1} increased by evacuating the sample at 423 K for 1 h, while the bands at 3367, 3272 and 1526 cm^{-1} disappeared (Fig. 2c). Since only one peak
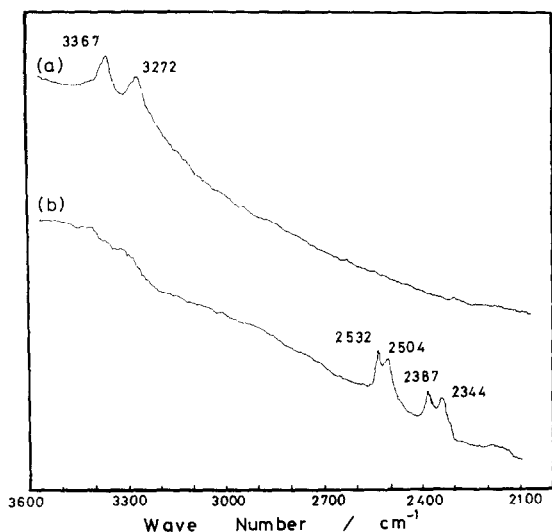
Fig. 3. IR spectrum of deuteration of Eu amide species. (a) Eu/K–Y evacuated at 353 K for 30 min. (b) Sample (a) contacted with D₂ (41 kPa) at 298 K for 30 min.

due to stretch vibration of N–H was observed, the band at 3068 cm⁻¹ is assigned as Eu imide species. This result suggests that Eu amide species is decomposed into Eu imide around 420 K. In the TDP spectrum [4], NH₃ desorption around 420 K was observed, corresponding to Eu amide transforming to the imide.

$$Eu(NH_2)_2 \rightarrow EuNH + NH_3 \qquad (2)$$

Howell et al. [10], reported that the thermal decomposition of the Eu(NH₂)₂ at 503 K gave rise to EuNH, and that the band of N–H stretch vibration due to EuNH was observed at 3150 cm⁻¹. The intensity of the band at 3068 cm⁻¹ decreased by increasing the evacuation temperature from 423 K to 473 K (Fig. 2d). This peak almost disappeared by evacuating the sample at 473 K for 1 h (Fig. 2e). This result suggests that the decomposition of Eu imide species is transformed into Eu nitride around 470 K, since TPD spectrum showed the hydrogen desorption around 500 K as reported earlier [4]. The bands due to Eu nitride species around 600 cm⁻¹ could not be detected by strong adsorption bands attributed to the frameworks of Y-zeolite.

The Eu amide species on K–Y was deuterated by contacting with D₂ (41 kPa) for 30 min at 298 K. As shown in Fig. 3, four new bands appeared

at 2523, 2504, 2387, and 2344 cm⁻¹, concomitant with the disappearance of the bands at 3367 and 3272 cm⁻¹. This result indicates that two different amide species exist on K–Y, although two different kinds of amide species could not be distinguished in the spectrum Fig. 2a.

The Eu imide species on K–Y was also deuterated. The intensity of the band at 3068 cm⁻¹ decreased to about half and a new band was observed at 2274 cm⁻¹ on contacting the sample Fig. 2c with D₂ (41 kPa) at 373 K for 2 h. This result indicates that a single kind of imide species is generated by the decomposition of two kind of Eu amide species.

3.3. Valence variation of Eu species

EXAFS spectroscopy was used to investigate the valence state of the Eu species. The Eu L₃-edge XANES spectra are shown in Fig. 4. The peaks of the L₃-edge XANES were observed at
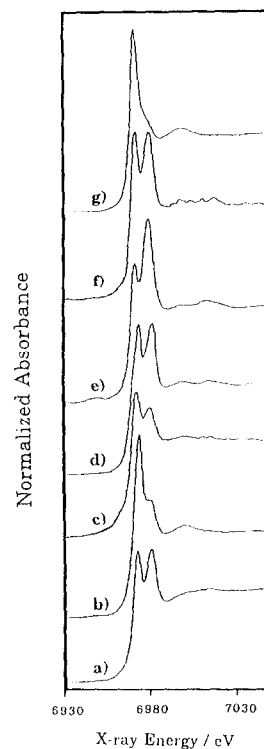

X-ray Energy / eV

Fig. 4. Eu L₃-edge absorption spectrum of Eu (8 wt%)/K–Y evacuated at (a) 303 K, (b) 423 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K, (g) 973 K for 1 h.
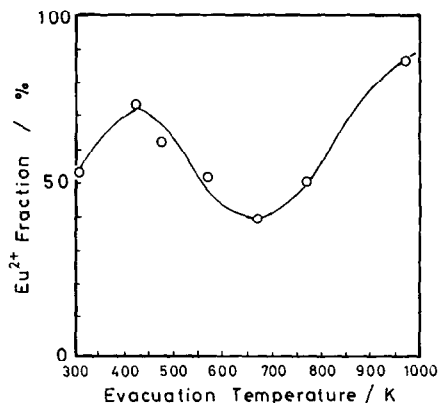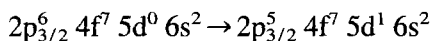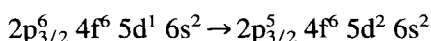
Fig. 5. Fraction of Eu^{2+} plotted against evacuation temperatures.

6970 and 6977 eV and the corresponding peaks of the L_2-edge XANES were observed at 7613 and 7621 eV, respectively. These energy values in L_3 and L_2 edges did not change by the changing the evacuation temperature.

The energy values due to the peaks of L_3 edge are very close to those of Eu^{2+} and Eu^{3+} in $EuCo_2Si_{2-x}Ge_x$ ($0 < x < 2$) [11] and $Eu_2Ni_3Si_5$ [12], and are attributed to the

$$2p^6_{3/2} \; 4f^7 \; 5d^0 \; 6s^2 \rightarrow 2p^5_{3/2} \; 4f^7 \; 5d^1 \; 6s^2$$

and

$$2p^6_{3/2} \; 4f^6 \; 5d^1 \; 6s^2 \rightarrow 2p^5_{3/2} \; 4f^6 \; 5d^2 \; 6s^2$$

transitions [13], respectively. These results indicate the existence of two valence states of the europium, i.e., Eu^{2+} and Eu^{3+}, and that there is no metallic europium species.

To estimate the fraction of Eu^{2+} and Eu^{3+}, the deconvolution of XANES spectra into two sets of curves, i.e., a Lorentzian line for absorption due to $2p \rightarrow 5d$ electron transition and an arctangent line for continuous absorption [14] was carried out.

The sum of the absolute peak areas due to Eu^{2+} and Eu^{3+} were constant for all the samples heated under vacuum at various temperatures (303–973 K). This result indicates that the areas are directly proportional to the amounts of the Eu^{2+} and Eu^{3+} species, respectively.

The fraction of Eu^{2+} thus determined was plotted against the evacuation temperature as shown in Fig. 5. The fraction of Eu^{2+} increased from

53% to 75% by increasing the evacuation temperature from 303 K to 423 K. In the TDP spectrum, the desorption of H_2 and N_2 was observed, corresponding to the decomposition of $Eu(NH_2)_3$ to EuNH. The oxidation states of europium in $Eu(NH_2)_3$ and in EuNH may be Eu^{3+} ($Eu(III)$) and Eu^{2+} ($Eu(II)$), respectively.

$$Eu(NH_2)_3 \rightarrow EuNH + 1/2H_2 + N_2 \qquad (3)$$
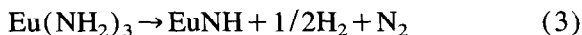
The fraction of Eu^{2+} decreased to 38% and the fraction of Eu^{3+} increased by increasing the evacuation temperature from 423 to 673 K. This is due to the decomposition of $Eu(II)$ imide (EuNH) to $Eu(III)$ nitride (EuN) with formation of hydrogen, whose desorption peak in the TPD spectrum was observed around 500 K [4].

$$EuNH \rightarrow EuN + 1/2H_2 \qquad (4)$$

The fraction of Eu^{2+} in Eu/K–Y gradually increased at an evacuation temperature higher than 673 K, and reached 88% at 973 K (Fig. 1). This is presumably caused by further decomposition of the $Eu(III)$ nitride species to nitrogen and $Eu(II)$ nitride, since the maximum nitrogen desorption in TPD spectrum was observed around 950 K.

3.4. Active species for catalytic reactions over Eu/K–Y

As shown in Fig. 1, the catalytic activities of Eu/K–Y for the isomerization of DB-1 and the Michael reaction of 1 with 2, increased sharply increased with increasing the evacuation temperature and reached a maximum activity around 420 K. In the case of the isomerization of but-1-ene, the maximum catalytic activity was observed around 470 K.

The fraction of Eu^{2+} gradually increased by increasing the evacuation temperature and reached maximum (75%) around 420 K (Fig. 5). Although the variation of catalytic activity is more extreme than that of the fraction of Eu^{2+}, the temperatures of the maximum activities for the three reactions are reasonably close to that where the maximum concentration of the Eu^{2+} species is

observed as shown in Fig. 5. Around this temperature, the Eu^{2+} species mainly exist in the imide form. Therefore, it is concluded that Eu(II) imide mainly acts as a catalyst for the isomerization of alkenes and the Michael reaction.

As mentioned above, Eu/K–Y evacuated around 420 K has little catalytic activity for ethene hydrogenation (Fig. 1). The activity for the hydrogenation gradually increased with increasing evacuation temperature from 673 to 973 K, concomitant with increasing the fraction of Eu^{2+} owing to the formation of Eu(II) nitride. Therefore, we can conclude that Eu(II) nitride mainly acts as a catalyst for the hydrogenation of ethene. It has already been reported that lanthanide nitride compounds have catalytic activity for hydrogenation of alkenes [15], the valence states of these compounds, however, were not given.

4. Conclusion

Eu(II) amide are generated by the reaction of Eu cations with ammonia on K–Y zeolite at ca. 350 K. Around 420 K, Eu(II) amide is decomposed to Eu(II) imide, which catalyzes the isomerization of alkenes and the Michael reaction. Eu(II) imide is decomposed to Eu(III) nitride around 670 K. Around 970 K, Eu(III) nitride is further changed to Eu(II) nitride, which shows catalytic activity for the hydrogenation of ethene.

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