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Catalytic Properties of Low-valent Lanthanide Species introduced into Y-Zeolite

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Low-valent ytterbium or europium species were introduced into Y-zeolites by impregnation from ytterbium or europium metal dissolved in liquid ammonia. The zeolites thus loaded with ytterbium or europium have a high catalytic activity for the isomerization of but-1-ene at 273 K, when they were heated under vacuum at *ca*. 500 K. Their catalytic activities are strongly influenced by the alkali-metal cations present in the Y-zeolite. The isomerization proceeds *via* an allylic carbanion-type intermediate. On the other hand, the zeolites heated under vacuum around 900 K are active for the hydrogenation of ethene at 273 K, and buta-1,3-diene at 323 K. The photoluminescence of europium supported on zeolites and temperature-programmed desorption spectra of gases desorbed from zeolites loaded with europium or ytterbium suggest that metal imides such as EuNH, and metal-like species may be formed by the zeolites under vacuum at *ca*. 500 and 900 K, respectively.

Homogeneous low-valent lanthanides have been developed into useful reagents in organic synthesis.[1-3] For example, Kagan and co-workers reported that SmI_2 and YbI_2 were effective reducing agents for deoxygenation of epoxides and reduction of conjugated double bonds.[1] Evans *et al.* demonstrated that low-valent organolanthanide complexes synthesized by the metal vapour technique were the first f-element complexes capable of homogeneously catalysing the activation of hydrogen.[4-6] The low-valent lanthanides, however, have been little explored as heterogeneous catalysts compared to the high-valent ones such as lanthanide oxides.[7] Recently, Imamura *et al.* reported that highly dispersed lanthanide metals such as Sm and Eu, prepared by depositing lanthanide metal vapour into a frozen tetrahydrofuran or benzene matrix at low temperature, catalysed the hydrogenation of alkynes and alkenes.[8,9]

Zeolites have distinct structures and unique properties that are attributed, in part, to the presence of intracrystalline cavities. We have tried to impregnate Yb or Eu complexes on Y-zeolites by evaporating the solvent from a solution of Yb or Eu metal dissolved in liquid NH_3, and have reported that the low-valent ytterbium or europium species thus introduced into Y-zeolites have high catalytic activities for the isomerization of but-1-ene.[10] In this work, we report the isomerization of but-1-ene in more detail together with the hydrogenation of ethene and buta-1,3-diene over these catalysts.

Experimental

Materials

Ingots of Yb (99.9% purity) and Eu (99.9% purity) were obtained from Soekawa Rigaku Inc.

Na-Y zeolite (Si/Al = 2.88) from TOSOH was used in all experiments after having been washed with dilute NaCl. Alkali-metal cation-exchanged Y-zeolites were prepared by ion exchange with an alkali-metal chloride solution of 0.2 mol dm^{-3} at 353-373 K, followed by washing with water and drying at 393 K overnight. The degree of alkali-metal cation exchange was determined by atomic absorption analysis.

Preparation of Catalysts

Alkali-metal cation-exchanged zeolites were calcined under air at 773 K for 10 h. The zeolite (0.1-0.5 g) introduced into a quartz reactor of volume 76 cm^3, was heated under vacuum to 10^{-3} Pa at 773 K for 3 h, and the ingot of Yb or Eu was placed in the reactor under nitrogen. After evacuating the reaction system to 10^{-3} Pa at room temperature, NH_3 was liquefied into the reactor which was cooled with a mixture of dry ice and ethanol, in order to dissolve Eu or Yb metal. The metal solution of liquid NH_3 was kept in contact with a Y-zeolite for 1 h. The zeolite was warmed to room temperature to remove most of the NH_3, and was then heated under vacuum at the prescribed temperature for 1 h.

Reaction Procedures

The isomerization of but-1-ene was performed in a conventional gas-circulating system of volume 422 dm^3. The reaction temperature was 273 K and the initial pressure of but-1-ene was 20.5 kPa.

The isomerization of 2,3-dimethylbut-1-ene or 3,3-dimethylbut-1-ene, at an initial pressure of 10.5 kPa, was carried out in the same circulating system at 314 K.

The hydrogenation of ethene and buta-1,3-diene were also performed in a similar gas-circulating system of volume 259 dm^3. The temperatures used for hydrogenation of ethene and butadiene were 273 and 323 K, respectively. The initial pressures of hydrogen and ethene or buta-1,3-diene were 13.3 kPa and 26.6 kPa, respectively.

The reaction products in the system were collected by a gas sampler and were analysed by gas chromatography with a 10 m column of OV-101 for the isomerization of but-1-ene, a 2 m column of Porapak-Q for ethene hydrogenation and a 10 m column of Sebaconitorile for buta-1,3-diene hydrogenation.

TPD Spectra

The TPD spectra of gases desorbed from Yb or Eu supported on K-Y were measured as follows: The zeolite, which was kept in contact with liquid NH_3 containing Yb or Eu, was warmed to room temperature and then heated under vacuum at the prescribed temperature for 1 h. The relative amount of gas desorbed from the zeolite was determined mass-spectrometrically (ULVAC MSQ-300) with a heating rate of 5 K min^{-1} up to 973 K.

Photoluminescence Spectra

The Eu/K-Y samples were placed in a quartz cell and sealed for the measurement of photoluminescence spectra after having been treated. The spectra were recorded on a Hitachi 850 fluorescence spectrometer at room temperature.

Results and Discussion

Isomerization of Alkenes

But-1-ene over Eu *supported on K-Y Zeolite*

The isomerization of but-1-ene was carried out at 273 K over Eu or Yb supported on Y-zeolite. The catalysts were prepared by heating them under vacuum at 473 K for 1 h after contacting the metal solution of liquid NH_3 with the Y-zeolites. Only the double-bond migration of but-1-ene into (*Z*)- and (*E*)-but-2-ene proceeded, whereas no skeletal isomerization was observed. No gaseous hydrocarbons other than butenes were detected in the reaction mixtures.

The change in the gas-phase composition with reaction time over 2.71×10^{-2} g (0.178 mmol) of Eu supported on 0.50 g of K-Y zeolite, is shown in Fig. 1. Eu supported on K-Y zeolite (Eu/K-Y) showed a high activity for isomerization, and the conversion of but-1-ene reached 86.4% in 10 min. The main product was (*Z*)-but-2-ene, the (*Z*) : (*E*) ratio being constant at *ca.* 10, until the conversion of but-1-ene reached *ca.* 80%. This indicates that the rate of isomerization of but-1-ene to (*Z*)-but-2-ene is considerably faster than that of the isomerization between but-2-enes.

Yb supported on Y-zeolites has also a high catalytic activity for isomerization. For instance, 3.31×10^{-2} g (0.179 mmol) of Yb introduced into 0.50 g of K-Y, gave 82.7% conversion of but-1-ene in 10 min under the same conditions. The (*Z*) : (*E*) ratio was constant at *ca.* 4.3.

Influence of the Type of Na-*exchanged Zeolite on the Isomerization Activity of* Yb

The various zeolites in their Na-exchanged form were used for supporting Yb (6.6 wt.%), and initial rates of the isomerization of but-1-ene were measured at 272 K. The pressure of but-1-ene was 20.5 kPa. The catalytic activity of Yb depended strongly on the type of zeolite, and Na-Y zeolite was the best support (Table 1). The activity of Yb/Na-Y was *ca.* 35 times higher than that of Na-ZSM-5 zeolite. No zeolite showed any isomerization activity without Yb. The (*Z*) : (*E*) ratio was independent of the type of zeolite and was constant at *ca.* 4.5.

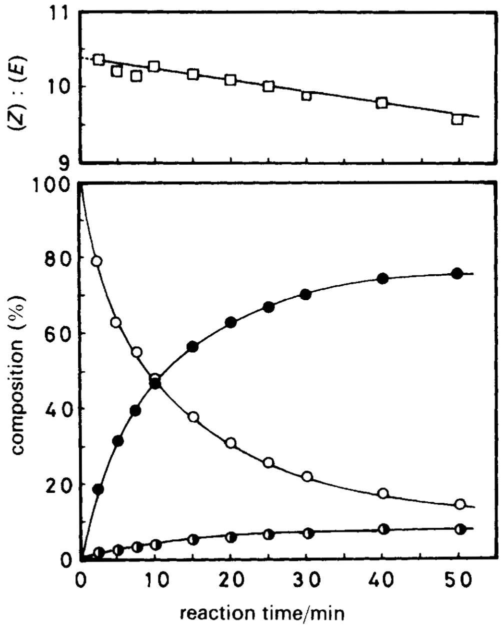

Fig. 1 Composition change in the reaction gas with reaction time. 0.027 g of Eu supported on 0.5 g of K-Y zeolite. Catalyst heated under vacuum at 473 K for 1 h after contacting Eu solution of liquid ammonia with K-Y zeolite. Reaction temperature 273 K, pressure of but-1-ene 20.5 kPa. ○, but-1-ene; ●,(*Z*)-but-2-ene; ◐,(*E*)-but-2-ene; □, (*Z*):(*E*) ratio

Table 1 Catalytic activities of Yb supported on various Na-exchanged zeolites for isomerization of but-1-ene

support	initial rate/10^{-5} mol g_{cat}^{-1} min^{-1}	(*Z*) : (*E*)
Na-Y	39	4.4
Na-X	5.2	4.3
Na-Mordenite	2.3	5.0
Na-A	1.9	4.1
Na-ZSM-5	1.2	4.2

Reaction temperature 273 K, Yb (6.7 wt.%) supported on zeolite, catalyst heated under vacuum at 473 K for 1 h, after contacting Yb solution of liquid ammonia with zeolite.

Effect of the Cation in Y-zeolite on the Isomerization Activity

The catalytic activity of Yb or Eu supported on alkali-metal cation-exchanged Y-zeolite was strongly dependent on the type of cation (Fig. 2). Eu/K-Y is the most effective catalyst, giving an initial rate of 3.9×10^{-3} mol g_{cat}^{-1} min^{-1}, *ca.* 100 times higher than that of Eu/Li-Y. The order of the catalytic activity of Eu supported on M^+-exchanged Y-zeolites was K > Rb > Cs > Na > Li (Fig. 2).

For Yb supported on Y-zeolites, K-Y was also the best support and the order of the catalytic activities of Yb supported on alkali-metal cation-exchanged Y-zeolites is the same as that for Eu supported on Y-zeolites.

The catalytic activity of Eu or Yb supported on Y-zeolites is much higher than that of proton-(H-Y) or Eu^{3+}-exchanged Y-zeolite (Eu-Y) (Fig. 2). The (*Z*) : (*E*) ratios were 0.93 and 0.90 over H-Y and Eu-Y, respectively. It is known that Eu^{3+}-exchanged zeolites have a solid-acid character because of the dissociation of water coordinated with Eu^{3+} in the zeolite as follows:[11]

$$Eu(H_2O)^{3+} \rightarrow Eu(OH)^{2+} + H^+ \qquad (1)$$

The (*Z*) : (*E*) ratios over Eu or Yb supported on the zeolites are very different from that of Eu^{3+}-exchanged Y-zeolite [(*Z*) : (*E*) = 0.9], and is nearly equal to that of H-Y, since the

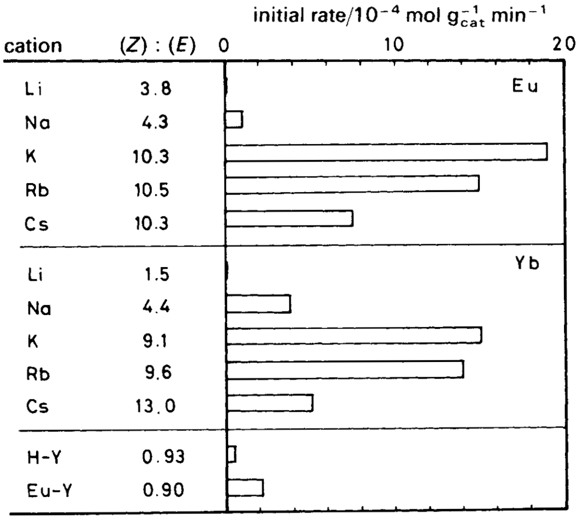

Fig. 2 Catalytic activity of Eu or Yb supported on alkali-metal cation-exchanged Y-zeolite. Degree of cation exchange: Li (67%), Na (100%), K (99%), Rb (47%) and Cs (39%). Reaction conditions: see Fig. 1

isomerization over Eu^{3+}-exchanged Y-zeolite proceeds by a carbocation mechanism. Therefore the character of Eu or Yb impregnated into alkali-metal cation-exchanged Y-zeolites by using a metal solution in liquid NH_3 is totally different from that of Eu^{3+}-exchanged Y-zeolite.

Dependence of the Isomerization Activity on the Amount of Eu *Supported on K-Y Zeolite*

The dependence of the initial rate of isomerization of but-1-ene at 273 K on the amount of Eu supported on K-Y is shown in Fig. 3. As mentioned above, K-Y did not have any catalytic activity on its own. The initial rate increased linearly with increasing Eu content, indicating that highly dispersed europium species are formed in zeolite pores. A maximum initial rate of 2.6×10^{-3} mol g_{cat}^{-1} min^{-1} was observed at 8.0 wt.%. This amount of Eu corresponds to 6 atoms per unit cell of K-Y. When the amount of Eu exceeded 8.0 wt.%, the catalytic activity decreased. Bigger Eu species presumably grew in the zeolite pores by introducing larger amounts of Eu species into the zeolite. The ratio $(Z):(E)$ ratio was nearly 9.5 and was independent of Eu loading.

Influence of Evacuation Temperature on the Isomerization Activity

The influence of evacuation temperature on the catalytic activities of Yb/Na-Y and Eu/K-Y for the isomerization of but-1-ene is shown in Fig. 4. In both catalysts, the activities for isomerization of but-1-ene sharply increased with increasing evacuation temperature and reached a maximum around 470 K. At higher evacuation temperature, the catalytic activities declined. Thus, the optimum evacuation temperature for isomerization of but-1-ene lies around 470 K.

The $(Z):(E)$ ratios were nearly constant at 4.5 and 10 over Yb/Na-Y and Eu/K-Y, respectively. Such high $(Z):(E)$ ratios suggest that the reaction proceeds *via* an allylic carbanion-type intermediate.

Mechanism of Isomerization of But-1-ene over Eu *Supported on Zeolite*

It has been reported that the isomerization of but-1-ene over base catalyst such as Na metal supported on Al_2O_3,[12] and on Na-Y zeolite[13] proceeds by a carbanion-type reaction mechanism, and the base catalysts give high $(Z):(E)$ ratios.

As shown in Fig. 2, the $(Z):(E)$ ratios are much higher than 1. These high ratios over Eu or Yb supported on alkali-metal cation-exchanged Y-zeolites are typical features of carbanion-type reaction mechanisms. The base-catalysed isomerizations of alkenes such as but-1-ene over Eu supported on Na^+, K^+ and Rb^+-exchanged Y-zeolites, over which the isomerizations proceed by a carbanion-type reaction mechanism, is confirmed by the fact that 3,3-dimethylbut-1-ene failed to react over these catalysts at 353 K. This molecule has no allylic proton and is therefore unable to form an allylic-type carbanion. The isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene did proceed over Eu supported on Y-zeolites as expected. For example, the initial rates were 1.2×10^{-6}, 1.7×10^{-5} and 4.9×10^{-5} mol g_{cat}^{-1} min^{-1} when the reaction was carried out over Eu (5.5 wt.%) supported on Na-Y, K-Y and Rb-Y zeolites, respectively, at 314 K with 10.5 kPa initial pressure of 2,3-dimethylbut-2-ene, after the catalyst was heated under vacuum at 473 K.

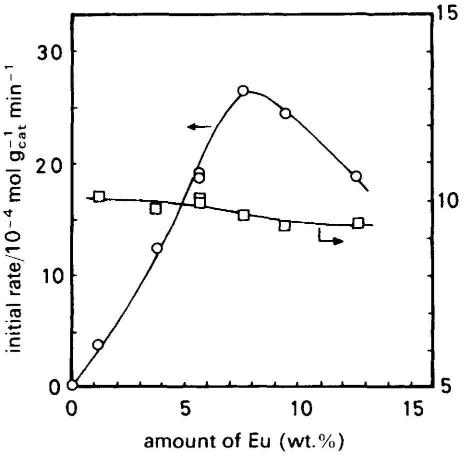

Fig. 3 Dependence of the initial rate of isomerization of but-1-ene on the amount of Eu supported on K-Y. Reaction conditions: see Fig. 1

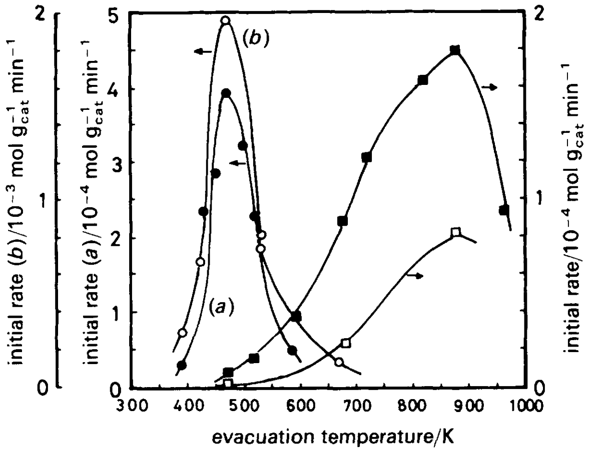

Fig. 4 Influence of evacuation temperature on the catalytic activity for isomerization of but-1-ene and hydrogenation of ethene. Isomerization of but-1-ene: ●, Yb (6.6 wt.%)/Na-Y; ○, Eu (5.5 wt.%)/K-Y. Reaction temperature 273 K, but-1-ene: 20.5 kPa. Hydrogenation of ethene: ■, Yb (6.6 wt.%) supported on K-Y zeolite; □, Eu (5.5 wt.%)/K-Y. Reaction temperature 273 K, hydrogen 26.6 kPa, Ethene 13.3 kPa

Hydrogenation of Alkenes

Ethene

As described above, Yb/K-Y or Eu/K-Y heated under vacuum around 500 K, is highly active for the isomerization of but-1-ene (Fig. 4). The influence of evacuation temperature on the hydrogenation of ethene was also examined. Yb/K-Y or Eu/K-Y heated around 500 K has little catalytic activity for ethene hydrogenation, as shown in Fig. 4. Eu/K-Y has a lower hydrogenation activity than the Yb catalyst. In both cases, the maximum catalytic activity appeared around 900 K. This result indicates that Yb or Eu species formed by heating under vacuum at *ca.* 500 K have changed to other chemical species.

Hydrogenation of Buta-1,3-diene over Yb *Supported on K-Y Zeolite*

To investigate further the catalytic character of Yb/K-Y heated under vacuum around 900 K, this catalyst was applied to the hydrogenation of buta-1,3-diene. The conversion of buta-1,3-diene and the distribution of reaction products with reaction time are shown in Fig. 5, when the reaction was carried out at 323 K over 0.013 g of Yb supported on 0.2 g of K-Y zeolite. The catalyst was heated under vacuum at 873 K for 1 h. The conversion of buta-1,3-diene increased linearly with reaction time and reached *ca.* 80% in 120 min, indicating that the hydrogenation of buta-1,3-diene proceeds with zero-order kinetics with respect to the pressure of both buta-1,3-diene and hydrogen.

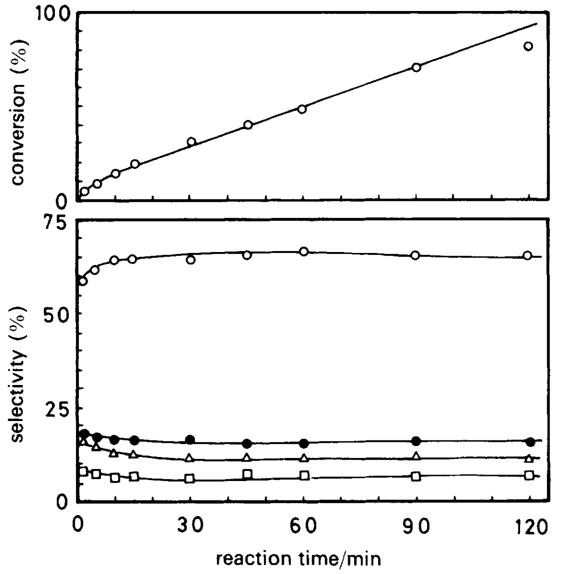

Fig. 5 Change in buta-1,3-diene conversion and selectivity to reaction products with reaction time. 0.013 g of Yb supported on 0.20 g of K-Y zeolite. Catalyst heated under vacuum at 873 K for 1 h after impregnation. Reaction temperature 323 K, hydrogen 26.6 kPa, buta-1,3-diene 13.3 kPa. ○, But-1-ene; △, (*Z*)-but-1-ene; ●, (*E*)-but-2-ene; □, butane

The main product was but-1-ene; the other products were (*Z*)-but-2-ene, (*E*)-but-2-ene and butane. The selectivities to butenes and butane varied little with reaction time, indicating that these products were formed with parallel reactions over the catalyst surface and that both isomerization and hydrogenation of butenes slightly proceeded. Thus, strong adsorption of buta-1,3-diene probably causes a high selectivity for butenes, since butenes produced on the catalyst surface would be easily displaced by buta-1,3-diene.

Dependence of the Catalytic Activity for Buta-1,3-diene Hydrogenation on the Amount of Yb *Supported on K-Y Zeolite*

Fig. 6 shows the influence of the amount of Yb supported on K-Y on the rate of hydrogenation of buta-1,3-diene and the product distribution at 323 K. The maximum rate appeared at *ca.* 4 wt.% Yb supported on K-Y zeolite. K-Y showed no catalytic activity for this reaction. The selectivities to butenes and butane changed slightly with the amount of Yb. The main product was but-1-ene.

Effect of the Cations in Y-zeolite on the Catalytic Activity for Hydrogenation of Buta-1,3-diene

As described above, the catalytic activities of Yb or Eu supported on Y-zeolite for isomerization of but-1-ene were strongly influenced by the type of cation in the zeolite. The effect of the cations in Y-zeolite on the catalytic activity for buta-1,3-diene was examined over Yb supported on alkali-metal cation-exchanged Y-zeolite at 323 K. The catalysts were prepared by heating under vacuum at 873 K for 1 h. The initial pressures of buta-1,3-diene and hydrogen were 13.3 and 26.6 kPa, respectively.

The catalytic activity of Yb supported on Y-zeolites for hydrogenation of buta-1,3-diene was also strongly dependent on the type of cation. The catalytic activities were in the following order at 323 K (rate/10^{-5} mol g_{cat}^{-1} min^{-1}):

$$Cs(6.4) > K(4.7) > Rb(4.6) > Na(2.8) > Li(1.6)$$

The strong influence of the type of cation on the catalytic activity suggests that the catalytically active species may be highly dispersed in the zeolite, and these active species remain in zeolite pores, even though the catalyst was heated under vacuum at temperatures as high as 873 K.

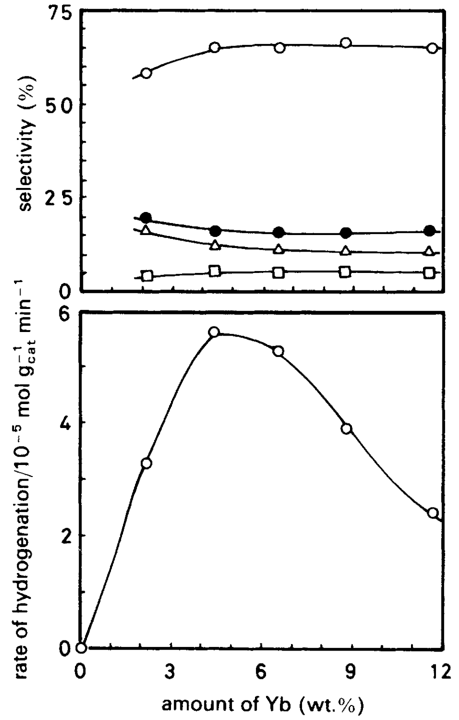

Fig. 6 Dependence of the catalytic activity for hydrogenation of buta-1,3-diene on the amount of Yb supported on K-Y zeolite. Reaction conditions: see Fig. 5

Influence of Evacuation Temperature on the Catalytic Activity for Hydrogenation of Buta-1,3-diene

For the hydrogenation of buta-1,3-diene, the maximum catalytic activity of Yb/K-Y appeared around 900 K, as in the case of ethene hydrogenation (Fig. 7). The Eu/K-Y or Yb/K-Y heated around 500 K, however, have very little catalytic activity for buta-1,3-diene hydrogenation.

The selectivity to butenes and butane was also strongly influenced by the evacuation temperature. When Yb or Eu supported on K-Y zeolite was heated under vacuum below 700 K, the main products were but-2-enes, the selectivity being *ca.* 90%. The product distribution changed markedly and but-1-ene was the main product instead of but-2-enes, when the catalyst was evacuated at higher than 700 K. Moreover, butane, which was not observed at the lower evacuation temperature, was formed at higher than 700 K. Hattori and co-workers[14] reported that but-2-enes are formed preferentially over solid-base catalyst during buta-1,3-diene hydrogenation, while Webb[15] reported that but-1-ene is the main product over conventional hydrogen catalysts such as Pt catalysts. As described above, Eu or Yb supported on Y-zeolite heated under vacuum around 500 K, works as a base catalyst. The predominant formation of but-1-ene over Yb/K-Y suggests that the characteristics of the catalyst change from basic to metallic by increasing the evacuation temperature from 500 to 900 K.

Characterization of Eu or Yb Species Introduced into Y-zeolites

Fluorescence Spectra

As described above, the catalytic character depends strongly on the evacuation temperature (Fig. 4 and 7). To investigate

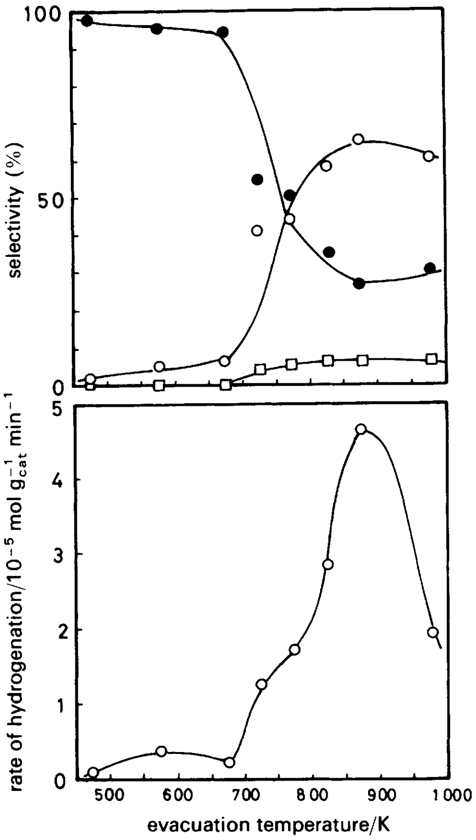

Fig. 7 Influence of evacuation temperature on the catalytic activity of Yb (6.6 wt.%)/K-Y. Reaction temperature 323 K, hydrogen 26.6 kPa, buta-1,3-diene 13.3 kPa. ○, But-1-ene; ●, but-2-enes; □, butane

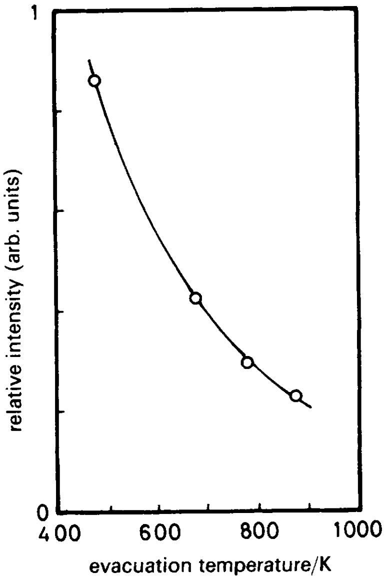

Fig. 8 Relative intensity of band emission for Eu^{2+} *vs.* evacuation temperature. Eu (5.5 wt.%) supported on K-Y zeolite. Eu/K-Y catalyst heated under vacuum at the prescribed temperature

the oxidation states of Eu or Yb species introduced into Y-zeolites, the photoluminescence spectra of Eu species were measured. When Eu/K-Y was heated under vacuum at 473 K for 1 h after K-Y was contacted with a solution of Eu in ammonia, the band excitation and the band emission were observed at 310 and 424 nm, respectively. The intensity of the band emission at 424 nm decreased with increasing evacuation temperature. A very slight emission was also observed at 625 nm. This band emission almost disappeared when Eu/K-Y was heated under vacuum at temperatures > 573 K.

Arakawa *et al.*[16] reported that the band emission of Eu^{II} in Na-Y and Na-mordenite zeolites due to the $4f^65d \rightarrow 4f^7$ transition is observed at 445 and 488 nm, respectively, by exciting the sample with radiation at 310 nm, and that the band emission of Eu^{III} in Na-mordenite is observed around 572 nm ($^5D_0$–$^7F_0$), 580 nm ($^5D_0$–$^7F_1$) and 624 nm ($^5D_0$–$^7F_2$).[17,18] Therefore, the emission band at 424 nm is due to the Eu^{II} cations, indicating that Eu^{II} species are formed in Y-zeolite pores by contacting Y-zeolites with a solution of Eu in liquid ammonia and then evacuating the sample at 473 K.

The relative intensity of the band emission (424 nm) for the Eu^{II} species is plotted as a function of the evacuation temperature. As shown in Fig. 8, the intensity of the band emission due to Eu^{II} species decreased monotonically with increasing evacuation temperature. This implies that Eu^{II} species are transformed into another species with an oxidation state < II by heating Eu/K-Y under vacuum.

TPD Spectra

In order to investigate further Eu or Yb species introduced into Y-zeolites, the measurements of gases desorbed from Eu (5.5 wt.%) or Yb (6.6 wt.%) supported on K-Y zeolite were carried out with TPD. To prepare the samples, K-Y was contacted with Eu or Yb in liquid ammonia for 1 h and was then evacuated at 303 K for 1 h. The gases desorbed from the catalyst were hydrogen ($m/z = 2$), NH_3 ($m/z = 17$) and nitrogen ($m/z = 28$). On the other hand, only the desorption of NH_3 was observed around 370 K, as shown by the dotted lines in Fig. 9 and 10, when K-Y was contacted with liquid ammonia. This desorption of NH_3 was caused by NH_3 physically adsorbed on K-Y.

Fig. 9 shows the profiles of H_2, NH_3 and N_2 desorption from Eu (5.5 wt.%) supported on K-Y zeolite. The NH_3 desorption peaks were observed around 370 and 450 K. The peak at 370 K is caused by the physical adsorption of NH_3

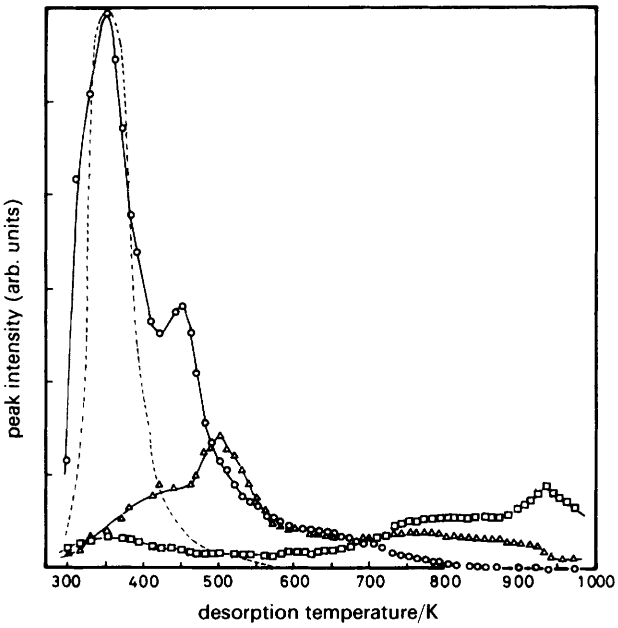

Fig. 9 TPD spectra of gases desorbed from Eu/K-Y. △, H_2; ○, NH_3; □, N_2. Eu (5.5 wt.%)/K-Y heated under vacuum at 323 K for 1 h after impregnation. (– – – –) NH_3 desorbed from K-Y heated under vacuum at 323 K, after contacting K-Y with liquid ammonia

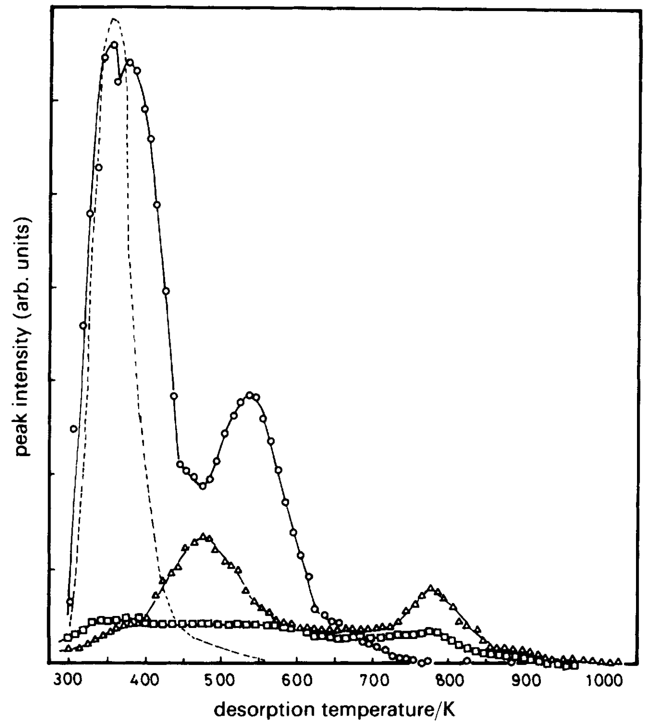

Fig. 10 TPD spectra of gases desorbed from Yb/K-Y. △, H_2; ○, NH_3; □, N_2. Yb (6.6 wt.%)/K-Y heated under vacuum at 303 K for 1 h after impregnation. (– – – –) see Fig. 9

on K-Y zeolite. The hydrogen desorption peaks were observed around 500 and 930 K.

It has been reported that $Eu(NH_2)_2$ is formed by evaporation of the solvent from a solution of Eu dissolved in liquid ammonia, and that the thermal decomposition of $Eu(NH_2)_2$ to the imide EuNH proceeds at 503 K and gives a brown-red product.[19] The colour of the Eu/K-Y was brown-red when Eu/K-Y was evacuated at 473 K, suggesting the formation of EuNH. According to the fluorescence spectra, Eu^{II} is observed by heating under vacuum around 500 K, and the amount of Eu^{II} species gradually decreases by heating the sample at higher temperatures (Fig. 8).

The desorption of NH_3 around 450 K may be caused by the decomposition of $Eu(NH_2)_2$ to EuNH:

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

The hydrogen desorption around 500 K presumably results from the decomposition of EuNH to the metal nitride, EuN:

$$2EuNH \rightarrow 2EuN + H_2 \qquad (3)$$

therefore, the maximum catalytic activity for the isomerization of but-1-ene over Eu/K-Y heated around 500 K may be explained by the formation of the imide; the catalytic activity is decreased by the formation of EuN by heating the sample above 500 K.

$Eu(NH_2)_2$ synthesized in liquid ammonia by using $Pd(NH_3)_4Cl_2$ was supported on K-Y by removing ammonia, and was then heated under vacuum at 473 K. This catalyst was applied to the isomerization of but-1-ene at 273 K, as in the case of Eu/K-Y. The initial rate of isomerization was 7.6×10^{-4} mol g_{cat}^{-1} min^{-1} at 273 K, and the ratio of (*Z*)-but-2-ene to (*E*)-but-2-ene was 9.8. This ratio is similar to the ratio (10.3) over Eu/K-Y; however, the initial rate is lower than that over Eu/K-Y. The decomposition of $Eu(NH_2)_2$ presumably gives EuNH, which is active for the isomerization of but-1-ene.

The nitrogen desorption at higher temperature is probably caused by further decomposition of the nitride to the metal-like species, which is active for the hydrogenation of alkenes:

$$EuN \rightarrow EuN_{(1-x)} + x/2N_2 \qquad (4)$$

Fig. 10 shows the profile of H_2, NH_3 and N_2 desorption from Yb (6.6 wt.%) supported on K-Y zeolite, after evacuating the sample at 303 K for 1 h. The NH_3 desorption peaks, apart from the physical adsorption of NH_3 from K-Y around 370 K, were observed around 400 and 540 K. The hydrogen desorption peaks were observed around 450 and 770 K. A small peak for nitrogen desorption was observed around 770 K.

It has been reported that the decomposition of a liquid ammonia solution of ytterbium gives the mixtures of diamide $Yb(NH_2)_2$ and triamide $Yb(NH_2)_3$, and that the thermal decomposition of $Yb(NH_2)_2$ proceeds at lower temperature than that of $Eu(NH_2)_2$ and gives YbN around 500 K.[20] In Fig. 10, the desorption of NH_3 around 400 K was observed. This suggests that YbNH formation proceeds by the decomposition of $Yb(NH_2)_2$ as in the case of $Eu(NH_2)_2$.

$$Yb(NH_2)_2 \rightarrow YbNH + NH_3 \qquad (5)$$

The hydrogen desorption around 450 K, may be caused by the decomposition of YbNH to YbN. It seems that the desorption of NH_3 results from the decomposition of $Yb(NH_2)_3$ to YbN, as follows:

$$Yb(NH_2)_3 \rightarrow YbN + 2NH_3 \qquad (6)$$

As in the case of EuN, at higher evacuation temperatures YbN decomposes to metal-like species, which are responsible for hydrogenation of alkenes. The small amount of hydrogen and nitrogen around 780 K might be caused by the decomposition of NH_3 molecules coordinated to Yb species.

Summary

(1) Catalysts prepared by heating under vacuum around 450 K show high catalytic activities for the isomerization of but-1-ene. (2) The isomerization proceeds *via* an allylic carbanion-type intermediate, and might be catalysed over metal imides. (3) Catalysts prepared by heating under vacuum around 900 K, are active for the hydrogenation of alkenes, which might proceed over the lanthanide metal-like species formed in the zeolite pores. (4) The catalytic activities of metal imides or metal-like species formed in Y-zeolites are strongly influenced by the cations present in the zeolite.

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