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Preparation and characteristics of various rare earth nitrides

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Abstract

Active nanocrystalline nitrides of EuN and YbN with high surface areas were successfully prepared by the thermal decomposition of the rare earth amides $(Eu(NH_2)_2, Yb(NH_2)_2 \text{ and } Yb(NH_2)_3)$. For the preparation of CeN, PrN and NdN, the direct reaction of the rare earth metals with ammonia was extensively studied to determine optimal conditions. In the reaction of rare earth metals with ammonia, hydrides besides the nitrides were competitively formed. The reaction conditions such as temperatures and ratios of ammonia to rare earth metal were crucial in preferential formation of nitride. The nanocrystalline YbN and EuN readily absorbed large amounts of ammonia even at room temperature upon contact with ammonia (13.3 kPa). The absorbed ammonia existed in at least two forms on/in the nitride; the one was surface-adsorbed ammonia and the other ammonia absorbed in the nitride in a decomposed state. The properties of ammonia absorbed by the nitride were further evaluated by temperature-programmed desorption (TPD), FT-IR and XRD techniques.

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1. Introduction

Recently there has been a growing interest in science and application of rare earth materials. We have studied catalytic properties of a variety of rare earth compounds. In particular, by taking advantages of the solubility of europium and ytterbium metals in liquid ammonia [1], we have proposed the preparative methods of novel rare earth catalysts and have extensively studied their catalytic properties [2]. Much attention has been given to heterogeneous catalysis of rare earth elements and their related compounds [3].

In this study, interest has centered on identifying the preparative conditions of various nanocrystalline nitride (CeN, PrN, NdN, EuN and YbN) obtained by thermal decomposition of rare earth amides (Eu(NH₂)₂, Yb(NH₂)₂ and Yb(NH₂)₃) or by direct reaction of rare earth metals (Ce, Pr and Nd) with ammonia. The optimal conditions for the preparation of nitrides were studied by X-ray diffraction analysis (XRD) and temperature-programmed desorption (TPD) combined with mass spectrometer. An interesting feature of rare earth nitrides such as EuN and YbN which show the ability to absorb a considerable amount of ammonia at room temperature has been extensively studied. It has been

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shown elsewhere [4,5] that the catalytic activity of YbN and EuN is higher than expected.

2. Experimental

2.1. Procedures of sample preparation

Ce, Pr, Nd, 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 $(Eu(NH_2)_2, Yb(NH_2)_2 \text{ and } Yb(NH_2)_3)$ were prepared using liquid ammonia according to a previous paper [5]. To obtain EuN and YbN, the rare earth amides were thermally decomposed under evacuation at 573 and 773 K, respectively. For the preparation of CeN, PrN and NdN, in a 50 cm³ stainless steel reactor were placed Ce, Pr or Nd 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, purified ammonia gas was liquefied. The reactor was allowed to stand at 523 K for 12 h, resulting in the formation of nitrides.

2.2. Characterization

X-ray diffraction (XRD) analyses of the nitrides were conducted with a Rigaku X-ray diffractometer (RINT 2200) using Cu K α radiation. Temperature programmed desorption (TPD) measurements were made *in vacuo* at a heating rate of 2.5 K min⁻¹ by continuously monitoring desorbed gases *via* quadrupolar mass spectrometer. Infrared spectra were recorded on a JASCO 7300 Fourier transform infrared spectrometer equipped with a MCT detector. The method for infrared spectra was similar to that previously described [6]. Infrared spectra were obtained from the ratio of the background spectrum of YbN to that of

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NH₃-treated YbN. All procedures of the rare earth samples were carried out without exposure to air.

The NH₃ uptake by the rare earth nitrides was carried out at 297, 473 or 573 K by introducing ammonia gas at varied pressures (0-13.3 kPa) into a reactor with a fixed volume. The amounts of NH₃ uptake were determined by changes in pressures.

3. Results and discussion

3.1. Preparation of EuN and YbN

The preparation of nanocrystalline europium and ytterbium nitrides with high activity and large surface areas $(107-146 \text{ m}^2 \text{ g}^{-1})$ was successfully achieved by the thermal decomposition of amides (Eu(NH₂)₂, Yb(NH₂)₂, and Yb(NH₂)₃) at 573–773 K [7]. This preparation method is characterized by taking advantage of the solubility of these particular rare earths in liquid ammonia [1], resulting in the quantitative formation of such amides as precursors of nitrides. However, this method for nitride preparation is not the case for other rare earths.

3.2. Preparation of CeN, PrN and NdN

For the preparation of nitrides for cerium, praseodymium and neodymium, the direct reaction of these rare earth metals with ammonia was carried out with a stainless steel reactor. However, it has been shown that rare earth hydrides besides nitrides are competitively formed, depending upon the reaction conditions of rare earth metals with ammonia [8]. Taking the reaction system of Ce-NH₃ as a typical example, the ratios of Ce metal to NH₃ in this reaction were crucial in determining the products as shown in XRD (Fig. 1). The Ce metal readily reacted with ammonia at 523 K to form the cerium nitride (CeN) and/or hydride (CeH_x). As depicted in Fig. 1, the preferential formation of CeN was observed with decreasing the relative amounts of ammonia to cerium. This is probably due to differences in NH₃ pressure dependence for the formation of CeN and CeH_x . Moreover the formation of the nitride (CeN) was found to be predominant at higher reaction temperatures above 623 K.

The reaction was followed by taking XRD spectra with the elapse of time. When the reaction was carried out at 623 K, the Ce



Fig. 1. Changes in XRD spectra of Ce–NH₃ system with different NH₃ to Ce metal ratios. The reaction was carried out at 523 K for (a) NH₃/Ce \simeq 4 for 12 h, (b) NH₃/Ce \simeq 8 for 12 h, (c) NH₃/Ce \simeq 20 for 48 h and (d) NH₃/Ce \simeq 200 for 48 h.

metal immediately reacted with ammonia to yield a mixture of nitride (CeN) and hydride (CeH_x). At the beginning of reaction the relative XRD peak intensity of hydride was stronger than that of CeN. Prolonged reaction led to the predominant formation of nitride, and a single-phase product with cubic structures was finally obtained after the reaction for 12 h. It is considered for the reaction of Ce with NH₃ that the following two reactions simultaneously occur:

$$Ce + NH_3 \rightarrow CeN + \frac{3}{2}H_2$$

 $Ce + NH_3 \rightarrow CeH_x + \frac{1}{2}N_2$

Taking into account that magnesium hydride (MgH_2) reacts with ammonia to yield magnesium amide $(Mg(NH_2)_2)$ [9] one can suppose that also the cerium hydride (CeH_x) formed here is further converted into the cerium amide.

$$MgH_2 + 2NH_3 \rightarrow Mg(NH_2)_2 + 2H_2$$

 $\text{CeH}_x + \text{NH}_3 \rightarrow (\text{cerium amide}) \rightarrow \text{CeN} + \frac{3+x}{2}\text{H}_2$

However, the cerium amide was not detected in XRD; probably it is immediately decomposed to CeN as evidenced by XRD. It has been quite often seen that rare earth amides thermally decompose to nitrides [7]. It has been also reported elsewhere [10,11] that the rare earth nitrides are effectively formed by the reaction of rare earth hydrides with ammonia at elevated temperatures. Thus the reaction successively progresses *via* the hydride to form the nitride.

The formation of other nitrides, namely PrN and NdN, showed the behavior similar to that for CeN; the reaction with ammonia was carried out for 12 h. The reaction of praseodymium or neodymium metal with ammonia at 623 K yielded the nitrides, which have cubic structures as shown in XRD.

3.3. Evaluation of ammonia absorbed by the nitride

An interesting feature of rare earth compounds is that the nitrides such as EuN and YbN showed the ability to absorb a considerable amount of ammonia even at room temperature. EuN or YbN was evacuated at 723 or 923 K, respectively, followed by introducing ammonia gas at 297 K into a reactor for NH₃ uptake. The amounts of NH₃ uptake were determined by changes in pressures. As shown in time dependencies of the NH₃ uptake by YbN (Fig. 2), the nitride readily absorbed ammonia at 297 K upon contact with the gas, simultaneously changing from dark brown to reddish brown. The NH₃ uptake rapidly occurred in the very initial stage and instantly reached about 0.3 in NH₃/YbN molar ratio.

The time dependencies of NH_3 uptake were similarly obtained when measured at 473 and 573 K. However, the NH_3 uptake decreased with increasing reaction temperatures. This is due to that it simultaneously includes considerable amounts of NH_3 adsorption on the surface. When the NH_3 uptake by YbN was measured at 573 K to record 0.20 in NH_3 /YbN, followed by dropping to 297 K, there was additional uptake of NH_3 up



Fig. 2. Time dependencies of NH_3 uptake by YbN at 273, 473 and 573 K. In the NH_3 uptake at 473 and 573 K, the temperature was changed to 297 K in the course of each run.

to about 0.28. This additional uptake of NH₃ is probably based on surface adsorption and reached fairly great amounts. This is consistent with the large surface areas of YbN, as described previously. The NH₃ uptake at 573 K seems to be very close to the amounts of NH₃ reacting with YbN itself, as shown later. EuN showed similar uptake behavior of NH₃ to YbN, but the quantity was about a third of that for YbN.

To evaluate the ammonia uptake by the nitride, TPD of the NH₃-treated YbN was first studied. The TPD traces showed a broad desorption peak of NH3 around 400 K and two desorption peaks of H₂ and N₂ at approximately equal temperatures of 800 K [7]. This strongly indicates that at least two types of ammonia species seem to be involved in the present NH₃ uptake by YbN; one, corresponding to the desorption at 400 K, is the molecularly adsorbed ammonia as explained above and the other, representing the desorption at 800 K, is the ammonia existing in a decomposed state in YbN. Judging from TPD of YbN treated in different NH₃/YbN molar ratios, it seems that first the ammonia strongly reacts with YbN itself and that subsequently excess ammonia is weakly adsorbed on the nitride surface. The NH₃-treated EuN showed similar TPD traces (Fig. 3); the desorption of molecular NH3 was observed at 410-460 K, while the desorption of H₂ and N₂ simultaneously occurred around 690 K.

FT-IR measurements afforded useful information about the ammonia uptake by YbN, especially about the ammonia



Fig. 3. TPD of EuN with NH₃ uptake of 0.04 in NH₃/EuN molar ratios. The sample was heated at a heating rate of 2.5 K min^{-1} *in vacuo* and the desorbed gases were continuously monitored by quadrupolar mass spectrometer.



Fig. 4. FT-IR for (a) YbN saturated with ammonia, NH_3 /YbN molar ratios: 0.28 and (b) after evacuation of NH_3 at 473 K.

undergoing some reaction with YbN (Fig. 4). For YbN with NH₃ uptake of 0.28 in NH₃/YbN, the bands of 3500–3000 and 1650–1550 cm⁻¹ were assigned to stretching and deformation vibrations of adsorbed ammonia, respectively [12]. When the sample was subjected to evacuation around 473 K to remove the adsorbed ammonia, there remained strong absorption bands around 2021 and 1209 cm⁻¹, indicating that the ammonia reacts with YbN and that the nitrogen of NH₃ exists as azido (N₃)-type compounds. Moreover, the IR bands observed at ~3200 and ~1500 cm⁻¹ suggests that the hydrogen of NH₃ forms amido species.

The nitride showed the XRD pattern with cubic structure. Upon uptake of NH_3 by YbN, the diffraction peaks were shifted to lower angles with increasing the amounts of NH_3 absorbed. This suggests that the ammonia was absorbed in the cubic crystal lattice, resulting in the expansion of lattice constants. In view of TPD of the NH_3 -treated YbN, evacuation around 470 or 970 K is required to remove the ammonia species on/in YbN. There were no changes in XRD patterns for the evacuation of 470 K, while upon evacuation at 970 K the ammonia incorporated in the YbN bulk was removed, resulting in the return of the XRD pattern to the original structure of YbN. Thus the NH_3 uptake responsible for the structural changes of ytterbium nitride was observed as desorption peaks of H_2 and N_2 around 900 K in TPD.

4. Conclusion

Active nanocrystalline nitrides of EuN and YbN with high surface areas were successfully prepared by the thermal decomposition of the rare earth amides. The preparation of CeN, PrN and NdN was extensively examined by the direct reaction of the rare earth metals with ammonia. The formation of nanopowders of EuN and YbN is probably due to the difference in preparative methods. The nanocrystalline EuN and YbN readily absorbed large amounts of ammonia even at room temperature upon contact with ammonia. The absorbed ammonia existed in at least two forms on/in the nitride; the one was surface-adsorbed ammonia and the other ammonia absorbed in the nitride in a decomposed state. FT-IR of the ammonia absorbed by YbN showed absorption bands assigned to amido and azido (N₃)-type compounds. Upon NH₃ uptake, XRD exhibited diffraction peaks shifted to lower angles, indicating that the ammonia entered the crystal lattice with the expansion of crystal constants.

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