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Catalysis of lanthanides deposited on oxide from Eu or Yb metal solutions in liquid ammonia

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Abstract

The catalytic properties of lanthanides (Ln) deposited on oxides (MnO, TiO_2 and MgO) from Eu or Yb metal solutions in liquid ammonia were studied. The catalysis of Ln/oxide varied markedly with differences in the oxides used and changes in levels of lanthanide content. The thermal treatment of Ln/oxide in vacuo also led to appreciable changes in catalytic activity. The lanthanides were used more efficiently for the hydrogenation and dehydrogenation when deposited on MnO. Ln/MnO showed the highest activity for the hydrogenation of ethene. Upon introduction of more than ca. 8 mass% Eu or Yb onto MnO, the activity for the hydrogenation appeared even at a reaction temperature of 199 K. The adsorption characteristics of hydrogen evaluated by temperature-programmed desorption (TPD) were improved at the same time. The lanthanide species present on MnO were characterized by FT-IR, combined with TPD studies. The increase in catalytic activity of Ln/MnO with evacuation temperature was responsible for changes of lanthanide amide to imide. In particular, when Ln/MnO was evacuated around 673 K, some synergetic actions between the lanthanides and MnO maximally develop, leading to enhanced activities.

Keywords: Catalysis; Lanthanide; MnO; Ytterbium; Europium; Liquid ammonia

1. Introduction

The catalytic properties of lanthanide elements and their related compounds have attracted a growing interest from the standpoint of heterogeneous catalysts. The use of dissolution of lanthanide metals (Ln: Eu and Yb) in liquid ammonia enables novel lanthanide-containing catalysts to be prepared [1]. We have showed that bimetallic catalysts are prepared by the reaction of transition metals (Co, Ni, Cu, Pd and Ag) with Eu or Yb metals dissolved in liquid ammonia [2–7]. The investigation can be further extended to include the lanthanides deposited on oxides (Ln/oxide), obtained by impregnating the oxide powders with solutions of dissolved Eu or Yb metals in liquid ammonia [8]. The novel lanthanide catalysts have been prepared by the reaction of silica [9] or active carbon [10] with the lanthanide metal solutions in liquid ammonia. In this study, interest has centered on understanding how the differences in oxide matrices (MnO, TiO_2 and MgO) affect the catalytic activity of lanthanides. The catalytic properties for the hydrogenation of ethene and the dehydrogenation of cyclohexane, largely for the Ln/MnO system, are investigated.

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2. Experimental

Eu and Yb (99.9%) were obtained from Santoku Metal Ind. Co., Ltd. MgO and TiO_2, referred to as JRC-MGO-3 and JRC-TIO-3 (reference catalyst of the Catalysis Society of Japan [11]), were used. MnO was conventionally prepared by a wetness technique; manganese nitrate was decomposed in basic solutions to form hydroxide precipitates. The resulting precipitates were filtered off, thoroughly washed with distilled water, dried and finally heated under an atmosphere of hydrogen at 673 K for 10 h. The formation of desired structures of MnO was confirmed by X-ray diffraction analyses (XRD).

In a typical preparation of the lanthanide catalysts deposited on MnO, the MnO powders were placed in a Schlenk tube flushed thoroughly with dry nitrogen. Eu or Yb metal chips were added to MnO suspended in liquid ammonia (15–20 cm^3) with stirring at 198 K. The Eu or Yb metals immediately dissolved in liquid ammonia to form a blue homogeneous solution which is characteristic of the solvated electrons [12]. The blue color gradually disappeared as a result of the reaction of MnO with the dissolved lanthanide metals in liquid ammonia. On completion of the reaction, the vessel was allowed to warm to room temperature and the excess ammonia was vaporized leaving Ln/MnO with varied levels of Eu or Yb content. Ln/TiO_2 and Ln/MgO were similarly prepared. Unless otherwise stated, the content of the lanthanide in Ln/oxide was represented by the fraction of mass%.

The catalytic reactions were examined using a Pyrex gas recirculation reactor with a fixed volume. IR spectra were recorded on a JASCO FT-IR 620 spectrometer equipped with MCT detector. The preparation of the samples was carried out as follows. To a solution of Eu or Yb in liquid ammonia at 198 K was added an IR pellet of MnO which had been previously treated at 673 K in a hydrogen flow. The Ln/MnO sample thus prepared was transferred to an IR cell of variable temperatures (293–673 K) without exposure to air and connected to a vacuum system. IR spectra were obtained from the ratio of the background spectrum of MnO to that of Ln/MnO.

3. Results and discussion

3.1. Catalytic activity of Ln/oxide

Ln/oxide catalysts were obtained by impregnating various oxides (MnO, MgO and TiO_2) with europium or ytterbium metal solutions in liquid ammonia. First their catalytic properties were tested by the hydrogenation of ethene (Table 1). The rate of hydrogenation generally increased markedly with increasing the level

Table 1
Results of ethene hydrogenation over lanthanides dispersed on various oxides[a]

Lanthanide/mass%	Oxide	Evacuation temperature[b] (K)	Reaction temperature (K)	Activity[c] ($min^{-1} g^{-1}$)
–	MnO	673	199	–[d]
Eu/8.8	MnO	673	199	6.5×10^{-2}
Yb/9.9	MnO	673	199	4.6×10^{-3}
Yb/14.2	MnO	673	199	7.8×10^{-3}
–	MgO[e]	873	300	–[d]
Eu/6.7	MgO	573	300	4.7×10^{-2}
Eu/15.4	MgO	573	300	1.4×10^{-1}
Yb/9.2	MgO	573	300	9.5×10^{-3}
Yb/15.9	MgO	573	300	3.1×10^{-2}
	TiO_2		383	–[d]
Yb/4.7	TiO_2	633	383	1.2×10^{-2}
Yb[f]	–	473	323	1.6×10^{-3}

[a] $C_2H_4 = 16$ Torr and $H_2 = 32$ Torr.
[b] For 2 h.
[c] Evaluated by the first-order rate constant.
[d] Almost zero within detection limit.
[e] For 10 h.
[f] Source: [22].

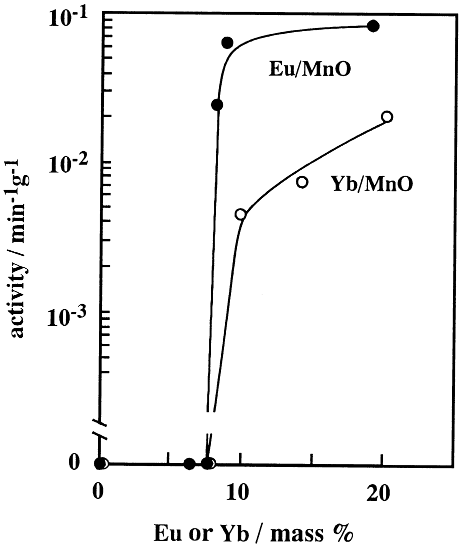


Fig. 1. Variation of hydrogenation activity (199 K) as a function of Eu or Yb content in Ln/MnO. The catalysts were evacuated at 673 K for 2 h prior to the reaction. Reaction conditions: C_2H_4 = 16 Torr and H_2 = 32 Torr.

of lanthanide content. However, as shown in Table 1, the influence of differences in the oxide matrix on the catalytic activity was pronounced; the lanthanide on MnO was very active.

MnO alone was virtually inactive for the hydrogenation for ethene, while the activity of lanthanide was moderate, but negligible at 199 K. The combined Ln/MnO system showed significant hydrogenation activity even at 199 K. As shown in Fig. 1, upon introduction of more than ca. 8 mass% of Eu or Yb onto MnO, the activity appeared at 199 K and abruptly increased as many as 10^2–10^3 times or above. The increase in activity for Eu/MnO was marked, but not so much for further lanthanide introduction as expected. Evidently the enhancement of hydrogenation activity in the lanthanide introduction region of 8–10 mass% was not necessarily proportional to the content of Eu or Yb, leading to speculations of some synergy between the lanthanide and MnO. For both Eu/MnO and Yb/MnO, essentially similar dependence of the activity as a function of lanthanide content was observed (Fig. 1). Ln/TiO_2 and Ln/MgO showed similar variation in activity upon introduction of lanthanide onto the oxide, but their activities were much lower.

The catalytic action of the lanthanide on the oxides varied markedly with pretreatment conditions for the catalysts. We observed that the evacuation treatment which was carried out prior to the reaction was an important factor in determining the catalytic properties. The hydrogenation activity increased markedly with an increase in evacuation temperatures. The activity of 14.2 mass% Yb/MnO was drastically changed in the evacuation temperature range of 373–923 K (Fig. 2). Upon evacuation above 373 K, the catalytic activity appeared at 199 K. The activity increased with increasing evacuation temperatures, and passed through a maximum around 673 K with an enhancement by over two orders of magnitude. Then, the catalyst was completely deactivated upon evacuation at 793 K. 20% of Eu/MnO also exhibited a similar dependence of activity on the evacuation temperature, which showed a maximal activity around 673 K. Upon such thermal treatments, the synergy for Ln/MnO seems maximally

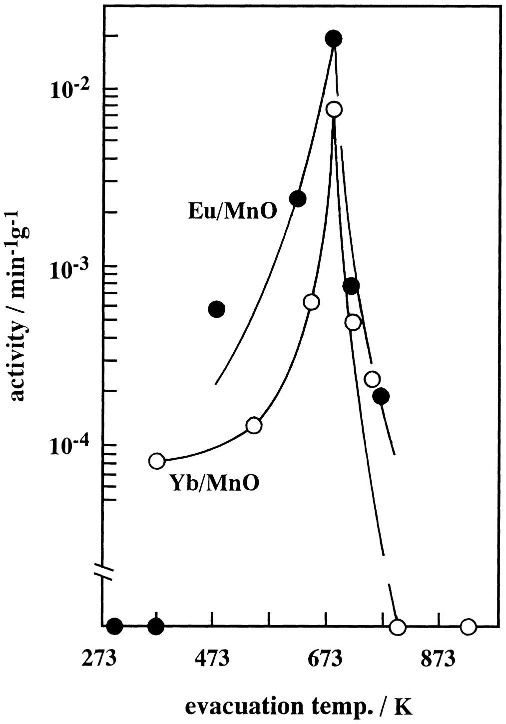


Fig. 2. Effects of evacuation temperatures of 20% Eu/MnO and 14.2% Yb/MnO on the hydrogenation activity (199 K). The catalysts were evacuated for 2 h prior to the reaction. Reaction conditions: C_2H_4 = 16 Torr and H_2 = 32 Torr.

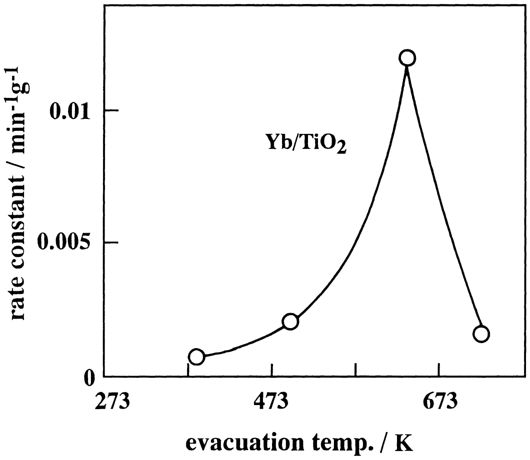


Fig. 3. Effects of evacuation temperatures of 4.7% Yb/TiO_2 on the hydrogenation activity (383 K). The catalysts were evacuated for 2 h prior to the reaction. Reaction conditions: C_2H_4 = 16 Torr and H_2 = 32 Torr.

to develop, leading to enhanced activities. The variation in activity of Yb/TiO_2 as a function of evacuation temperatures are shown in Fig. 3; a maximal activity was reached upon evacuation around 633 K.

The lanthanides dispersed on MnO which had a high hydrogenation ability also exhibited the activity for the dehydrogenation of cyclohexane to benzene at 473 K. The appearance of dehydrogenation activity was similarly observed upon introduction of more than 10 mass% of ytterbium (Fig. 4); thus the activity dependence as a function of lanthanide content was similar to that for the hydrogenation. The high benzene selectivity was obtained regardless of alteration in proportion of lanthanide incorporated. The evacuation treatment of Yb/MnO at elevated temperatures (373–873 K) resulted in the similar effects on the catalytic activity for the dehydrogenation (Fig. 5). The activity of 30% Yb/MnO increased by over two orders of magnitude with an increase in the evacuation temperature from 373 to 673 K and then decreased upon evacuation at higher temperatures.

3.2. Characteristics of lanthanides on oxide matrices

In X-ray diffraction (XRD) spectra for Ln/MnO with varied levels of Ln, the parent MnO phase alone was observed; there were no XRD peaks assigned

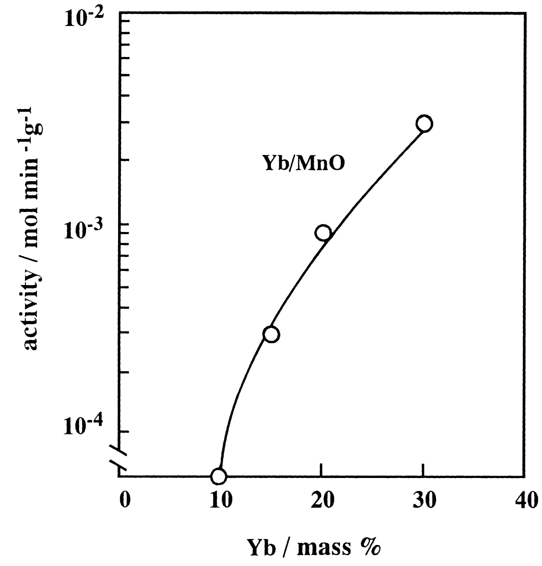


Fig. 4. Variation of dehydrogenation activity (473 K) as a function of Yb content in Yb/MnO. The catalysts were evacuated at 673 K for 2 h prior to the reaction. Reaction conditions: C_6H_{12} = 16 Torr.

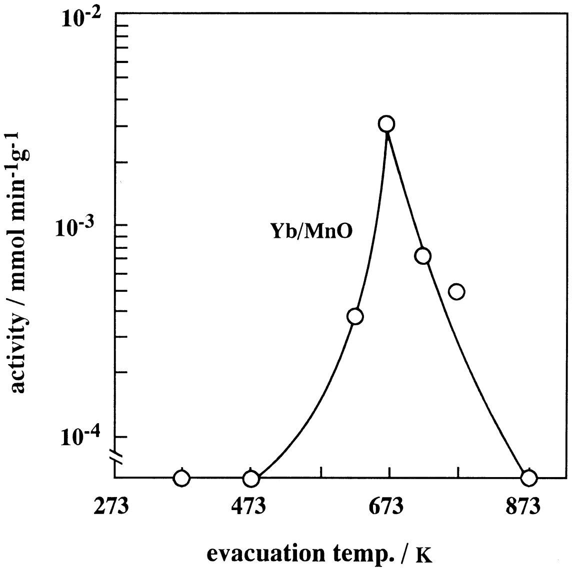


Fig. 5. Effects of evacuation temperatures 30% Yb/MnO on the dehydrogenation activity (473 K). The catalysts were evacuated for 2 h prior to the reaction. Reaction conditions: C_6H_{12} = 16 Torr.

to the lanthanides regardless of the content of lanthanides. Thus the lanthanides are considered to exist on MnO in a high dispersion state. XRD measurements did not afford any information about the thermal treatment of Ln/MnO up to 673 K which led to enhanced activity for the hydrogenation (Fig. 2) and dehydrogenation (Fig. 5). However, additional diffraction peaks newly emerged upon evacuation of 30% Yb/MnO at 793 K. It seems that changes in catalyst structures during such thermal treatments are involved in a rapid decrease in activity of Ln/MnO to almost zero as shown in Figs. 2 and 5.

3.2.1. IR of Ln/MnO

The IR spectra (Fig. 6) of 30% Yb/MnO showed strong absorptions at 3330, 3275 and 1529 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], alkaline amides [16], and alkaline earth amides [17]. The absorption bands observed here were also close to those for Yb/SiO_2 [9] and $Yb(NH_2)_2$ [10] obtained from lanthanide metal solutions in liquid ammonia. Yb/TiO_2 showed IR bands at 3377, 3260 and 1599 cm^{-1} which could be assigned to the NH_2 stretching and bending vibration, respectively. When Yb/MnO was subjected to thermal treatments from 293 to 653 K in vacuo, the absorption intensity gradually decreased. Upon heating above 673 K, these bands completely disappeared, indicating the occurrence of conversion into the nitride, YbN. It is known that thermal decomposition products of liquid ammonia solutions of Eu and Yb metals are finally the nitride (EuN and YbN) through amides or imides [14,18].

The IR spectra (Fig. 7) of 30% Eu/MnO showed absorptions at 3294 and 3230 cm^{-1}, other than 3255 and 3195 cm^{-1} which were very close to the NH_2 stretching vibration observed for $Eu(NH_2)_2$ [10]. Moreover, two bands at 1564 and 1506 cm^{-1} were observed as NH_2 bending vibration. Incidentally, it is known that

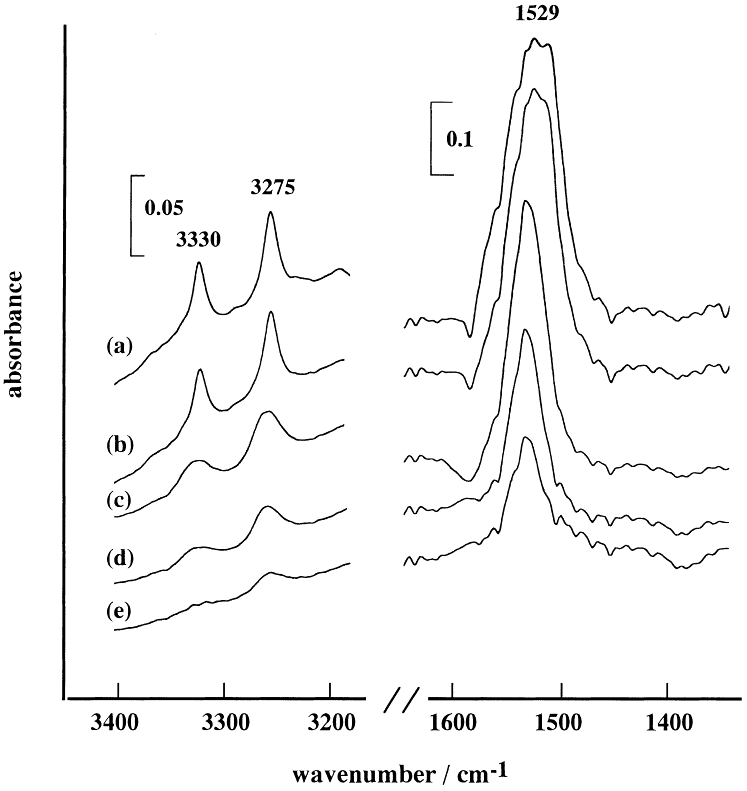


Fig. 6. IR spectra of 30% Yb/MnO (a) as prepared; after evacuation at (b) 373; (c) 473; (d) 573; and (e) 653 K.

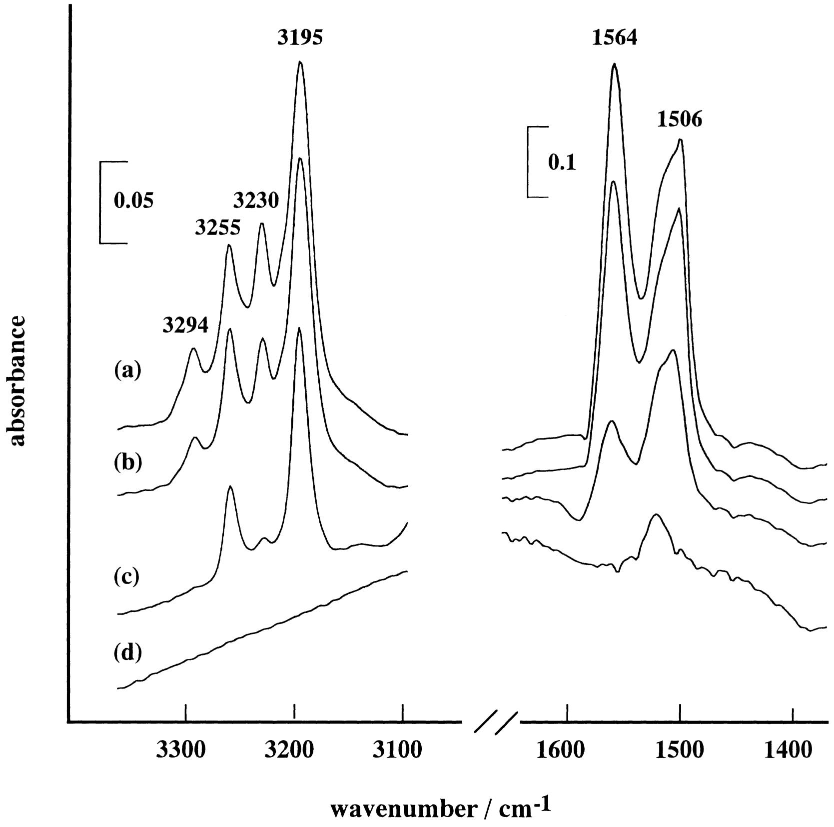


Fig. 7. IR spectra of 30% Eu/MnO (a) as prepared; after evacuation at (b) 373; (c) 473; and (d) 573 K.

the IR of $Eu(NH_2)_2$ shows the NH_2 stretching bands at 3259 and 3196 cm^{-1} and the NH_2 bending band at 1501 cm^{-1} [10]. The thermal stability of the IR bands at 3255, 3195 and 1506 cm^{-1} were higher than that for 3294, 3230 and 1564 cm^{-1}. These facts obviously indicate that there are at least two types of europium amide species on MnO. In the thermal treatment of Ln/MnO in vacuum, the absorption bands of the NH_2 groups for Yb/MnO were observed up to higher temperatures compared to those for Eu/MnO.

3.2.2. *TPD of Ln/MnO*

To further clarify what the evacuation treatments cause, temperature programmed desorption (TPD) measurements for Ln/MnO were made in vacuo by continuously monitoring desorbed gases via quadrupole mass spectrometry. When Ln/MnO as prepared was heated at a heating rate of 2 K min^{-1} under evacuation, the gases desorbed from the sample were exclusively hydrogen ($m/z = 2$), ammonia ($m/z = 17$) and nitrogen ($m/z = 28$). TPD for MnO which was contacted simply with liquid ammonia was first measured for comparison; the gases desorbed from MnO were hardly detected. Fig. 8 shows the profiles of H_2, NH_3 and N_2 desorption from 30% Eu/MnO. The broad desorption peaks of H_2 and NH_3 were observed around 473 K, but not pronouncedly for N_2 desorption. This was, on the whole, similar in peak temperature and relative peak intensity to TPD spectra for $Eu(NH_2)_2$ prepared separately. It has been shown that europium amide is normally formed as diamide $Eu(NH_2)_2$, and that the thermal decomposition of $Eu(NH_2)_2$ occurs at 503 K to yield EuNH, which further decomposes to EuN [19]. However, there have been many discussions about the formation of EuNH. XRD studies for $Eu(NH_2)_2$ have proved that

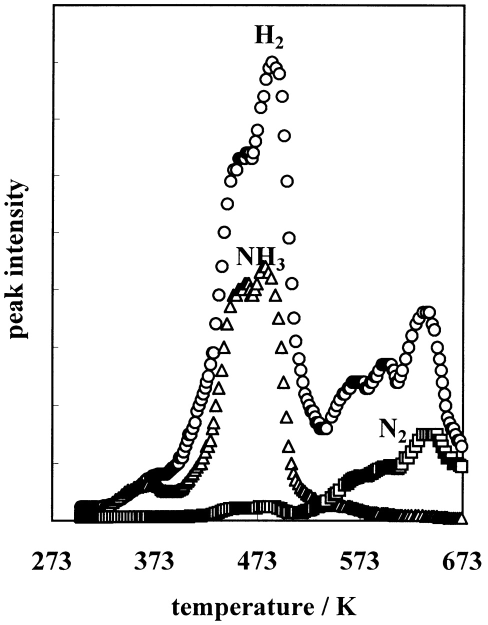


Fig. 8. TPD of 30% Eu/MnO.

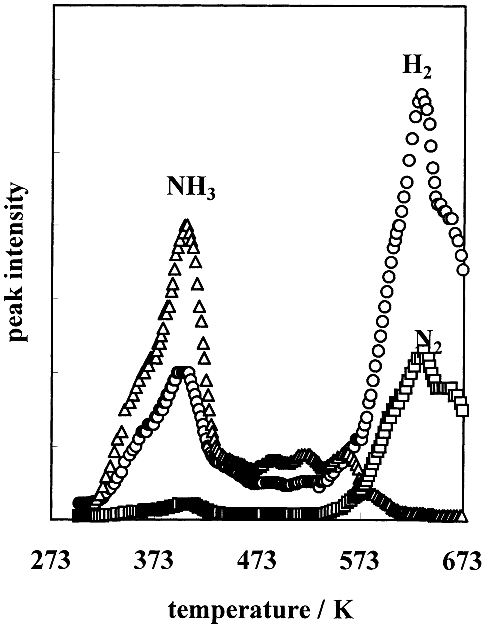


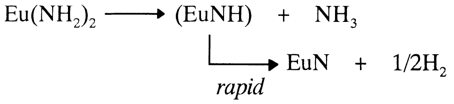
Fig. 9. TPD of 30% Yb/MnO.

the thermal decomposition to EuN occurs without any detectable formation of EuNH in the temperature range of 503–573 K [10].

For TPD spectra for 30% Eu/MnO (Fig. 8), the simultaneous desorption of H_2 and NH_3 around 473 K may be caused by direct decomposition of $Eu(NH_2)_2$ to EuN to some extent as follows:

$$Eu(NH_2)_2 \rightarrow EuN + \frac{1}{2}H_2 + NH_3$$

The possibility that the decomposition of $Eu(NH_2)_2$ to EuNH, followed by rapid conversion of EuNH to EuN with evolution of hydrogen occurs in the range of 400–550 K, cannot be ruled out.



$$Eu(NH_2)_2 \longrightarrow (EuNH) + NH_3, \quad (EuNH) \xrightarrow[rapid]{} EuN + 1/2H_2$$

However, there was no indication of europium imide in the IR spectra of Fig. 7. In TPD measurements of 5.5 mass% Eu/K–Y zeolite, Baba [20] has reported that the decomposition of $Eu(NH_2)_2$ to EuNH around 450 K with subsequent decomposing of EuNH to EuN around 500 K occurs.

Unlike Eu/MnO, the TPD spectra for 30% Yb/MnO showed broad desorption peaks of NH_3, H_2 and N_2 around 400 K (Fig. 9). According to TPD measurements of ytterbium amide carried out for comparison, this was similar to TPD spectra for $Yb(NH_2)_3$ rather than $Yb(NH_2)_2$. This indicates that the ytterbium on MnO exists predominantly as triamide although ytterbium amide obtained from Yb metal solutions in liquid ammonia normally yields a mixture containing di- and tri-amide with varied compositions [21]. It has been revealed by XRD studies that the decomposition of ytterbium amide begins around 423 K and is complete up to about 453 K, and that the diffraction peaks attributable to ytterbium imide YbNH are observed in the range of 423–773 K [10]. In view of the fact that the gases desorbed from Yb/MnO was rich in ammonia, $Yb(NH_2)_3$ on MnO may decompose to YbN, other than YbNH. Moreover, the ytterbium which exists partly as diamide decomposes to YbNH with evolution of NH_3.

$$Yb(NH_2)_3 \rightarrow YbNH + NH_3 + H_2 + \frac{1}{2}N_2$$

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

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

It seems that the H_2 desorption in the range of about 573–673 K or above results from the decomposition of YbNH to YbN.

$$\mathrm{YbNH} \rightarrow \mathrm{YbN} + \tfrac{1}{2}\mathrm{H}_2$$

However, the formation of imide, YbNH, was not observed in the IR spectra of Yb/MnO, as well as Eu/MnO.

Thus, upon thermal treatment of Eu/MnO and Yb/MnO, the changes from the amide to the nitride via a imide intermediate are responsible for an increase in catalytic activity for the hydrogenation and dehydrogenation [10,19].

3.3. Effects of lanthanides on hydrogen adsorption

Scarcely any studies have been reported with catalytic reactions over MnO or lanthanides alone. Normally MnO alone is catalytically inactive for the hydrogenation and dehydrogenation. The lanthanide metal catalysts which are prepared by the metal vapor technique have proved to be active for the hydrogenation of olefins [22]. Moreover, it is known that the lanthanides deposited from Eu or Yb metal solutions in liquid ammonia are changed through varied steps [19,23], and simultaneously their catalytic properties vary markedly [10,24]. For the Ln/MnO system, the effects of lanthanide content on the catalytic properties strongly indicates that the existence of some synergetic interactions between MnO and lanthanide rather than each component itself constitutes active sites. The activation of Ln/MnO was found to be a consequence of introduction of more than a certain amount of lanthanides, although the extent of promotion effect of lanthanides was dependent upon the type of reactions carried out.

The introduction of more than a certain quantity of lanthanide onto MnO led to drastic changes in TPD characteristics of hydrogen. The TPD spectra were measured for Eu/MnO and Yb/MnO which had been subjected to evacuation at 673 K for 2 h, followed by contact with hydrogen of 150 Torr at room temperature for 180 min. As shown in Fig. 10, the adsorption characteristics of hydrogen on Ln/MnO varied markedly upon introduction of more than ca. 8% lanthanide on MnO, leading to an enhanced catalytic activity. Pure MnO showed negligible adsorbing power for hydrogen at room temperature, but upon introduction of lanthanides, TPD showed the existence of newly adsorbed hydrogen species at 300–550 K. The amounts of such adsorbed hydrogen increased with increasing the lanthanide content (6.5–19.1%) in Eu/MnO, probably resulting in enhanced hydrogenation activity.

The rates of ethene hydrogenation over Ln/MnO were proportional to the pressure of hydrogen and were almost independent of the pressure of ethene, in the lanthanide content range studied. This strongly suggests that the catalytic activation of hydrogen on Ln/MnO is an important step in a series of hydrogenation processes in which the hydrogen species participate. Therefore, Ln/MnO which have the high ability for hydrogen adsorption seems to show high catalytic activity.

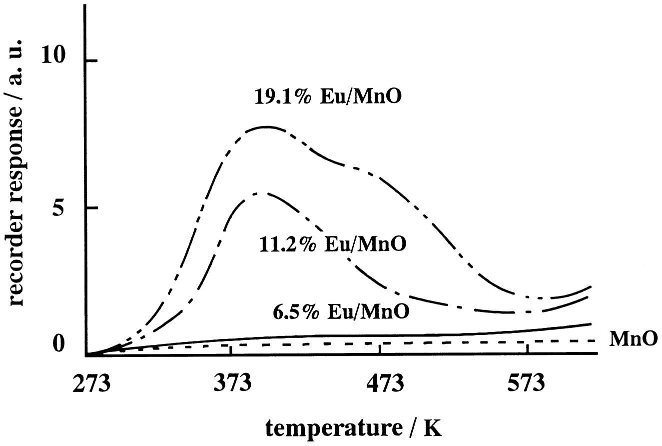


Fig. 10. TPD of hydrogen on MnO and Eu/MnO.

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