ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 903–907

Journal of ALLOYS AND COMPOUNDS

Catalytic properties of lanthanide amide, imide and nitride formed by thermal degradation of liquid ammonia solutions of Eu and Yb metal

Hayao Imamura*, Katsuhiko Mizuno, Kazutaka Ohishi, Eisaku Suda, Kenzo Kanda,
Yoshihisa Sakata, Susumu Tsuchiya

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755, Japan

Abstract

The catalytic properties of lanthanide amide, imide and nitride prepared by the use of liquid ammonia solutions of lanthanide metals (Ln=Eu and Yb) were studied for catalytic hydrogenation. The reaction of Eu or Yb metal solutions in liquid ammonia with silica yielded SiO_2-grafted lanthanide amide in the divalent state. The divalent amide showed catalytic activity for the selective hydrogenation of dienes and benzene. It was found that partial hydrogenation of benzene occurred with a very high selectivity for cyclohexene. Amides of calcium, strontium and barium were examined similarly in connection with catalytic studies on divalent amides. Imide and nitride, into which the lanthanide (Ln/AC) deposited by impregnation of active carbon (AC) with liquid ammonia solutions of lanthanide metals were converted thermally, were studied catalytically. It was concluded that imide or imide-like species generated during the thermal degradation of lanthanide amide to nitride were very active in the hydrogenation of ethene. Lanthanide nitride was virtually inactive, but the nitride highly dispersed on active carbon was activated when subjected to evacuation treatment above about 1000 K. © 1998 Elsevier Science S.A.

Keywords: Lanthanide amide; Lanthanide imide; Lanthanide nitride

1. Introduction

Recently there has been growing interest in lanthanides and their derivatives for their potential synthetic and catalytic activity [1]. However, there have been few studies published of the heterogeneous catalysis of lanthanide elements.

It has been shown that the use of dissolution of lanthanide metals (Ln=Eu and Yb) in liquid ammonia enables the preparation of novel heterogeneous catalysts of lanthanides which exhibit specific catalytic properties [2]. When matrix substrates are impregnated with liquid ammonia solutions of lanthanide metals, the way in which the lanthanide species exist on the matrix changes from matrix to matrix and, simultaneously, the catalytic properties vary markedly [3,4]. When silica is used as a matrix, the dissolved lanthanide in liquid ammonia preferentially reacts with surface hydroxyl group on silica to form amide species such as $\equiv Si–O–Ln–NH_2$ [4]. More recently, for lanthanides introduced into zeolite by impregnation from liquid ammonia solutions, the changes in their chemical state with evacuation temperature have been reported [5,6]. It is accepted that the thermal degradation of liquid ammonia solutions of Eu and Yb metals finally leads to the formation of nitride through amide and/or imide [7,8]. In this paper, the catalytic properties of lanthanide amide, imide and nitride formed during the thermal treatment of lanthanide catalysts (Ln/SiO_2 or Ln/AC), obtained by impregnation of silica or active carbon (AC) as a matrix with Eu or Yb metal solutions in liquid ammonia, were studied. It is of great interest to investigate the relationship between the chemical state of the lanthanides and their catalytic nature.

2. Experimental

2.1. Materials

Eu and Yb ingots (99.9%) were obtained from Shin-Etsu Chemical Co. Ltd. Calcium (Nacalai Tesque Inc.), Sr (Koch Chemicals Ltd.) and Ba (Wako Pure Chemical Ind., Ltd.) were available commercially and used in the form of chips or granules. Before use, active carbon (AC; Nacalai Tesque Inc.) was evacuated at 873 K, and SiO_2 (Degussa Aerosil; 380 $m^2 g^{-1}$), MgO (Ube Ind. Ltd.) and ZrO_2

---

*Corresponding author.

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00481-2

(Tosoh-Zirconia TZ-3Y) were evacuated at 1073 K. Ammonia gas (Iwatani Ind. Ltd.) was dried by passing through a calcium oxide column and subsequently through a sodium hydroxide column.

2.2. Catalyst preparation and reaction

2.2.1. Ln/SiO$_2$ and other SiO$_2$-grafted catalysts

In a typical preparation of 15 wt% Yb/SiO$_2$, SiO$_2$ which had been previously evacuated at 1073 K for 10 h, was placed in a Schlenk tube, in which purified ammonia was liquefied at 198 K. Yb was added to the SiO$_2$ powders suspended in liquid ammonia (ca. 20 cm^3) with vigorous stirring at 198 K. Upon dissolution of the lanthanide metal in liquid ammonia, a blue homogeneous solution was formed, characteristic of divalent metal cations and solvated electrons [9]. The blue color of the solution faded gradually with stirring as a result of the reaction of the dissolved lanthanide metal with SiO$_2$. On disappearance of the blue color, excess ammonia was removed under vacuum at 198 K leaving 15 wt% Yb/SiO$_2$ catalyst. 3.6 wt% Ca/SiO$_2$, 7.7 wt% Sr/SiO$_2$ and 12 wt% Ba/SiO$_2$ were similarly prepared.

2.2.2. Ln/AC

Eu or Yb was similarly added to the AC powder suspended in liquid ammonia with stirring to prepare Ln/AC with different levels of lanthanide loading.

2.2.3. Lanthanide amides

Basically according to the method of Hadenfeldt et al. [10], lanthanide amides were prepared as supported and unsupported. For the preparation of supported lanthanide amide, in a 100 ml stainless steel reactor was placed a measured amount of lanthanide metal and support (active carbon, MgO or ZrO$_2$) under an atmosphere of dry nitrogen. The reactor was briefly evacuated, cooled by a dry ice/methanol bath and about 0.8 mol of purified ammonia was liquefied. The mixture was allowed to stand for 20 h at room temperature. The formation of lanthanide amide (II) and (III) was confirmed by XRD. For the preparation of unsupported amides, the same procedures were carried out without the use of a support.

2.2.4. Hydrogenation reactions

The hydrogenation reactions were studied using a Pyrex gas-recirculation reactor. Prior to the reaction the catalysts were subjected to evacuation treatment at 298–1373 K for 2 h, set at a reaction temperature of 203–373 K, and then the reaction was initiated by introducing mixed gases of hydrogen and reactants. The reacting gas was periodically collected by a gas sampler and analyzed by a Shimazu FID or TCD gas chromatograph.

2.2.5. Analyses

IR spectra were recorded on a JASCO FT-IR 7000 spectrometer equipped with a MCT detector. To a solution of alkaline earth metals (Ca, Sr and Ba) in liquid ammonia was added an IR disc of SiO$_2$, which had been evacuated at 973 K, treated in an oxygen flow at 723 K, and again evacuated at 723 K for 0.5 h. In a dry-nitrogen glove bag, the IR disc thus treated was carefully loaded into the IR cell, which was attached to a vacuum apparatus. IR spectra were obtained from the ratio of the background spectrum of silica to that of each sample.

3. Results and discussion

3.1. Catalysis of lanthanide amides and lanthanide grafted onto SiO$_2$

Lanthanide metals (Eu and Yb) dissolved in liquid ammonia reacted with SiO$_2$ to form active Ln/SiO$_2$ catalysts. The behavior of lanthanides present on SiO$_2$ varied markedly with the level of lanthanide loading [4]. For low loadings (13–15 wt%), lanthanide catalysts immobilized on SiO$_2$, formed by the preferential reaction of lanthanides with surface hydroxyl groups on SiO$_2$ which have been shown by Fourier-transform infrared studies to have the structure $\equiv$Si–O–Ln–NH$_2$, exhibited selective hydrogenation properties, discriminating between conjugated and non-conjugated dienes. Thus, buta-1,3-diene, isoprene, penta-1,3-diene and cyclohexa-1,3-diene were readily reduced to the corresponding monoenes at 298 K, whereas penta-1,4-diene and hexa-1,4-diene remained unchanged. An interesting property in this connection is that such lanthanide amide catalysts show negligible or very low reducing power for monoenes (propene and but-1-ene), in marked contrast to their reactivity with conjugated dienes. Europium and ytterbium showed rather similar catalytic behavior, but the activity of ytterbium was much higher than that of europium.

A further important characteristic of the ytterbium catalyst grafted onto SiO$_2$ and Al$_2$O$_3$ is that partial hydrogenation of benzene to cyclohexene occurred with a selectivity of 96–100% [11], which is much higher than previously reported. As described above for the catalysis of $\equiv$Si–O–Yb–NH$_2$, cyclohexa-1,3-diene was readily reduced to cyclohexene with almost 100% selectivity at 298 K, whereas cyclohexene was virtually inactive. This is the reason why the SiO$_2$-grafted lanthanide amide catalysts can realize extremely high selective hydrogenation of benzene to cyclohexene.

It is known that europium and ytterbium amide can exist in a divalent or trivalent state [12,13]. When the supported and unsupported lanthanide amides (II and III) were examined, interestingly, selectivity for partial hydrogenation of benzene was observed for the divalent amide (Table 1). This is consistent with the data for 15% Yb/

Table 1
Hydrogenation of benzene at 373 K over various catalysts[a]

Catalyst	Activity (mmol min^{-1} g^{-1})	Product (%)[b]	Ref.
13% Eu/SiO_2	None (298 K)		[11]
15% Yb/SiO_2	1.8×10^{-4} (298 K)	Cyclohexene (100%)	[11]
$Yb(NH_2)_2$	2.5×10^{-5}	Cyclohexene (100%)	
$Yb(NH_2)_3$	None		
$Yb(NH_2)_3$/AC	None		
$Yb(NH_2)_2$/MgO	2.8×10^{-5}	Cyclohexene (95%)	
$Yb(NH_2)_2/ZrO_2$	3.2×10^{-5}	Cyclohexene (91%)	

[a] The reaction was carried out with benzene (20 Torr) and hydrogen (120 Torr).
[b] Selectivity (%) for the products.

SiO_2 [11]. However, upon thermal treatment of Yb/SiO_2 above ca. 575 K, the catalyst was deactivated, owing to the decomposition of the active ≡Si–O–Ln–NH_2 species as shown from the IR spectra [4]. Alkaline earth metals [9], which were similarly dissolved in liquid ammonia to form divalent amides, were examined. The IR spectra (Fig. 1) show that the reaction of liquid ammonia solutions of Ca, Sr or Ba metals with SiO_2 occurs similarly to the case of Yb/SiO_2. For Sr/SiO_2 as an example, the vibration band at 3748 cm^{-1} of SiO_2, which is assigned to free hydroxyl groups, decreased immediately upon contact with strontium. New absorptions were simultaneously observed at 3384 and 3252 cm^{-1}, which could be assigned to the NH_2 group bound to the alkaline earths by comparison with published data [14]. These bands are very close to 3384 and 3288 cm^{-1} obtained for Yb/SiO_2 [4]. The surface density of hydroxyl groups on silica, which is known to be a function of the evacuation temperature, was estimated here to be ~1.5 OH nm^{-2} for SiO_2 evacuated at 1073 K [15]. The alkaline earth loadings of 3.6% Ca/SiO_2, 7.7% Sr/SiO_2 and 12% Ba/SiO_2, as well as 15% Yb/SiO_2 [4], were determined by assuming an alkaline earth metal to OH group ratio of 1:1 in the surface complex. The IR spectra of Ca/SiO_2, Sr/SiO_2 and Ba/SiO_2 are shown in Fig. 1, and suggest that alkaline earth amides are similarly grafted onto silica in the form of ≡Si–O–M–NH_2 (M=Ca, Sr and Ba). These SiO_2-grafted catalysts exhibited slight activity for the selective hydrogenation of benzene to cyclohexene at the start of the reaction, followed by inactivation.

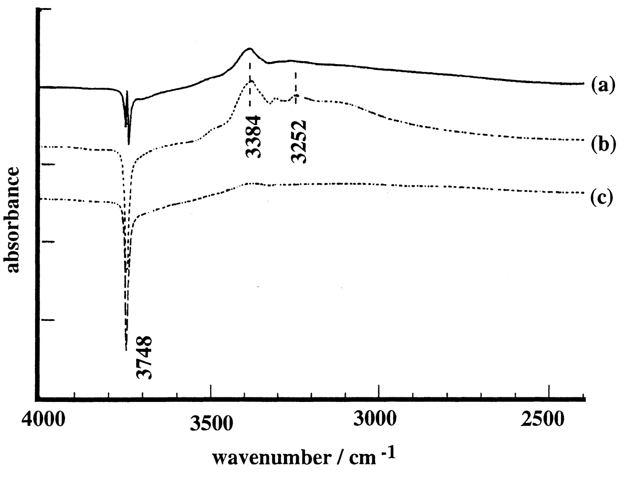

Fig. 1. IR spectra of (a) 3.6% Ca/SiO_2, (b) 7.7% Sr/SiO_2 and (c) 12% Ba/SiO_2.

3.2. Catalysis of lanthanide imide and nitride formed on AC

The catalysis of lanthanide amide, imide and nitride was further examined for Eu/AC and Yb/AC obtained by impregnation of active carbon (AC) with liquid ammonia solutions of Eu or Yb metal. The lanthanide deposited on active carbon was consecutively changed through varied steps (metal, amide, imide or nitride) by thermal treatment (298–1373 K) [7,8] and simultaneously the hydrogenation activity varied, depending on the mode of variation [16].

The catalytic behavior of Eu/AC and Yb/AC depends upon the thermal pretreatment in vacuo and upon the degree of lanthanide loading during preparation, especially higher loading (60%) and lower loading (<30%) (Fig. 2). Upon evacuation of 60% Yb/AC above 473 K, the hydrogenation activity of ethene appeared even at 203 K; the activity increased with increasing evacuation temperature up to 773 K, and passed through a maximum around 773 K with an enhancement by over two orders of magnitude. Then, 60% Yb/AC was completely deactivated upon evacuation at 1373 K. 60% Eu/AC exhibited a similar temperature dependence of the catalytic activity (Fig. 2).

Lanthanide amides (II and III), $Yb(NH_2)_2$ and $Yb(NH_2)_3$/AC, exhibited almost no activity for the hydrogenation of ethene [16], which is consistent with the conclusion drawn in the previous section. Upon evacuation of 60% Yb/AC above 773 K, XRD spectra showed conversion to nitride YbN. The formation of europium nitride EuN was also observed upon thermal treatment of Eu/AC above 573 K. The nitrides of europium and ytterbium thus obtained showed negligible activity for the hydrogenation of ethene. It has been shown that transient intermediates, imide (EuNH, YbNH) or imide-like spices, generated during thermal degradation (503–573 K for europium and 423–773 K for ytterbium) of lanthanide

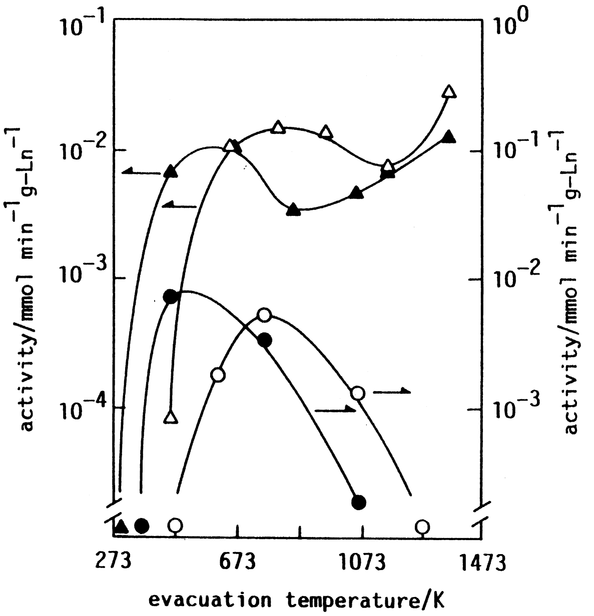

Fig. 2. Effect of the evacuation temperature of Ln/AC on the hydrogenation rates of ethene. Hydrogenation at 253 K over 30% Eu/AC (▲) and 30% Yb/AC (△). Hydrogenation at 203 K over 60% Eu/AC (●) and 60% Yb/AC (○). The catalysts were evacuated for 2 h prior to the reaction.

amides to nitride exhibit very high hydrogenation activity at 203 K [16].

As shown in Fig. 2, Eu/AC and Yb/AC with lower lanthanide loadings exhibit a different dependence of the activity on the evacuation temperature than catalysts with higher loadings, particularly at higher temperatures above ca. 1000 K. Thus, upon evacuation at 1373 K, 30% Ln/AC was highly activated, whereas 60% Ln/AC was completely deactivated. It was found that the variation of the activity of 15% Ln/AC as a function of evacuation temperature was quite similar to that of 30% Ln/AC. Regardless of the degree of Yb loading (15, 30 and 60%), only nitride diffraction peaks were observed upon evacuation of Yb/AC above 773 K, but the catalytic behavior was quite different between 30 and 60% Yb/AC, as shown in Fig. 2. For 15 and 30% Yb/AC, a broadening of the XRD peaks was observed due to the high dispersion of ytterbium. However, for evacuation treatment between about 300 and 900 K, the variations in activity of 30% Eu/AC and 30% Yb/AC closely resemble those observed for 60% Eu/AC and 60% Yb/AC with a maximum activity around 573 and 773 K, respectively. Hence, it is deduced that 30% Ln/AC is essentially similar to 60% Ln/AC in the catalytic nature induced by thermal treatment from about 300 to 900 K. Thus, there are definite differences in the catalytic properties between lower loading (15 and 30%) and higher loading (60%) of lanthanides on active carbon, in particular when Ln/AC catalysts are subjected to evacuation above ca. 1000 K.

This difference similarly reflects the kinetic behavior for the hydrogenation of ethene. For 30% Yb/AC, the hydrogenation rates of the catalyst evacuated at 673 K are represented by a first-order rate equation with respect to the hydrogen pressure, while evacuation at 1373 K results in a different pressure dependence; the reaction orders with respect to hydrogen and ethene were about +1.0 and −1.0, respectively. For evacuation at 673 K, there were no differences in the pressure dependence of the rates between 30 and 60% Yb/AC. Furthermore, for the catalysts evacuated at 673 K, the apparent activation energies of the hydrogenation were nearly equal and were estimated as 30 kJ mol^{-1}. This seems to reveal catalysis of lanthanide imide formed on AC upon evacuation at 673 K [16]. On the other hand, an activation energy of 6 kJ mol^{-1} was determined for the 30% Yb/AC catalyst evacuated at 1373 K.

When lanthanides introduced into Y-zeolite by impregnation from liquid ammonia solutions of Eu or Yb metal are evacuated around 900 K, the Ln/zeolite catalyst is active for the hydrogenation of ethene [5,6]. Baba et al. conclude that lanthanide nitride species catalyze the hydrogenation. However, the reasons why only Ln/AC with lower lanthanide loadings was highly activated upon evacuation above 1000 K are unknown.

4. Conclusions

1. The immobilization of lanthanide amide on silica from liquid ammonia solutions of Eu and Yb metals results in specific catalysis for hydrogenation.
2. Ytterbium amide in the divalent state shows catalytic activity for the partial hydrogenation of benzene with high selectivity.
3. Imide or imide-like species formed by thermal decomposition of lanthanide deposited by impregnation of active carbon with lanthanide metal solutions in liquid ammonia are catalytically active for the hydrogenation of olefins.

Acknowledgements

We are grateful to The Ministry of Education, Science and Culture for financial support. We would like to thank DuPont Company for a research grant that allowed this research to be carried out.

References

[1] T. Imamoto, Lanthanides in Organic Synthesis, Academic Press, London, 1994; Y. Kamochi, Kudo, Rev. Heteroatom. Chem. 11 (1994) 165; G.A. Molander, Chem. Rev. 92 (1992) 29; J.A. Soderquist, Aldrichim. Acta 24 (1991) 15.

[2] H. Imamura, K. Igawa, Y. Kasuga, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 90 (1994) 2119.

[3] H. Imamura, H. Yoshimochi, Y. Sakata, S. Tsuchiya, J. Mol. Catal. 66 (1991) L33.

[4] H. Imamura, T. Konishi, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 88 (1992) 2251.

[5] T. Baba, S. Hikita, R. Koide, Y. Ono, T. Hanada, T. Tanaka, S. Yoshida, J. Chem. Soc., Faraday Trans. 89 (1993) 3177.

[6] T. Baba, S. Hikita, Y. Ono, T. Yoshida, T. Tanaka, S. Yoshida, J. Mol. Catal. A: Chem. 98 (1995) 49.

[7] S. Salot, J.C. Warf, J. Am. Chem. Soc. 90 (1968) 1932.

[8] R. Juza, C. Hadendeldt, Naturwissenschaften 55 (1968) 229.

[9] J.C. Thompson, Electrons in Liquid Ammonia, Clarendon Press, Oxford, 1976.

[10] C. Hadenfeldt, H. Jacob’s, R. Juza, Z. Anorg. Allg. Chem. 379 (1970) 144.

[11] H. Imamura, T. Konishi, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Chem. Commun. (1993) 1852.

[12] T. Tanaka, T. Hanada, S. Yoshida, T. Baba, Y. Ono, Jpn. J. Appl. Phys. 32 (1993) 481.

[13] T. Tanaka, T. Hanada, S. Yoshida, T. Baba, Y. Ono, Physica B 208–209 (1995) 687.

[14] P. Bouclier, A. Novak, J. Portier, P. Hagenmuller, C.R. Hebd. Séanc. Acad. Sci. Paris 263 (1966) 875.

[15] L.T. Zhuravlev, Langmuir 3 (1987) 316.

[16] H. Imamura, T. Konishi, E. Suda, Y. Sakata, S. Tsuchiya, Bull. Chem. Soc. Jpn. 69 (1996) 77.