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Preparation and catalytic properties of rare earth amides obtained by reactions of Eu or Yb metals with liquid ammonia

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Abstract

By controlling the preparative conditions, rare earth amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$) were successfully prepared from the reaction of Eu or Yb metals with liquid ammonia. The reaction of Yb metals with ammonia gradually proceeded to produce $Yb(NH_2)_2$ with subsequent conversion into $Yb(NH_2)_3$, while the Eu/NH_3 system yielded exclusively $Eu(NH_2)_2$. The different decomposition products obtained during thermal treatments of the rare earth amides were characterized by temperature-programmed desorption (TPD) and XRD techniques. The decomposition products such as imide and nitride were identified and the temperature ranges suitable for forming these products were also determined. The structural changes of the Eu/NH_3 and Yb/NH_3 systems through varied steps were related to the catalytic activity for the hydrogenation of ethene or benzene. The rare earth imide and nitride showed high hydrogenation activity.

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1. Introduction

Recently there has been a growing interest in catalytic properties of rare earths (R) and related compounds. It is known that europium and ytterbium among rare earth elements readily dissolve in liquid ammonia to yield homogeneous solutions with a deep blue color, being characteristic of the ammonia-solvated electrons [1]. The rare earth metal/NH_3 systems are known to change through varied steps [2–4]. The thermal decomposition products of the Eu/NH_3 and Yb/NH_3 finally yield nitride (EuN and YbN) through diamide, triamide or imide, respectively.

In this study, interest has centered on identifying the preparative conditions of rare earth amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$) obtained by reactions of Eu or Yb metals with liquid ammonia. The thermal decomposition processes of these rare earth amides are characterized by temperature-programmed desorption (TPD), combined with XRD studies. The rare earth amides and their derivatives are also examined from the viewpoint of the catalytic properties for the hydrogenation reactions. By taking advantage of the solubility of Eu and Yb in liquid ammonia, we have developed methods for preparing novel rare earth catalysts and have demonstrated that they exhibit unexpected activity and selectivity for various reactions [5].

2. Experimental

2.1. Procedures of sample preparation

Eu and Yb (99.9%) were obtained from the Santoku Co. Ammonia gas (Iwatani Ind. Ltd.) was purified through a calcium oxide column and subsequently through a sodium hydroxide column.

The rare earth amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$) were prepared using liquid ammonia as follows. In a 50 cm^3 stainless steel reactor were placed Eu or Yb metals (ca. 0.5 g) under an atmosphere of dry nitrogen. The reactor was briefly evacuated, cooled by a dry ice/methanol bath, and then, about 1350 cm^3 of purified ammonia gas

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was liquefied. The Eu and Yb metal readily dissolved in liquid ammonia to yield a homogeneous rare earth metal solution [1]. The solutions were allowed to stand at 273 K, resulting in the formation of amide products as a precipitate. Ammonia was subsequently removed from the reactor leaving powdery products. The thermal treatment of rare earth amides was subjected to evacuation at elevated temperatures for 1 h.

The X-ray diffraction (XRD) patterns of the Eu/NH_3 and Yb/NH_3 systems were obtained with a Rigaku X-ray diffractometer (RINT 2200) using Cu Kα radiation. The XRD measurements of the samples were made without exposure to air.

2.2. Catalytic reactions

The catalytic properties of rare earth samples were examined with the hydrogenation of ethene and benzene. The hydrogenation of ethene was studied at 298 K using a Pyrex gas-recirculation reactor. The liquid-phase hydrogenation of benzene was carried out at 483 K under H_2 pressures of 3 MPa.

3. Results and discussion

3.1. Preparation of rare earth amides obtained by use of reaction of Eu or Yb metals with liquid ammonia

The Eu and Yb metal readily dissolved in liquid ammonia to yield a blue homogeneous solution containing the divalent metal cations and ammoniated electrons [1]. The solutions were allowed to stand at 273 K, resulting in the formation of amide products as a precipitate. To obtain information as to the structural changes of the Eu/NH_3 and Yb/NH_3 systems, XRD powder patterns were recorded at regular time intervals (Fig. 1(a) and (b)). According to XRD obtained when the Yb metal in liquid ammonia was permitted to stand for 1 h, unreacted Yb metals still remained, but the new diffraction peaks at $2\theta = 29.8$, 34.5, 49.7 and 59.0°, corresponding to the formation of tetragonal diamide $Yb(NH_2)_2$, appeared simultaneously. The reaction of Yb metals with liquid ammonia gradually proceeded, and upon reaction for 12 h the products consisted primarily of the Yb diamide. However, as shown in Fig. 1(a), further reaction for 24 h led to the conversion of reddish brown diamide into white triamide, $Yb(NH_2)_3$.

On the other hand, the reaction of Eu metals with liquid ammonia took place more rapidly. Upon reaction for only 1 h, the Eu metal was completely converted into diamide, $Eu(NH_2)_2$, with tetragonal structures (Fig. 1(b)). Judging from XRD, the Eu/NH_3 system yielded exclusively $Eu(NH_2)_2$ as a product unlike the Yb/NH_3 system [6].

For the reaction of Eu or Yb metals with NH_3, the reaction temperatures and the amounts of liquid ammonia used were crucial factors in determining the products; in the case of the Yb/NH_3 system, higher temperatures (>323 K) or larger amounts (>2000 cm^3) of NH_3 preferentially led to the formation of $Yb(NH_2)_3$.

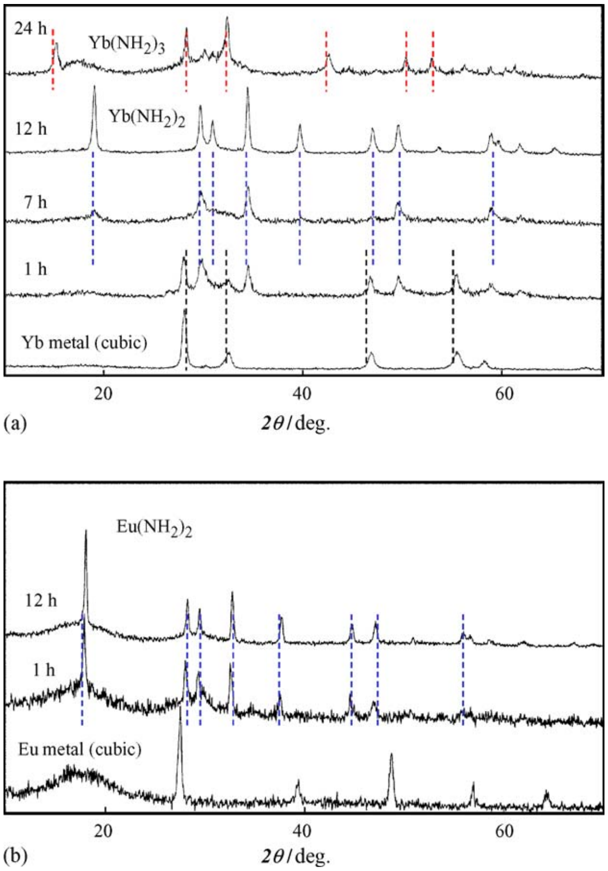

Fig. 1. (a) Changes in XRD of the Yb/NH_3 system at 273 K. (b) Changes in XRD of the Eu/NH_3 system at 273 K.

3.2. TPD of europium and ytterbium amides

To further clarify what the thermal treatments of rare earth amides caused, temperature-programmed desorption (TPD) measurements for $Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$ were made in vacuo by continuously monitoring desorbed gases via quadrupole mass spectrometry. When $Eu(NH_2)_2$ as prepared was heated at a heating rate of 2 K min^{-1} under evacuation, the gases desorbed from the sample were exclusively hydrogen, ammonia and nitrogen. Fig. 2 shows the profiles of H_2, NH_3 and N_2 desorption from $Eu(NH_2)_2$. The desorption peaks of H_2 and NH_3 were observed around 530 K, and upon further heating above 630 K, the desorption of H_2 became pronounced again. It has been shown that the thermal decomposition of $Eu(NH_2)_2$ occurs at 503 K to yield EuNH (Eq. (1)), which subsequently decomposes to EuN (Eq. (2)) [2]:

$$Eu(NH_2)_2 \rightarrow EuNH + NH_3 \tag{1}$$

$$EuNH \rightarrow EuN + 1/2H_2 \tag{2}$$

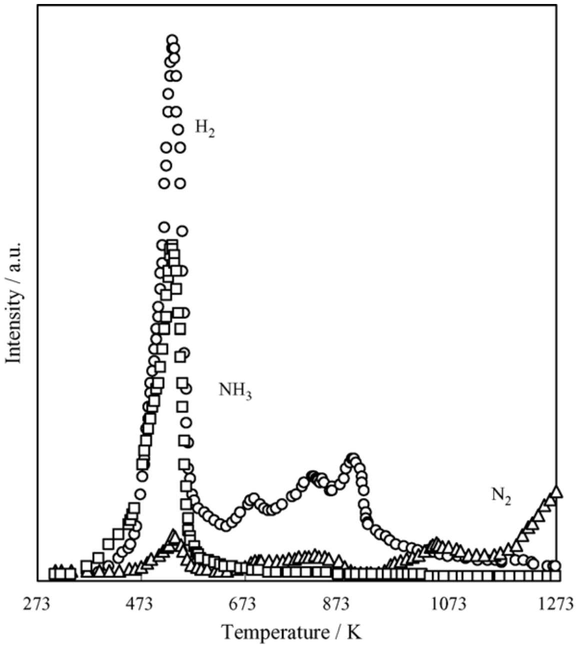

Fig. 2. TPD of $Eu(NH_2)_2$.

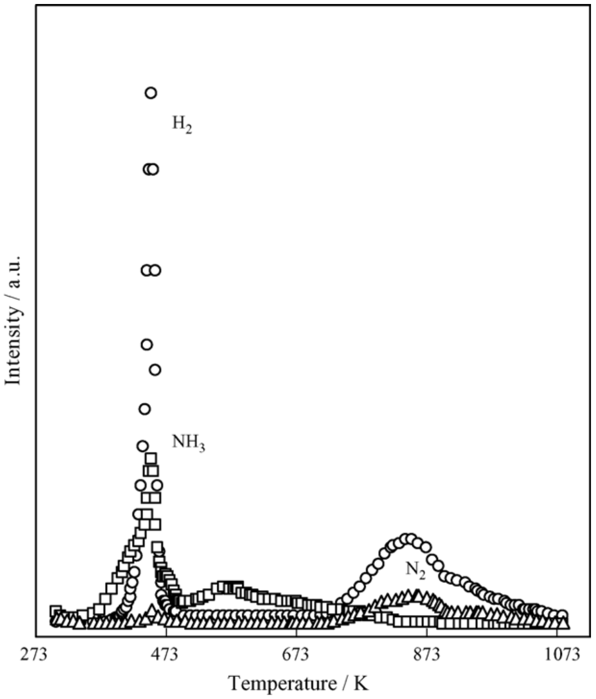

Fig. 4. TPD of $Yb(NH_2)_2$.

However, there have been many discussions about the formation of EuNH. According to TPD (Fig. 2) for $Eu(NH_2)_2$, the simultaneous desorption of H_2 and NH_3 around 530 K may be caused by direct decomposition of $Eu(NH_2)_2$ to EuN to some extent as follows:

$$Eu(NH_2)_2 \rightarrow EuN + 1/2H_2 + NH_3$$

Upon heating above about 630 K, the conversion (Eq. (2)) of EuNH into EuN with liberation of hydrogen seems to occur in TPD. However, judging from XRD (Fig. 3) recorded with the thermal treatment of $Eu(NH_2)_2$, the decomposition to EuN occurred without any detectable formation of EuNH in the temperature range of 503–573 K [7].

The TPD results (Fig. 4) for $Yb(NH_2)_2$ was, on the whole, similar to that for $Eu(NH_2)_2$. $Yb(NH_2)_2$ showed sharp desorption peaks of H_2 and NH_3 around 450 K and further desorption of H_2 from around 730 K. It was proved by XRD (Fig. 5) that the decomposition of $Yb(NH_2)_2$ to YbNH began from approximately 373 K and was completed up to about

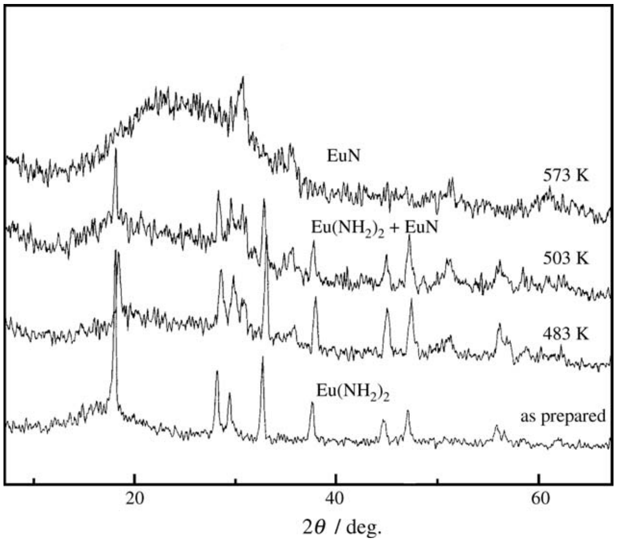

Fig. 3. Changes in XRD of $Eu(NH_2)_2$ with the thermal treatment. $Eu(NH_2)_2$ was subjected to evacuation for 1 h at the following temperatures: (a) as prepared, (b) 483 K, (c) 503 K and (d) 573 K.

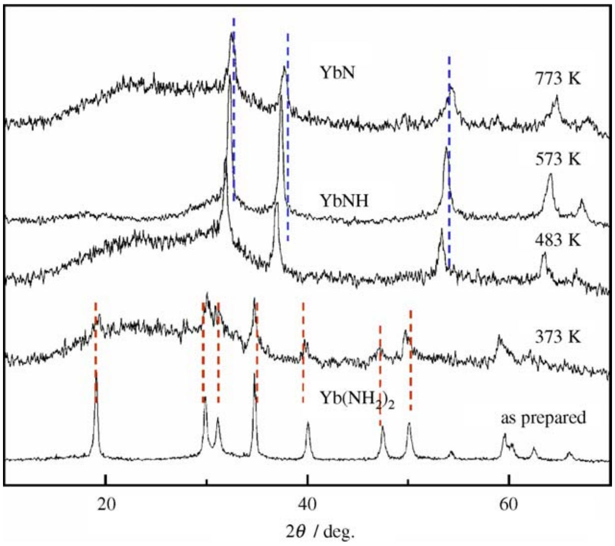

Fig. 5. Changes in XRD of $Yb(NH_2)_2$ with the thermal treatment. $Yb(NH_2)_2$ was subjected to evacuation for 1 h at the following temperatures: (a) as prepared, (b) 373 K, (c) 483 K, (d) 573 K and (e) 773 K.

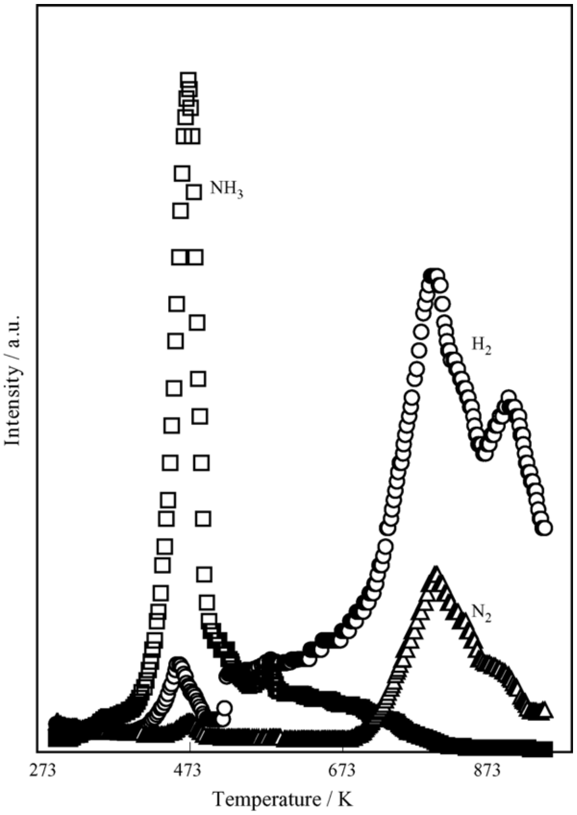

Fig. 6. TPD of $Yb(NH_2)_3$.

483 K. The diffraction peaks assigned to YbNH was observed in the range of 423–773 K [7]. Compared to $Eu(NH_2)_2$, the decomposition temperature of $Yb(NH_2)_2$ fell, but the conversion of YbNH into YbN occurred at higher temperatures as shown in TPD and XRD. In contrast to $Yb(NH_2)_2$, $Yb(NH_2)_3$ showed a strong desorption peak of NH_3 with simultaneous desorption of H_2 and N_2 around 470 K (Fig. 6). $Yb(NH_2)_3$ may partly decompose to YbN (Eq. (4)), other than YbNH (Eq. (3)):

$$Yb(NH_2)_3 \rightarrow YbNH + NH_3 + H_2 + 1/2N_2 \quad (3)$$

$$Yb(NH_2)_3 \rightarrow YbN + 2NH_3 \quad (4)$$

It seems that the H_2 desorption observed from about 710 K results from the change of YbNH to YbN.

In Figs. 2, 4 and 6, the desorption of N_2 observed at elevated temperatures is probably due to further decomposition of RN to RN_{1-x}.

3.3. Catalytic properties

The different decomposed states obtained during the thermal treatment of rare earth amides are responsible for variations in catalytic properties. Upon evacuation of $Yb(NH_2)_2$ above 473 K, the hydrogenation of ethene occurred at 298 K [7]. The activity increased with increasing evacuation temperatures, passed through a maximum around 773 K with an enhancement by over three orders of magnitude and then, the sample was completely deactivated upon evacuation at 1373 K (Fig. 7). $Eu(NH_2)_2$ also exhibited a similar temperature dependence of activity. $Eu(NH_2)_2$ showed the highest

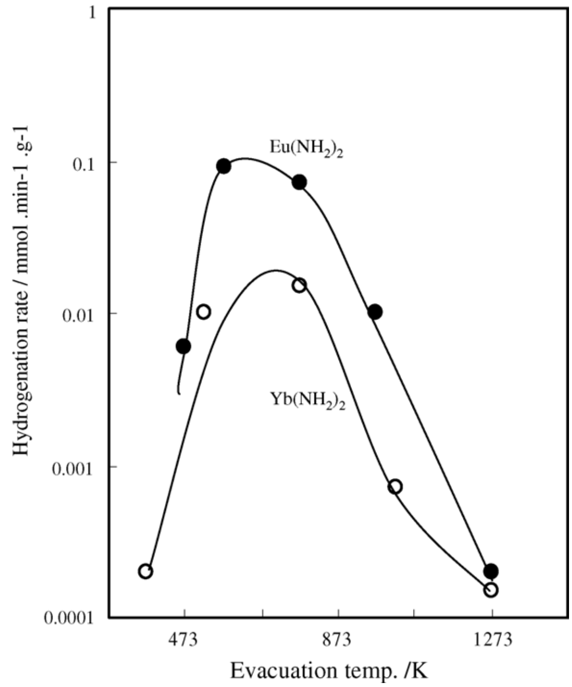

Fig. 7. Dependence of the hydrogenation activity of ethene on the evacuation temperatures of $Eu(NH_2)_2$ and $Yb(NH_2)_2$. The hydrogenation of ethene (C_2H_4: 20 Torr, H_2: 40 Torr) was carried out at 298 K.

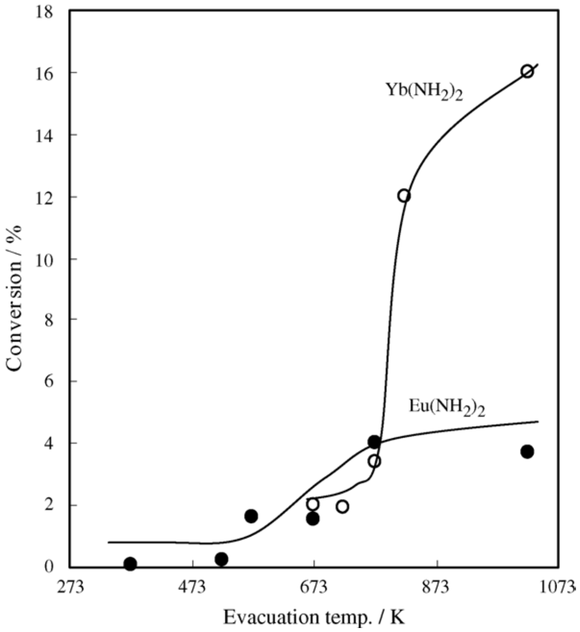

Fig. 8. Dependence of the conversion of benzene on the evacuation temperatures of $Eu(NH_2)_2$ and $Yb(NH_2)_2$. The conversion was expressed by the fraction of benzene consumed in 3 h for the hydrogenation of benzene; C_6H_6: 5 cm^3, H_2: 3 MPa, catalyst: 0.2 g, temperature: 483 K.

activity when evacuated around 573 K. Thus, for the hydrogenation of ethene, the imide or imide-like species generated in the thermal decomposition processes of rare earth amides to nitride seem to be active catalysts. On the other hand, EuN and YbN obtained by thermal decomposition of the rare earth amides were excellent in catalytic activity for the liquid-phase hydrogenation of benzene (Fig. 8) [8]. It was proved that the rare earth imide and nitride showed high catalytic activity for the hydrogenation. Considering that the hydrogenation of benzene was usually carried out under H_2 pressures of 3 MPa, one of the causes of such differences in hydrogenation of ethene and benzene seems to be differences in the H_2 pressure dependence of imide and nitride on activity.

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