Preparation and catalytic properties of europium and ytterbium hydrides using liquid ammonia solutions of lanthanide metals

Hayao Imamura *, Yoshiaki Maeda, Toshiko Kumai, Yoshihisa Sakata, and Susumu Tsuchiya
Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,
2-16-1 Tokiwadai, Ube 755-8611, Japan

Received 17 December 2002; accepted 11 March 2003

Active carbon (AC)-supported dihydrides of europium and ytterbium were prepared by depositing finely divided metallic lanthanide on AC from liquid ammonia solutions of Eu and Yb metals, respectively, followed by hydriding under a hydrogen flow at 298–673 K. Upon heat treatment of YbH_2/AC and $EuH_{1.9}$/AC in vacuum, hydrogenation activity for olefins appeared.

KEY WORDS: lanthanide dihydride; europium hydride; ytterbium hydride; olefin hydrogenation; hydride catalysts.

1. Introduction

Recently, there has been growing interest in lanthanides and their derivatives for potential synthetic and catalytic activity. It has been shown that the use of dissolution of lanthanide metals (Ln: Eu and Yb) in liquid ammonia allows the preparation of novel lanthanide-containing catalysts which exhibit specific properties for various reactions [1]. In this paper, we report a new method for the preparation of active carbon (AC)-supported hydrides of europium and ytterbium and their catalytic properties for the hydrogenation of ethane. Europium and ytterbium react with hydrogen to form only the dihydrides, which have orthorhombic structures [2–4]. The AC-supported dihydrides were prepared by depositing finely divided metallic lanthanide on AC from liquid ammonia solutions of Eu and Yb metals, followed by hydriding. Few studies have been published on the catalytic properties of lanthanide hydrides (LnH_x) to the best of our knowledge, particularly for supported hydride catalysts.

2. Experimental

Eu and Yb ingots (99.9%) were obtained from Santoku Metal Industries. Active carbon (1064 m^2/g) obtained from Nacalai Tesque was evacuated at 873 K for 20 h before use. Ammonia gas (Iwatani Industries) was dried through a calcium oxide column and subsequently through a sodium hydroxide column.

2.1. Catalyst preparation

In a typical preparation of AC-supported dihydride of europium ($EuH_{1.9}$/AC), AC (1.0 g) which had previously been subjected to evacuation at 873 K was placed in a Schlenk tube, cooled in a dry ice–methanol bath and then mixed with purified liquid ammonia (about 15 cm^3). Eu metal chips (0.6 g) were added to the AC powder suspended in liquid ammonia with stirring at 198 K. The Eu metal immediately dissolved in the liquid ammonia to form a homogeneous solution containing solvated electrons with an intense blue color [5], which gradually faded as a result of the deposition of europium on active carbon. Subsequently, liquid ammonia was immediately removed by evacuation at 198 K. This led to the deposition of europium (Eu/AC) in the metallic state on active carbon as shown in figure 1; the metallic europium existed in a cubic structure. AC-supported dihydride of europium was prepared by hydrogenation of Eu/AC with a flow of hydrogen for 12 h at 298–423 K and was identified as orthorhombic hydride $EuH_{1.9}$ [6] by X-ray diffraction (XRD). The XRD measurements were made with a Rigaku RINT 2200 X-ray diffractometer using Cu K_α radiation.

AC-supported dihydride of ytterbium (YbH_2/AC) was similarly prepared by the hydrogenation of Yb/AC.

2.2 Hydrogenation reactions

The catalytic reactions were carried out using a Pyrex gas-recirculation reactor. Prior to the reaction, $EuH_{1.9}$/AC and YbH_2/AC were subjected to evacuation treatment at 298–1273 K for 1 h, set at a reaction temperature of 300 K and then the reaction was initiated by admitting hydrogen (33 Torr) and ethene (33 Torr). The reacting gas was periodically collected by a gas sampler and analyzed using a Shimadzu TCD gas chromatograph.

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* To whom correspondence should be addressed.
E-mail: hi-khm@yamaguchi-u.ac.jp

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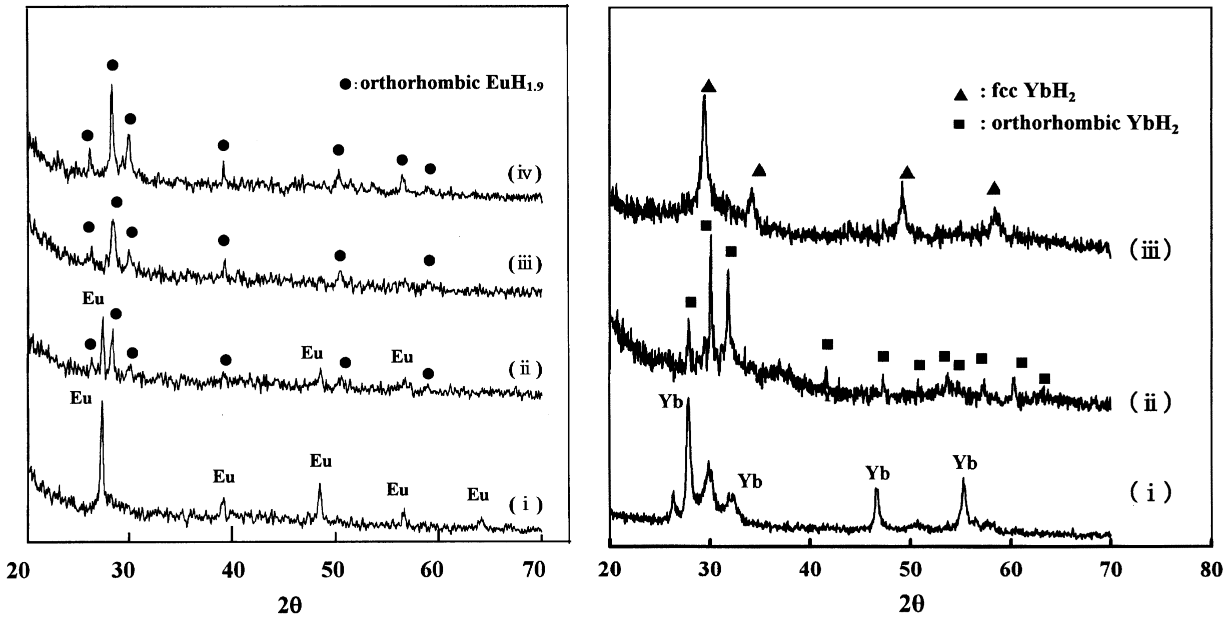

(a) (b)

Figure 1. (a) XRD of (i) Eu/AC and of $EuH_{1.9}$/AC hydrogenated at (ii) 298, (iii) 373 and (iv) 423 K. (b) XRD of (i) Yb/AC and of YbH_2/AC hydrogenated at (ii) 423 and (iii) 673 K.

3. Results and discussion

3.1. Hydrides obtained by hydrogenation of lanthanide metals deposited from liquid ammonia solutions of Eu and Yb metals

As shown by XRD (figure 1) of Eu/AC and Yb/AC, the europium and ytterbium were deposited in fine particle form of the metal on active carbon from liquid ammonia solutions of Eu and Yb metals, respectively. The dihydrides of europium and ytterbium were prepared by direct hydrogenation of the metals highly dispersed on active carbon with a flow of hydrogen at atmospheric pressure. The XRD patterns of the products hydrogenated at different temperatures (298–673 K) are shown in figure 1(a) and (b). It has been shown that the reaction of ytterbium or europium metal with hydrogen at less than 1 atm pressure and moderate temperatures yields only the dihydrides, which have orthorhombic structures [2–4]. The formation of higher hydrides of ytterbium, YbH_x ($x > 2$), is successfully achieved by reaction of the metal with hydrogen at higher pressures and elevated temperatures [7,8]. As shown in figure 1, the europium metal reacted readily with hydrogen even at 298 K. The XRD data for the hydrides of europium and ytterbium thus obtained coincided with those for $EuH_{1.9}$ [6] and YbH_2 [9] with orthorhombic structures, respectively. On hydriding ytterbium metal above 673 K, the hydride product had a face-centered cubic (fcc) structure (figure 1(b)). This is consistent with the fact that orthorhombic hydrides of ytterbium are transformed into the fcc modification when heated to 473–673 K [9].

The catalytic behavior of the europium and ytterbium hydrides depended on the heat treatment in vacuum. The evacuation treatment of LnH_x/AC at elevated temperatures (298–1273 K) for 1 h, before the reaction, strongly affected the hydrogenation activity for ethene. When $EuH_{1.9}$/AC was used as a catalyst, upon evacuation above 473 K the hydrogenation activity appeared at a reaction temperature of 300 K (figure 2). The activity increased with increasing evacuation temperature up to 573 K, and passed through a maximum around 573 K. Subsequently, the catalyst was completely deactivated upon heating to 773 K. On the other hand, YbH_2/AC exhibited a different temperature dependence of catalytic

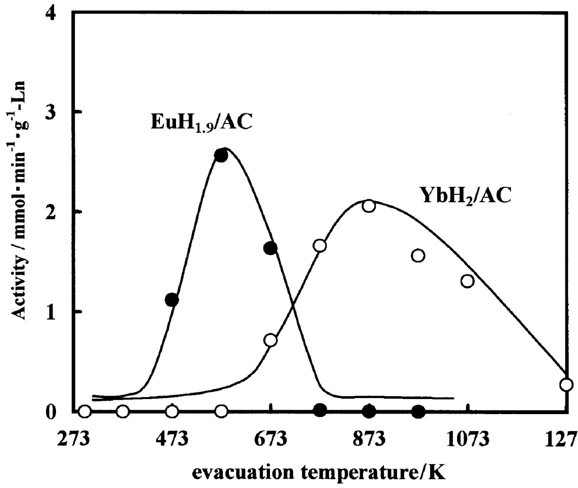

Figure 2. Effects of evacuation temperature on the hydrogenation activity of ethene. The hydrogenation was carried out at 300 K with ethene (33 Torr) and hydrogen (33 Torr).

activity (figure 2); evacuation at around 873 K led to maximum activity. The dependence of the activity almost remained unaltered even though the dihydride of YbH_2/AC with either an orthorhombic or fcc structure was used. YbH_2/AC was similar in specific activity to $EuH_{1.9}$/AC. However, the reasons why there was a difference in evacuation temperatures leading to the maximum activity between YbH_2/AC and $EuH_{1.9}$/AC are unknown. It may be partly associated with differences in hydride structures relating to the activity; $EuH_{1.9}$/AC was orthorhombic, whereas YbH_2/AC was face-centered cubic, as shown later.

XRD of YbH_2/AC as prepared at 423 K showed only the orthorhombic structure, which changed to the fcc structure on heating to 673 K (figure 3). On further heat treatment at 1273 K, additional XRD peaks assigned to the nitride YbN were only just observed. On the other hand, $EuH_{1.9}$/AC had an orthorhombic phase, which remained unchanged even if heat treatment was conducted. However, the diffraction intensity of the dihydride gradually diminished with increasing evacuation temperature, and EuN instead of the dihydride was clearly observed in XRD. At an evacuation temperature of 773 K, at which the hydrogenation activity disappeared, XRD of $EuH_{1.9}$/AC showed only diffraction peaks of EuN. The formation of YbN and EuN is probably due to the transformation of the amide, formed simultaneously upon dissolution of lanthanide metals in liquid ammonia, into the nitride on heating [10,11], or to the reaction of hydrides with residual ammonia on active carbon at elevated temperatures. The decrease in the diffraction peaks of $EuH_{1.9}$ is associated with hydride stability, but there are no thermodynamic data available for $EuH_{1.9}$ [12]. As described in the next section, it seems unlikely that the lanthanide nitrides formed are involved in the catalytic hydrogenation of olefins observed here. For YbH_2/AC and $EuH_{1.9}$/AC, the catalytic activity was observed with the fcc and orthorhombic structure of the hydrides, respectively.

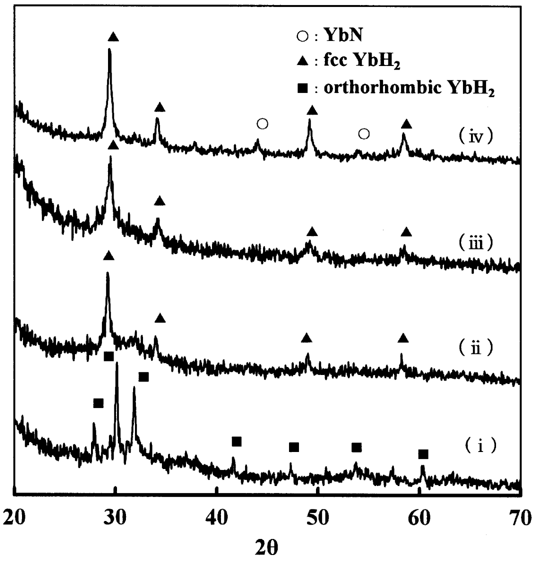

Figure 3. XRD of YbH_2/AC evacuated at (i) 423, (ii) 673, (iii) 1008 and (iv) 1273 K. YbH_2/AC was prepared by hydrogenation of Yb/AC at 423 K.

To clarify what effect the evacuation treatment causes, temperature-programmed desorption (TPD) measurements on YbH_2/AC and $EuH_{1.9}$/AC were made *in vacuo* by continuously monitoring the desorbed gases via quadrupole mass spectrometry. TPD showed characteristic profiles of H_2, NH_3 and N_2 desorption from the samples, when measured at a heating rate of 2 K/min in vacuum. It can be seen from comparison of figures 2 and 4 that the TPD traces for YbH_2/AC correspond

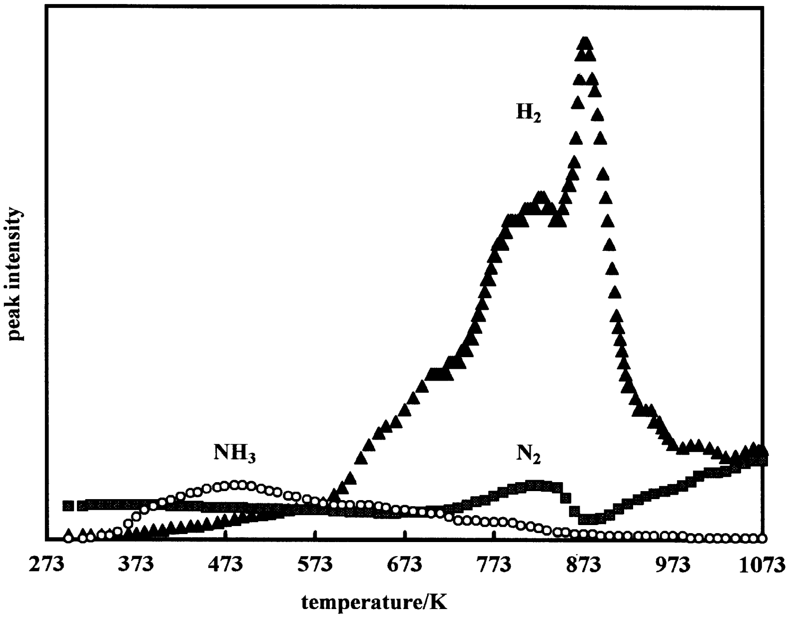

Figure 4. TPD measurements of YbH_2/AC.

well with the dependence of catalytic activity as a function of evacuation temperature; maximum activity emerged in the range of evacuation temperatures in which the TPD peak of hydrogen had a maximum. When the dihydride was heated under vacuum, the hydrogen in the surface layer was desorbed to some extent, resulting in the formation of non-stoichiometric hydride surfaces which acted just as active catalysts. The desorption of H_2 from $EuH_{1.9}$/AC was maximally recorded around 550 K. This is very close to the evacuation temperature of 573 K at which the maximum activity was observed in figure 2.

3.2. Hydrides obtained by hydrogenation of powdered Yb turnings

The influence of differences in the method of preparation of the lanthanide hydrides was examined. Ytterbium was used for comparison in the form of powdered turnings of the metal, which was further hydrogenated at 473 K. The ytterbium hydride was obtained similarly to YbH_2/AC with an orthorhombic structure. As mentioned previously, the catalytic activity also varied markedly with changes in evacuation temperature. Evacuation at around 873 K resulted in maximum hydrogenation activity with simultaneous transformation of orthorhombic hydride to fcc hydride. This was very similar to the results obtained for YbH_2/AC. TPD measurements indicated that the defects formed by desorption of hydrogen with the phase transformation constituted active sites for the hydrogenation of ethene. Moreover, the results obtained so far strongly suggest that the nitrides observed when $EuH_{1.9}$/AC and YbH_2/AC were treated at elevated temperatures are hardly associated with the catalytic activity for ethene hydrogenation.

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