Catalytic Properties of Lanthanide Metals Introduced into Y-Zeolites

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Ytterbium or europium metal introduced into Y-zeolites, prepared by the impregnation method from ytterbium or europium metal dissolved in liquid ammonia, has a high catalytic activity for the isomerization of but-1-ene at 273 K, and their catalytic activities are dramatically influenced by the kind of alkaline metal cations in Y-zeolite.

Evans *et al.* have demonstrated that low-valent organolanthanide complexes synthesised by the metal vapour technique,[1] are the first f block element complexes capable of homogeneously catalysing the activation of hydrogen.[2–4] The lanthanide metals, however, have been little explored as heterogeneous catalysts. Recently, Imamura *et al.* reported that highly dispersed lanthanide metals, such as Sm and Eu, which are prepared by depositing lanthanide metal vapour into a frozen tetrahydrofuran (THF) or benzene matrix, catalyse the hydrogenation of alkynes and alkenes.[5–6] Fujiwara *et al.* have also reported that lanthanide metals, such as Yb, can be useful for carbon–carbon bond formation in organic synthesis.[7]

Zeolites have distinct structures and unique properties attributed, in part, to the presence of intracrystalline cavities. In this work, we demonstrate that ytterbium and europium metals introduced into Y-zeolites have very high catalytic activities for the isomerization of but-1-ene. The approach we tried was the impregnation of the metal from a solution of Yb or Eu metal dissolved in liquid ammonia.

Na-Y zeolite (Si : Al = 2.88) (TOSOH Co. Ltd.) was used after washing with a dilute NaCl solution. Alkaline cation exchanged Y-zeolites were prepared by ion exchange with an aqueous solution of alkaline chloride (0.2 mol dm^{-3}) at 353–373 K. They were dried at 393 K for 12 h and then calcined at 773 K for 10 h. The degree of the cation exchange was determined by atomic absorption analysis. The zeolite was pretreated in the reactor by evacuating to 10^{-3} Pa at 773 K for 3 h, and a piece of Yb (purity 99.9%) or Eu (purity 99.9%) ingot was introduced into the reactor under nitrogen. After evacuating the reaction system at room temperature, NH_3 was introduced into the reactor cooled with dry-ice–ethanol to dissolve Yb or Eu into liquid NH_3. The Yb or Eu solution of the liquid NH_3 was kept in contact with the zeolite for 1 h. The sample was warmed to room temperature, while collecting the NH_3 into a liquid nitrogen trap, and was then evacuated at 473 K for 1 h.

The isomerization of but-1-ene was performed in a conventional gas circulation system (reaction volume 422 dm^3). The reaction temperature was 273 K and the pressure of but-1-ene was 20.5 kPa. The reaction products in the system were collected by a gas sampler and were analysed by GC.

Yb or Eu supported on K-Y zeolite showed a very high catalytic activity for the double bond migration of but-1-ene at 273 K. Thus, the conversion of but-1-ene reached 86.4 and 82.7% within 10 min, when 3.31×10^{-2} of Yb and 2.71×10^{-2} g of Eu, respectively, were supported on 0.500 g of K-Y. These amounts of Yb and Eu are equal to 4.5 atoms per unit cell (u.c.) of K-Y. The main product was *Z*-but-2-ene, the ratio of *Z*-but-2-ene to *E*-but-2-ene (*Z* : *E*) being 9.1 and 10.3 over Yb and Eu, respectively, supported on the zeolite, until the conversion of but-1-ene reached *ca.* 80%. This result indicates that the rate of isomerization of but-1-ene to but-2-enes is considerably faster than that of isomerization beween but-2-enes. No skeletal isomerization was observed and no gaseous hydrocarbons, other than butenes, could be

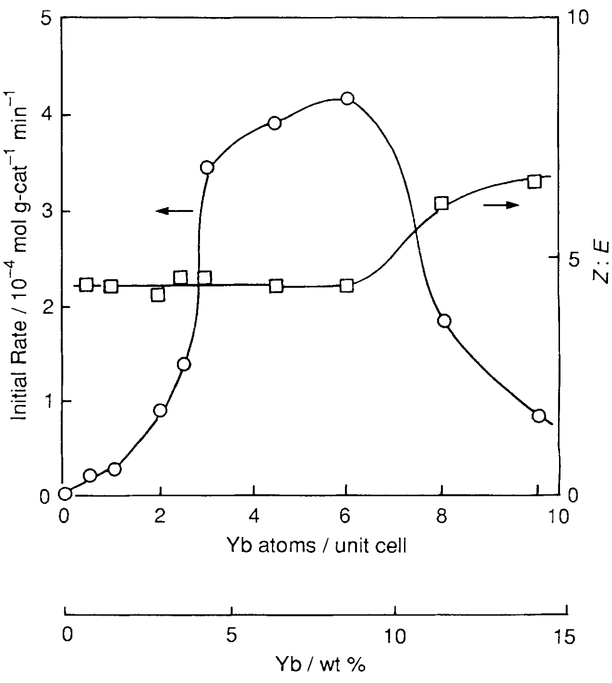

Fig. 1 The effect of the amount of Yb supported on Na-Y zeolite on the catalytic activity for the isomerization of but-1-ene. Reaction temperature; 273 K, pressure of but-1-ene; 20.5 kPa.

Table 1 Catalytic activities of Yb supported on Y-zeolites for the isomerization of but-1-ene

Cation	Degree of cation exchange (%)	Initial rate/ mol g-cat^{-1} min^{-1}	$Z:E$
Li	64	0.15×10^{-4}	1.5
Na	100	3.9×10^{-4}	4.4
K	99	15×10^{-4}	9.1
Rb	47	14×10^{-4}	9.6
Cs	39	5.1×10^{-4}	13
H[a]	75	0.55×10^{-4}	0.93

[a] H-Y zeolite without Yb; reaction temperature 273 K, but-1-ene at 20.5 kPa, 4.5 atoms of Yb per unit cell supported on Y-zeolite.

detected in the reaction mixtures. K-Y itself had no catalytic activity for this reaction. Eu and Yb and Y-zeolites exposed to oxygen did not show the catalytic activities either.

The dependence of the amount of Yb loaded on Na-Y zeolite (Yb/Na-Y) on the initial rate of isomerization at 273 K is shown in Fig. 1, the amount of Yb is expressed as the number of Yb atoms per u.c. of Na-Y. The catalytic activity strongly depends on the amount of Yb on Na-Y. Na-Y did not have a catalytic activity by itself for this reaction. When the amount of Yb was more than *ca.* 2 atoms of Yb per u.c., the rate sharply increased. The maximum initial rate of 4.2×10^{-4} mol g-cat^{-1} min^{-1} was observed at *ca.* 6 atoms of Yb per u.c. When the amount of Yb was more than 6 atoms per u.c., the catalytic activity decreased. These results indicate that the active sites for the catalysis are monoatomic species or very small metal clusters. The $Z:E$ ratio was *ca.* 4.5, the number of Yb being $\leqslant 6$ atoms. The $Z:E$ ratio increased when more than 6 atoms of Yb per u.c. were introduced.

It is well-known that the acid–base property of zeolites can be modified by exchanging Na^+ in zeolite with various cations. Table 1 shows that the catalytic activity dramatically depends on the kind of cations. K-Y is the best support, giving an initial isomerization rate 15×10^{-4} mol g-cat^{-1} min^{-1}. This catalytic activity of Yb/K-Y is about 100 times higher than Yb supported on Li-Y. For the isomerization of but-1-ene over Eu supported on Y-zeolites, K-Y was also the best support, the catalytic activity of Eu/K-Y being almost as high as that of Yb/K-Y. Yb and Eu supported on Y-zeolites exchanged with alkali metal cations have much higher catalytic activity than H^+ exchanged Y-zeolite.

The $Z:E$ ratio increased with the ionic radii of alkaline cations, as shown in Table 1. High $Z:E$ ratio over Yb or Eu clusters indicates that the isomerization over lanthanide metals in Y-zeolites proceeds by a carbanion type reaction mechansim, since the base catalysts such as MgO,[8] Na/Al_2O_3,[9] and Na/Na-Y[10] generally gives the high $Z:E$ ratio in but-1-ene isomerization. The base-catalysed isomerization over Yb on alkali cation exchanged Y-zeolites is further illustrated by the fact that 3,3-dimethylbut-1-ene fails to react over these catalysts at 354 K. This molecule has no allylic hydrogen, and is, therefore, unable to form an allylic type carbanion. The isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene does proceed over Yb supported on alkaline cation exchanged Y-zeolites, as expected. For example, the initial rates of isomerization were 1.5×10^{-5} and 4.9×10^{-5} mol g-cat^{-1} min^{-1} over 4.5 atoms of Yb per u.c. supported on K-Y and Rb-Y, respectively, at 314 K with 10.5 kPa of the initial pressure of 2,3-dimethylbut-1-ene.

Understanding of the exact nature of the catalytically active species require further studies. ESR and photoluminescence studies showed the presence of divalent species in the system. It is difficult, however, to decide that the active centres are monoatomic divalent species like metal amide or very small metal clusters, at this stage.

The features of lanthanide metals introduced into alkaline cation exchanged Y-zeolites from liquid ammonia solutions may be summarized as followed; (*i*) The catalysts, thus prepared, show very high activities for the isomerization of but-1-ene; (*ii*) The catalytic activities of the metals are dramatically influenced by the cations in the zeolite; (*iii*) The isomerization proceeds *via* an allylic carbanion type intermediate.

Received, 27th December, 1990; Com. 0/05797E

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