



Preparation of Cerium Nitride by Reaction of Cerium Hydride with Ammonia

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Abstract. The preparation of cerium nitride (CeN) was extensively studied to determine optimal conditions, in which the conversion method of cerium amide into cerium nitride was adopted as an effective way to synthesize active nanocrystalline cerium nitride. The cerium nitride was successfully prepared by the thermal decomposition of cerium amide or cerium amide-like compounds formed by the reaction of cerium hydride and ammonia. The preparation of cerium amide as a precursor of cerium nitride was important in this procedure and the amide was here prepared by reactive ball milling of dihydride (CeH₂) under 0.3 MPa ammonia pressure. The thermal decomposition processes of cerium amide to nitride was studied by XRD and temperature-programmed desorption techniques. Active nanocrystalline CeN was obtained by the decomposition of cerium amide around 873 K.

Keywords: Materials; Solid state; Catalysis; Synthesis

1. Introduction

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.^{1, 2, 3, 4} It has been recently found that rare earth nitrides show specific activity as catalysts; thus EuN and YbN are active as selective catalysts for the partial hydrogenation of benzene to cyclohexene.⁵ Europium amide, Eu(NH₂)₂, and the ytterbium amides Yb(NH₂)₂ and Yb(NH₂)₃ obtained by taking advantage of the solubility of europium and ytterbium metals in liquid ammonia are effective precursors for EuN and YbN, respectively; thus the thermal decomposition of these amides leads to catalytically active rare earth nitrides with high surface areas.^{4, 6, 7}

Other rare earth metals than Eu and Yb exhibit poor solubility toward liquid ammonia, and hence a similar procedure for the preparation of rare earth nitrides cannot be adopted. For the preparation of cerium nitride, CeN, the direct reaction of cerium metal with ammonia at elevated temperatures has been previously studied, but it is difficult to prepare stoichiometric cerium nitride.⁶

In this study, the use of cerium amide as a precursor for cerium nitride is investigated to synthesize active nanocrystalline CeN. According to previous studies,^{8, 9, 10} there is much expectation of the synthesis of cerium amide in good yield by taking advantage of the reaction of cerium hydride and ammonia. Optimal conditions for the preparation of CeN using cerium amide thus obtained has been extensively studied by X-ray diffraction analysis (XRD) and temperature-programmed desorption (TPD) combined with mass spectrometer.

¹ H. Imamura, in: *Handbook on the Physics and Chemistry of Rare Earths*, K. A. Gschneidner, Jr., L. Eyring (Eds.), Vol. 29, North-Holland, Amsterdam, **2000**, pp. 45-74, and references therein.

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⁶ H. Imamura, T. Imahashi, M. Zaimi, Y. Sakata, *J. Alloys Compd.* **2008**, *451/1-2*, 636.

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⁸ H. Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe, H. Fujii, *J. Phys. Chem. B* **2004**, *108*, 8763.

⁹ R. Kieffer, P. Etmayer, and S. Pajakoff, *Monatsh. Chem.*, **1972**, *103*, 1285.

¹⁰ D. E. LaValle, *J. Inorg. Nucl. Chem.* **1962**, *24*, 930.

2. Experimental

2.1 Procedures of sample preparation

Ce metal (99.9%) was purchased from the Santoku Co. and used in powder form by filing. Ammonia gas (Iwatani Ind. Ltd.) was purified through a calcium oxide column and subsequently through a sodium hydroxide column.

To prepare cerium hydride, the reaction of Ce metal with hydrogen was carried out with a glass apparatus provided with a high vacuum system (ca. 2.7×10^{-2} Pa). Prior to the reaction, the powdered Ce metal was subjected to an evacuation treatment at 473 K for 2 h, and the hydrogen absorption by the Ce metal was carried out at room temperature by introducing hydrogen gas of 0.066 MPa into a reactor with a fixed volume. The amount of hydrogen absorption was determined by change in pressure, and cerium hydride with a composition of CeH₂ was obtained.

The reaction of CeH₂ with ammonia was carried out using a planetary-type ball mill (P-6; Fritsch Ltd.), being capable of operating at 650 rpm. In a typical preparation of cerium amide, CeH₂ (0.25 g) was placed in a grinding bowl (made of zirconia; volume of 45 cm³), followed by introduction of 0.3 MPa ammonia. The mixtures were subjected to ball milling with zirconia balls (diameter: 3 mm, 55 g) for 0.25–20 h. To obtain CeN, the cerium amide thus prepared was thermally decomposed under evacuation at 300–1073 K.

2.2 Characterization

X-ray diffraction (XRD) analyses of the cerium samples obtained 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 3 Kmin⁻¹ by continuously monitoring desorbed gases *via* quadrupolar mass spectrometer. All procedures of the cerium samples were carried out without exposure to air.

3. Results and discussion

3.1 Preparation of cerium amide or cerium amide-like compounds by ball milling of CeH₂ and NH₃

For the preparation of cerium hydride, the direct reaction of the cerium metal with hydrogen gas was carried out with measuring the amounts of absorbed hydrogen. The cerium metal reacts normally with hydrogen to form the dihydride. Upon increasing the hydrogen pressure, the dihydride additionally absorbs hydrogen until a composition near trihydride is reached.¹¹ The cerium hydride with the composition of CeH₂ was successfully prepared for use in the present study and the formation of CeH₂ was confirmed to have a cubic structure by XRD.¹²

To carry out the reaction of cerium hydride with ammonia, CeH₂ thus prepared was first placed in a grinding bowl made of zirconia, followed by introduction of ammonia gas at a pressure of 0.3 MPa. The mixtures were subjected to high-energy ball milling for 0.25–20 h. As shown by time courses of changes in XRD (Fig. 1), the

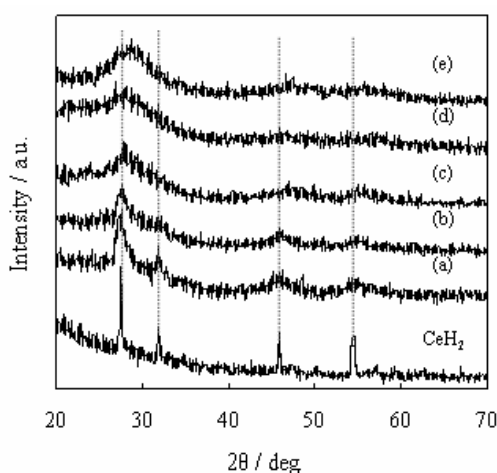


Figure 1. Time courses of changes in XRD with ball milling of CeH₂ and NH₃; (a) 0.25 h, (b) 1 h, (c) 3.5 h, (d) 7 h and (e) 20 h

cerium hydride immediately reacted with ammonia upon ball milling, simultaneously changing from dark gray to brown. The diffraction peaks corresponding to cerium hydride were considerably broadened and gradually diminished with milling times, due to the occurrence of nanocrystallization and reactions with ammonia. After ball milling of 7 h, the XRD peaks of CeH_2 were hardly observed. However, there were no additional diffraction peaks which suggested new phases or products resulting from ball milling of CeH_2 and NH_3 . Although cerium amide was most likely formed upon ball milling, regrettably, the formation of cerium amide was not confirmed by XRD, probably due to it being nanostructured or amorphous.

However, the sample obtained after ball milling of CeH_2 and NH_3 was found to be converted into cerium nitride when subjected to thermal treatment around 873 K as described in the next section. This indicates that the reaction product of CeH_2/NH_3 is certainly cerium amide or an amide-like compound, which decomposes to CeN as described later in XRD and TPD results. Upon ball milling of CeH_2 in an atmosphere of NH_3 , thus cerium hydride readily reacts with ammonia, resulting in the formation of the nanostructured cerium amide as shown in eq. (1).



3.2 Thermal decomposition of cerium amide to cerium nitride

Next the conversion of cerium amide to the cerium nitride was followed by taking XRD spectra with increasing in temperatures for the pretreatment. As shown by changes in XRD (Fig. 2) for CeH_2/NH_3 ball-milled for 7 h, the conversion started at about 673 K and the diffraction peaks of cerium nitride (CeN) were clearly observed upon the thermal treatment above 873 K. This indicates that the reaction of CeH_2 with NH_3 certainly occurs to form amide or amide-like products as a precursor of cerium nitride. It has been shown in previous studies⁶ that the reaction of cerium hydride (CeH_x) with ammonia at 623 K exclusively yields cerium nitride as evidenced by XRD; even if the cerium amide is temporarily formed in this case, it is not observed due to rapid decomposition to nitride at elevated temperatures around 623 K. It was found that upon treatment at higher temperatures considerable crystallization of CeN proceeded further.

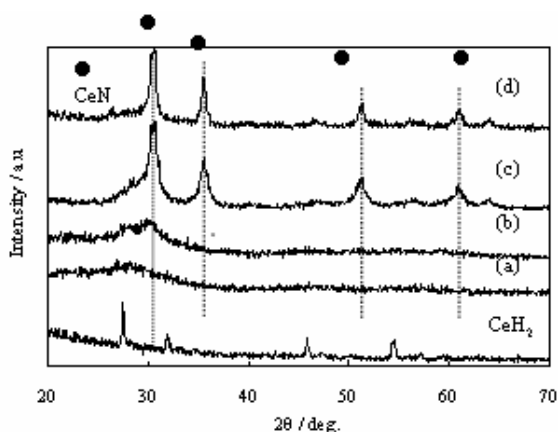


Figure 2. Changes in XRD of (a) 7-hour milling products of CeH_2 and NH_3 with the thermal treatment. The products were subjected to evacuation for 1 h at the following temperatures: (b) 673 K, (c) 873 K and (d) 1073 K.

To evaluate the processes of the conversion into CeN , TPD of the CeH_2/NH_3 products was studied (Fig. 3). The TPD traces (Fig. 3(c)) of the product after 7-hour milling of CeH_2 and NH_3 showed a broad desorption peak of NH_3 around 400 K, two desorption peaks of H_2 at temperatures around 430 and 500 K and small desorption of N_2 at 880 K. Taking into account the conversion processes of ytterbium and europium amide, $Yb(NH_2)_2$ and $Eu(NH_2)_2$, to the nitrides, YbN and EuN ,^{4,7} the change of cerium amide to nitride are considered as follows. Cerium amide, $Ce(NH_2)_2$, decomposes to form the imide, $CeNH$, with the evolution of NH_3 according to eq. (2) and subsequently the conversion into the nitride, CeN , accompanying the evolution of H_2 occurs as shown in eq. (3).

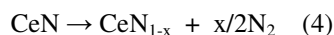
¹¹ G. G. Libowitz, A. J. Maeland, in: *Handbook on the Physics and Chemistry of Rare Earths*, K. A. Gschneidner, Jr., L. Eyring (Eds.), Vol. 3, North-Holland, Amsterdam, 1984, pp. 299-336, and references therein.

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The amide is usually converted into nitride through imide,^{13, 14, 15} Thus the thermal decomposition from the amide to the nitride successively occurs. However, the formation of CeNH was not confirmed in XRD studies (Fig. 2). In the decomposition reaction of rare earth amides, the formation of imide intermediates often has not been recognized. Juza et al.¹⁵ report that there is no evidence of imide formation in the conversion process of $\text{Eu}(\text{NH}_2)_2$ to EuN . However, TPD results obtained here were consistent with the conversion of cerium amide into nitride expressed by eqs. (2) and (3).

The evolution of N_2 observed around 880 K is probably due to further decomposition of CeN to CeN_{1-x} .



By the way, TPD of CeH_2 itself as a starting material showed two desorption peaks of hydrogen around 500 and 980 K as shown in Fig. 3(a). In the structural properties of cerium hydrides, the hydrogen atoms are distributed in the tetrahedral and octahedral sites of the fluorite-type structure and usually the tetrahedral sites are

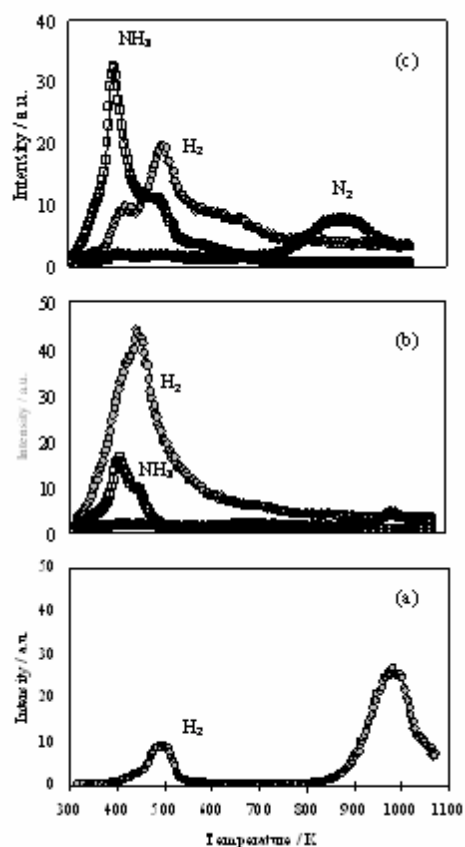


Figure 3. TPD for (a) CeH_2 as a starting material, (b) products after ball milling of CeH_2 and NH_3 for 15 min, and (c) products after ball milling of CeH_2 and NH_3 for 7 h.

preferentially occupied in CeH_2 dihydride.^{11,12} It can be seen by comparison of TPD traces between CeH_2 (Fig. 3(a)) and ball-milled CeH_2/NH_3 (Figs. 3(b) and 3(c)) that the hydrogen in CeH_2 which was observed around 500 K and 980 K disappeared after ball milling of CeH_2 and NH_3 for 7 h, due to reaction with ammonia according to eq. (1). Upon initial ball milling (Fig. 3(b)), hydrogen observed around 500 and 980 K started to disappear,

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while newly desorbed hydrogen from the reaction products of CeH_2/NH_3 was observed around 450 K. The hydrogen of CeH_2 observed around 980 K completely disappeared after only 15-minute milling. Taking into account the XRD results (Fig. 1), the TPD peaks of hydrogen in CeH_2 gradually diminished with ball milling and almost disappeared with the completion of reaction (1) by 7-hour ball milling, as shown in Fig 3(c). For the 7-hour ball-milled CeH_2/NH_3 , the TPD peaks of hydrogen observed around 430 and 500 K are assigned to hydrogen arising from the decomposition of cerium imide to nitride according to eq. (2). Probably, if cerium triamide is in part formed, the following decomposition process is possible: $\text{Ce}(\text{NH}_2)_3 \rightarrow \text{CeNH} + \text{H}_2 + 1/2\text{N}_2 + \text{NH}_3$. This leads to additional hydrogen desorption in the TPD traces. In TPD studies, it was proven that cerium amide thermally decomposes to form the imide, followed by the conversion to the nitride.

Thus, cerium nitride was successfully prepared by the thermal decomposition of cerium amide obtained by the reaction of cerium hydride with ammonia, compared to the preparation method using the direct reaction of the cerium metal with ammonia reported previously.⁶

4. Conclusion

The preparation method of cerium nitride by taking advantage of the reaction of cerium hydride with ammonia has been studied extensively. Nanostructured CeN was successfully prepared by thermal decomposition of cerium amide obtained by ball milling of CeH_2 and NH_3 . The formation of cerium amide as a precursor of nitride was important in the whole steps for the preparation and was strongly suggested by XRD and TPD studies. The cerium amide obtained by ball milling of CeH_2 and NH_3 for 7 h was subjected to a thermal treatment to be converted into cerium nitride. The conversion processes of cerium amide into nitride were evaluated with XRD and TPD. Consequently, the cerium amide decomposed to imide with evolution of ammonia around 400 K, followed by conversion into nitride from about 500 K with evolution of hydrogen.

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