Reactivities and Properties of Lanthanide Catalysts Prepared by Thermal Degradation of Liquid Ammonia Solutions of Eu or Yb Metal

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Studies of X-ray diffraction, Fourier-transform infrared spectra and catalytic properties of lanthanide catalysts (Eu/AC and Yb/AC) prepared by impregnation of active carbon (AC) with liquid ammonia solutions of Eu or Yb metal were carried out for the catalytic hydrogenation of ethene. The lanthanides thus deposited on AC were changed through varied steps (metal, amide, imide or nitride) by thermal treatments and simultaneously the hydrogenation activity varied markedly. Eu/AC and Yb/AC which were subjected to the evacuation treatment around 573 and 773 K, respectively, showed a high activity even at 203 K. The catalytic properties of lanthanide amide ($Eu(NH_2)_2$, $Yb(NH_2)_2$, and $Yb(NH_2)_3$) prepared separately, imide and nitride were investigated for comparison. It was concluded that imide or imide-like species formed during the thermal decomposition processes of europium(II) and ytterbium(II and III) amides to nitride at 503—573 and 423—773 K was active catalysts for Eu/AC and Yb/AC, respectively.

Recently there has been a growing interest in lanthanides and their derivatives for potential synthetic and catalytic activity.[1] However, there have been few studies published of heterogeneous catalytic properties of lanthanide elements.

It has been shown that the use of dissolution of lanthanide metals (Ln=Eu and Yb) in liquid ammonia enables the preparation of novel lanthanide-dosed catalysts which exhibit specific catalytic properties.[2] Lanthanide-dosed SiO_2 (or Al_2O_3) prepared by the reaction of SiO_2 (or Al_2O_3) with liquid ammonia solutions of lanthanide metals shows selective hydrogenation properties, discriminating between conjugated and non-conjugated dienes.[3] The catalyst consists of amide species, such as $\equiv$Si–O–Ln–NH_2, which can catalyze the partial hydrogenation of benzene to cyclohexene with a very high selectivity of 96—100%.[4] It has been found that the catalytic properties vary markedly with varieties of matrix substrates, due to changes in the way in which the lanthanide species exist in the matrix.[5] More recently, for lanthanides introduced into zeolite by the reaction with Eu or Yb metal solutions in liquid ammonia, the changes in their chemical state with evacuation temperature are reported.[6,7] In view of these facts, a great deal of attention has been here devoted to understanding how the lanthanide metals in liquid ammonia exist on the matrix substrate under varying conditions, in particular varied temperatures of evacuation, and how this affects the catalytic properties for the hydrogenation of alkene. In this paper, the lanthanide catalysts (Ln/AC) obtained by impregnation of active carbon (AC) as a matrix with liquid ammonia solutions of Eu or Yb metals have been dealt with. Lanthanide amide, imide, and nitride have been studied for comparison.

Experimental

Materials. Eu and Yb ingots (99.9%) were obtained from Shin-Etsu Chemical Co., Ltd. and used in the form of turnings or granules. Active carbon (designated hereafter as AC; 1064 $m^2 g^{-1}$) obtained from Nacalai Chemicals Ltd. was evacuated at 873 K for 20 h before use. Ammonia gas (Iwatani Ind. Ltd.) was dried through a calcium oxide column and subsequently through a sodium hydroxide column.

Catalyst Preparation and Reaction. Ln/AC: In a typical preparation of 60% Yb/AC, the active carbon (AC; 0.57 g) which had previously been subjected to evacuation at 873 K was placed in a Schlenk tube and then ammonia of about 0.6 mol was liquefied at 198 K. Yb turnings (0.85 g) in limited amounts were added to the AC powder suspended in liquid ammonia with stirring at 198 K. The lanthanide metal immediately dissolved in liquid ammonia to form a homogeneous solution containing solvated electrons with an intense blue color,[8] which gradually faded as a result of the occurrence of ytterbium deposition on active carbon. On completion of the deposition, the excess ammonia was removed under vacuum at 198 K leaving AC-supported ytterbium catalysts (Yb/AC). The content of lanthanides in the catalysts was represented by the fraction of wt%.

Lanthanide Amides: According to the method of Hadenfeldt et al.,[9] lanthanide amides were prepared in a supported and unsupported type. For the preparation of AC-supported lanthanide amide, in a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed a measured amount of lanthanide metals and active carbon under an atmosphere of dry nitrogen. For example, Eu of 0.77 g and active carbon of 0.52 g were used for the preparation of 64% $Eu(NH_2)_2$/AC. The reactor was briefly evacuated, cooled by a dry ice/methanol bath and then about 0.8 mol of purified ammonia was liquefied. The mixture was stirred at room temperature for one day in Yb amide/AC and for four days in Eu amide/AC. For the preparation of unsupported amides, the same procedures were carried out without use of active carbon.

Hydrogenation Reactions: The hydrogenation of ethene was studied using a Pyrex gas-recirculation reactor. Prior to the reaction the catalysts were subjected to evacuation treatment at 298—1373 K for 2 h, set at the reaction temperature of 203—298 K and then the reaction was initiated by admitting hydrogen (40 Torr) and ethene (20 Torr, 1 Torr = 133.322 Pa). The reacting gas was periodically collected by a gas sampler and analyzed by a Shimadzu TCD gas chromatograph.

Analyses. IR spectra were recorded as Nujol mull samples on a JASCO FT-IR 7000 spectrometer equipped with MCT detector. The preparation of the samples was carried out as follows. The lanthanide amide after evacuation treatments at various temperatures for 2 h was embedded in paraffin oil in a dry-nitrogen glove bag. The samples thus prepared were carefully loaded into the IR cell. IR spectra were obtained from the ratio of the background spectrum of paraffin oil to that of each sample.

The X-ray diffraction (XRD) patterns of the samples were obtained with a Shimadzu X-ray diffractometer (VG-107R) using Cu $K\alpha$ radiation.

Results and Discussion

Eu/AC and Yb/AC. The catalytic behavior of Eu/AC and Yb/AC depended upon the thermal pretreatment in vacuo (Fig. 1). The evacuation treatment of Ln/AC at elevated temperatures (298—1373 K) for 2 h, before the reaction, strongly affected the hydrogenation activity of ethene. When 60% Yb/AC was used as a catalyst, upon evacuation above 473 K the catalytic activity appeared even at 203 K; the activity increased with increasing evacuation temperatures up to 773 K, and passed through a maximum around 773 K with an enhancement by over three orders of magnitude. Then, the catalyst was completely deactivated upon evacuation at 1373 K. On the other hand, 60% Eu/AC also exhibited a similar temperature dependence of catalytic activity. However, on the whole the tendency of Eu/AC as a function of the evacuation temperature was shifted about 200 K to lower temperature side compared with that of Yb/AC. The hydrogenation activity of Ln/AC was comparable to that of 10% Ni/SiO_2 (3.2×10^{-3} mmol min^{-1} g^{-1} at 203 K).

As shown in Fig. 2, XRD spectra of 60% Yb/AC revealed the existence of metallic ytterbium in the cubic structure, and a further increase in the evacuation temperature from 298 to 623 K resulted in the occurrence of crystallization to a significant extent. Furthermore, it was found that the lanthanide on active carbon began to be converted into the nitride (YbN) when subjected to the thermal treatment above 773 K. For 60% Eu/AC, the mode of XRD changes with temperature was different from that of 60% Yb/AC (Fig. 3). 60% Eu/AC as prepared showed diffraction patterns of europium amide, $Eu(NH_2)_2$, which was maintained up to about 453 K. Upon evacuation above 503 K, the amide and nitride coexisted in the XRD spectra. It was found that for Eu/AC the conversion to the nitride occurred upon evacuation at lower temperatures compared with Yb/AC.

The solution of Eu and Yb metals in liquid ammonia shows a deep blue color, being characteristic of the solvated electrons.[8] The lanthanide metal solutions are changed by thermal decomposition through varied steps.[10] From the results on Ln/AC described above, the solution processes of lanthanide metals in liquid ammonia with subsequent related reactions are described through the following equations:

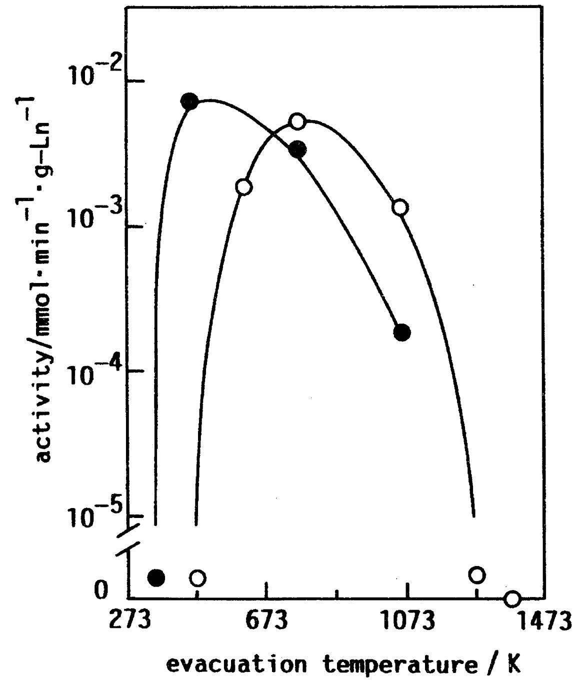

Fig. 1. Effect of the evacuation temperatures of Ln/AC on the hydrogenation rates of ethene. The catalysts were evacuated for 2 h prior to the reaction. Hydrogenation at 203 K over 60% Eu/AC (●) and 60% Yb/AC (○).

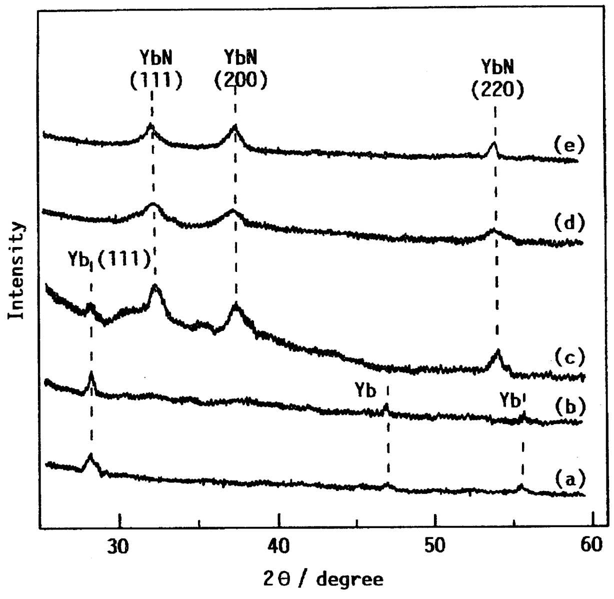

Fig. 2. XRD spectra of 60% Yb/AC. (a) as prepared; (b) 623 K; (c) 773 K; (d) 1073 K; (e) 1373 K. The samples were evacuated at prescribed temperatures for 2 h.

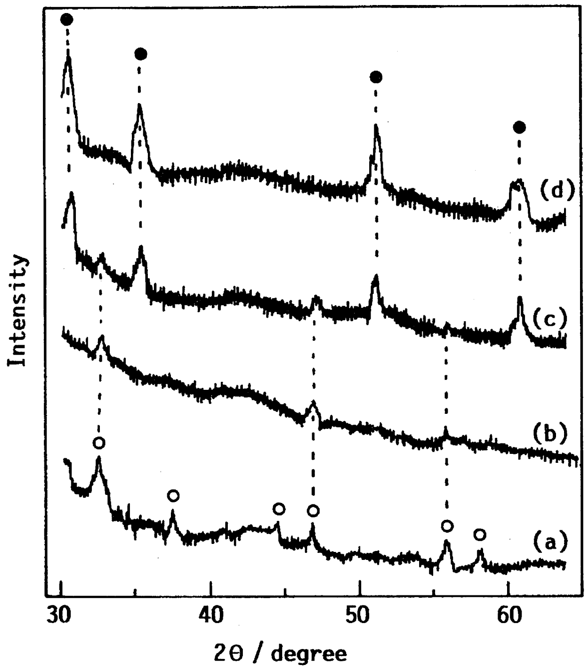

Fig. 3. XRD spectra of 60% Eu/AC. (a) as prepared; (b) 453 K; (c) 503 K; (d) 773 K. The d spacings correspond to: $Eu(NH_2)_2$ (○); EuN (●). The samples were evacuated at prescribed temperatures for 2 h.

$$\mathrm{Ln} \rightleftarrows \mathrm{Ln}^{2+} + 2\mathrm{e}_{\mathrm{am}}^{-} \quad (1)$$

$$\mathrm{e}_{\mathrm{am}}^{-} + \mathrm{NH_3} \rightarrow \mathrm{NH_2}^{-} + 1/2\mathrm{H_2} \quad (2)$$

$$\mathrm{Ln}^{2+} + 2\mathrm{NH_2}^{-} \rightarrow \mathrm{Ln(NH_2)_2} \quad (3)$$

$$\mathrm{Ln}^{2+} + 3\mathrm{NH_2}^{-} \rightarrow \mathrm{Ln(NH_2)_3} + \mathrm{e}_{\mathrm{am}}^{-} \quad (4)$$

$$\mathrm{Ln(NH_2)_2} \rightarrow \mathrm{LnN} + \mathrm{NH_3} + 1/2\mathrm{H_2} \quad (5)$$

$$\mathrm{Ln} = \mathrm{Eu,\ Yb}$$

The metallic lanthanide detected here (Fig. 2) is probably deposited on active carbon from liquid ammonia solutions of Yb through a reversal of Eq. 1.[11] The nitride is formed by the thermal decomposition of lanthanide metal solutions in liquid ammonia at elevated temperatures according to the steps shown above. However, the nitride can be also formed by the reaction of lanthanide metals with ammonia;[12] since active carbon as a support adsorbs large amounts of ammonia, the lanthanide metals deposited on active carbon can react with adsorbed ammonia to yield the nitride when Ln/AC was treated at elevated temperatures. Furthermore, it is also supposed that the reaction of lanthanide metals with ammonia gas yields lanthanide amides,[13] followed by decomposition to the nitride.

It is accepted that the thermal decomposition product of liquid ammonia solutions of Eu and Yb metals is finally the nitride (EuN and YbN) through amides or imides.[14,15] Europium metal solutions decompose to form the diamide exclusively at 223 K and further thermal degradation leads to imide (EuNH) under some circumstances,[16] finally crystalline EuN. Hadenfeldt et al.[9] have shown that thermal decomposition of $Eu(NH_2)_2$ at 523 K directly leads to formation of nitride (EuN). Decomposition of liquid ammonia solutions of ytterbium at 223 K gives rise to the ytterbium(II)–ytterbium(III) amide mixture and their decomposition also yields the nitride (YbN).

XRD gave no indication of lanthanide amides and/or imides in the present Eu/AC and Yb/AC samples. The existence of nitride was observed in XRD of Eu/AC and Yb/AC evacuated at higher temperatures, and such catalysts were deactivated as shown in Fig. 1. This might lead to speculations that species other than nitride are generated with changes in the pretreatment conditions (ca. 473—773 K) of Ln/AC and that they effectively catalyze the hydrogenation of ethene at such low temperatures of 203 K. However, for ytterbium introduced into Y-zeolite by impregnation from a liquid ammonia solution of lanthanide metals, the hydrogenation activity of ethene reaches a maximum upon evacuation temperatures, ca. 600—900 K, and consequently it has been claimed that YbN formed at this temperature ranges is catalytically active species.[6,17]

Although the lanthanide in metallic form is known to be active for the catalytic hydrogenation of alkenes,[18—20] the following facts make it very unlikely that the lanthanide metal detected here is active species for the present hydrogenation: (i) in the evacuation treatment of 60% Yb/AC at 773 K which led to a maximum activity, the diffraction peaks of Yb metal completely disappeared as shown in Fig. 2, (ii) the activity of lanthanide metal catalysts prepared by the metal vapour technique[21] for comparison was not so high as that observed at 203 K and (iii) judging from the results on lanthanide amides described in the following section.

AC-Supported and Unsupported Lanthanide (Eu and Yb) Amides. To clarify what the active lanthanide species are and under what conditions they are formed, the catalytic properties of lanthanide amide, as well as of imide and nitride derived from the amide, were studied. According to Ref. 9, the europium and ytterbium amide were first prepared in the form of a supported and unsupported catalyst. XRD of the active carbon-supported ytterbium amide displayed trivalent $Yb(NH_2)_3$ (Fig. 4A), while the unsupported ytterbium amide showed the diffraction pattern of divalent $Yb(NH_2)_2$ (Fig. 4B). This feature is one of the more interesting aspects of the present study since ytterbium amide prepared from Yb metal solutions in liquid ammonia normally yields a mixture containing di- and tri-amide with varied compositions, depending on the preparative conditions.[9,16] For the europium system, it was found that both the AC-supported and unsupported europium amide existed in the divalent state. It has been shown that the europium amide is always obtained exclusively as $Eu(NH_2)_2$.[9,15,16] In the XRD spectra, upon evacuation up to about 373 K, the structure of Yb(III) and Yb(II) amide was still maintained. When both samples were further evacuated at 423 K, new diffraction peaks around 31.7, 36.5, 52.8 and 62.0° appeared and coexisted with the lines attributable to amides. As shown in Fig. 4, above 453

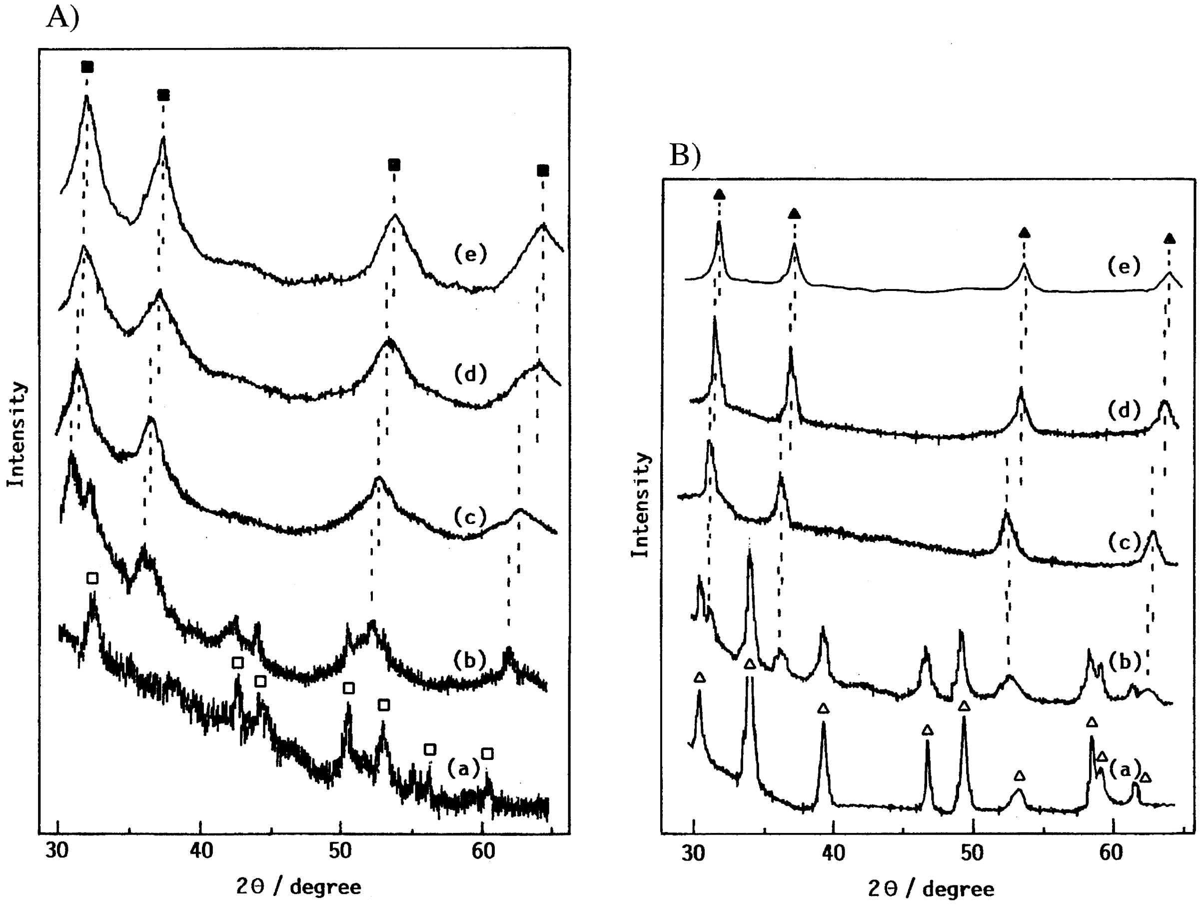

Fig. 4. A) XRD spectra of active carbon-supported Yb amide. (a) as prepared; (b) 423 K; (c) 453 K; (d) 723 K; (e) 873 K. The *d* spacings correspond to: $Yb(NH_2)_3$ (□); YbN (■). The samples were evacuated at prescribed temperatures for 2 h. B) XRD spectra of unsupported Yb amide. (a) as prepared; (b) 423 K; (c) 453 K; (d) 673 K; (e) 773 K. The *d* spacings correspond to: $Yb(NH_2)_2$ (△); YbN (▲). The samples were evacuated at prescribed temperatures for 2 h.

K the peaks of amides completely disappeared. The newly peaks observed at 503 K could be satisfactorily indexed to cubic lattice, a=4.85 Å, being in substantial agreement with the results of ytterbium imide (obtained at 513 K) characterized by Hadenfeldt.[9] These peaks gradually shifted to higher diffraction angles in the range of ca. 423 to ca. 773 K. X-Ray diffraction patterns of $Yb(NH_2)_3$/AC (Fig. 4A) and $Yb(NH_2)_2$ (Fig. 4B) eventually displayed lines attributable to a face-centered cubic lattice,[22] a=4.78 Å, in which YbN crystallized above about 873 and 773 K, respectively. It seems that active carbon as a support is effectively operative in thermal stability.

$$\begin{array}{ccccc} & & \mathrm{YbNH} & & \\ \mathrm{Yb(NH_2)_2,\ Yb(NH_2)_3} & \longrightarrow & \text{or} & \longrightarrow & \mathrm{YbN} \\ & & \text{imide-like species} & & \\ (<373\ \mathrm{K}) & & (423\text{—}773\ \mathrm{K}) & & (773\text{—}873\ \mathrm{K}<) \end{array} \qquad (6)$$

On the other hand, XRD of the supported and unsupported Eu(II) amide was held as $Eu(NH_2)_2$ up to approximately 503 K. The mixture of di-amide and nitride coexisted above this temperature and then, XRD was completely converted into the nitride EuN alone upon evacuating above 573 K. It was found that this changes in XRD with evacuation temperatures were very similar to those of 60% Eu/AC (Fig. 3) and moreover, that the conversion into the Eu nitride occurred upon treatment at lower temperatures compared with that for the ytterbium system. Howell et al.[16] claim that during the thermal decomposition of $Eu(NH_2)_2$, the imide, EuNH, is formed at 503 K. However, no indications of imide formation were recognized, despite our various attempts. Juza and Hadenfeldt[15] report that EuN is formed at 523 K, finding no evidence of imide formation.

$$\begin{array}{ccccc} & & \mathrm{Eu(NH_2)_2} & & \\ \mathrm{Eu(NH_2)_2} & \longrightarrow & \text{and} & \longrightarrow & \mathrm{EuN} \\ & & \mathrm{EuN} & & \\ (<503\ \mathrm{K}) & & (503\text{—}573\ \mathrm{K}) & & (573\ \mathrm{K}<) \end{array} \qquad (7)$$

IR spectra of europium(II) amide and ytterbium(II) amide were studied as a function of pretreatment temperatures. In Fig. 5A, $Yb(NH_2)_2$ as prepared showed strong absorptions at 3339, 3272, and 1527 cm^{-1}, which could be assigned to the NH_2 groups bound to the lanthanide by comparison with IR data reported on lanthanide amides,[13,15,23] alkali amides,[24] and alkaline earth amides.[25] These absorption bands are also analogous to those of Hewkin[26] for amido–metal complexes. The band positions and shapes of the

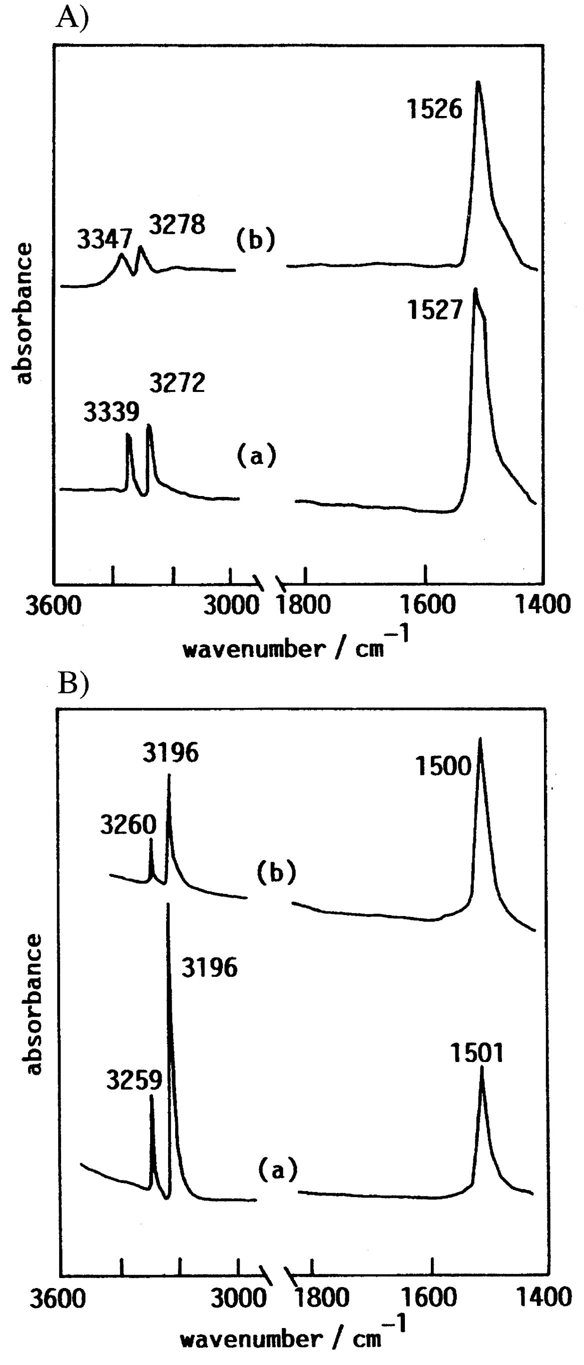

Fig. 5. A) IR spectra of $Yb(NH_2)_2$ (a) as prepared and (b) a sample after treatment at 453 K. B) IR spectra of $Eu(NH_2)_2$ (a) as prepared and (b) a sample after treatment at 503 K.

spectra (Fig. 5A) changed to 3347, 3278, and 1526 cm^{-1} when the sample was subjected to evacuation treatments at 453 K, leading to marked changes in XRD shown in Fig. 4B. For imide-like species $Yb_{0.62}N_{1.00}H_{1.13}$,[9] IR spectra indicate the presence of bands at 3346, 3280, and 1533 cm^{-1}, which are very close to those observed for the present Yb sample treated at the temperatures indicated. Upon a further increase in the temperature above 773 K, the observed bands completely disappeared, indicating the occurrence of conversion into the nitride, YbN. $Eu(NH_2)_2$ showed the NH_2 stretching bands at 3259 and 3196 cm^{-1} besides a band at 1501 cm^{-1} (Fig. 5B). In marked contrast with $Yb(NH_2)_2$, the vibrational spectra of $Eu(NH_2)_2$ exhibited negligible changes in band positions by alterations in the evacuation temperature. The absorption gradually decreased with increasing the temperature and disappeared around 573 K; thus, the formation of Eu imide was hardly observed in the course of conversion into Eu nitride. These observations for the Eu system are in agreement with the results on XRD as shown above.

For the active carbon-supported ytterbium(III) amide, the hydrogenation activity of ethene also varied with evacuation temperatures (Fig. 6). 65% $Yb(NH_2)_3$/AC exhibited a negligible activity upon evacuation between 298 and 373 K, and upon further evacuation at 503 K the activity appeared even at 203 K. The hydrogenation activity increased markedly with an increase in evacuation temperatures and also passed through a maximum around 773 K with an enhancement by over three orders of magnitude. Then, upon evacuation at 1073 K the activity steeply dropped below one-hundredth. This mode of variations in activity was very similar to that of 60% Yb/AC. Concerning the unsupported ytterbium(II) amide, $Yb(NH_2)_2$ itself showed no activity at such low temperatures of 203—253 K. The mode of the temperature dependence of activity was the same as for the 65% $Yb(NH_2)_3$/AC even though there were relative differences in specific activities (Fig. 6). In the present catalyst system, the possibility of ytterbium(II and III) amide as ac-

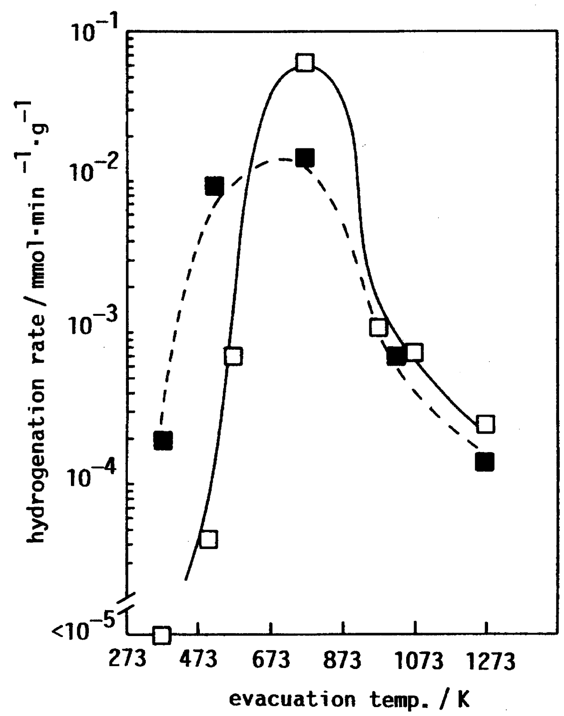

Fig. 6. Effect of the evacuation temperatures of supported and unsupported Yb amide on the hydrogenation rates of ethene. The catalysts were evacuated for 2 h prior to the reaction. Hydrogenation at 203 K over 65% $Yb(NH_2)_3$/AC (☐). Hydrogenation at 298 K over $Yb(NH_2)_2$ (■).

tive species available at such a low temperature (203 K) can be consequently ruled out. It is highly probably that transient intermediates formed during the thermal degradation (423—773 K) of ytterbium(II and III) amides to nitride are active for the present hydrogenation. XRD (Fig. 4) and IR (Fig. 5A) studies certainly indicate the formation of imide (YbNH) or imide-like species by the thermal decomposition of $Yb(NH_2)_2$ and $Yb(NH_2)_3$ at the temperatures indicated. Unlike the case of ytterbium amides, Yb/AC showed no definite evidences of imide formation, but it seems likely that the high catalytic activity of Yb/AC generated by evacuation in the similar temperature ranges (473—773 K) is attributed to ytterbium imide. We have recently found that the imide-like species formed from the lanthanide amides and Yb/AC also exhibit selective cyclization activity of alkynes.[27] The nitride YbN derived from the thermal decomposition of 65% $Yb(NH_2)_3$/AC and $Yb(NH_2)_2$, as well as 60% Yb/AC, showed very low activity for the hydrogenation of ethene. Baba et al.[17] report that ytterbium introduced into zeolite rapidly lost the hydrogenation activity upon evacuation above 900 K.

For the europium system, it was found that $Eu(NH_2)_2$ and 64% $Eu(NH_2)_2$/AC behaved similarly to 60% Eu/AC as a function of the evacuation temperature (Fig. 7); thus the hydrogenation activity exhibited a maximum around 503—573 K. As described previously, the europium existed in the mixture of amide and nitride in this temperture ranges. Howell[16] reports the observation of imide (EuNH) at 503 K during the thermal decomposition of $Eu(NH_2)_2$ to EuN. For Ln/zeolite, the formation of EuNH during similar thermal treatments is also suggested by Baba.[6] Unlike the ytterbium system, the existence of europium imide was not observed here, but the possibility that the imide species generated slightly or fleetingly on the catalyst surface by the thermal treatment catalyze the present hydrogenation is high.

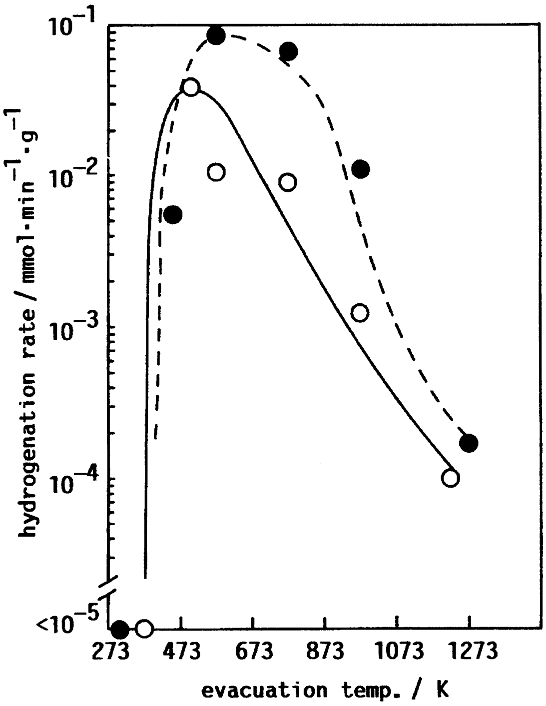

Fig. 7. Effect of the evacuation temperatures of supported and unsupported Eu amide on the hydrogenation rates of ethene. The catalysts were evacuated for 2 h prior to the reaction. Hydrogenation at 203 K over 64% $Eu(NH_2)_2$/AC (○). Hydrogenation at 298 K over $Eu(NH_2)_2$ (●).

Scarcely any studies have been reported with heterogeneous catalytic reactions on metal amide or imide either deposited from a liquid ammonia solution onto supports. However, there have been some of the works published of alkaline species supported by impregnating alumina with liquid ammonia solutions.[28,29] Potassium amide on Al_2O_3 is characterized as superbase with the basic strength of $H_- > 37$.[28] It has been reported that the lanthanide amide or imide-like species shows similarly basic catalysis for the isomerization of alkenes.[6] We have shown that the lanthanide amide species deposited from liquid ammonia onto silica exhibit a greater activity for butadiene than for ethene in hydrogenation,[3] possibly indicating the characteristics of base-catalyzed hydrogenation.[30] However, such hydrogenation behavior for butadiene and ethene was not observed for Ln/AC throughout the entire range of evacuation temperatures examined.

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