Lanthanide metal overlayers by deposition of lanthanide metals dissolved in liquid ammonia on Co and Ni. Effects of particle sizes of parent Co and Ni metals

Hayao Imamura [1], Yoshie Kasuga, Koji Abe, Yoshihisa Sakata
and Susumu Tsuchiya

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

Received 22 December 1994; accepted 28 February 1995

Lanthanide metals (Ln = Eu and Yb) dissolved in liquid ammonia and reacted readily with reduced Co or Ni powders to form lanthanide metal overlayers (Ln–Co or Ln–Ni). The surface properties of Ln–Co and Ln–Ni prepared from Co and Ni precursors with different particle sizes (15–28 nm) were characterized by the hydrogenation of propene. The hydrogenation behaviors varied markedly with changes in metal particle sizes of the Co and Ni precursors and the lanthanide content. The hydrogenation activity decreased with lanthanide content, passed through a minimum and increased with increasing content. The active surfaces of parent cobalt and nickel were gradually covered with the lanthanide metals and simultaneously synergetic interactions between the lanthanide and 3d-transition metals occurred, indicating the formation of hydrogen-absorbing surface intermetallic phases. This synergy showed a tendency to appear in the region of higher lanthanide contents with decreasing average metal sizes of the Co and Ni precursors.

Keywords: lanthanide; propene hydrogenation; lanthanide metal overlayer; liquid ammonia; bimetallic catalysts

1. Introduction

By using the solvating ability of liquid ammonia for the lanthanide metals (Ln = Eu and Yb) [1], we have recently developed methods for the preparation of new catalytic materials containing lanthanides and have demonstrated that they exhibit specific catalytic properties [2,3]. When reduced Co or Ni metal powder is added to a solution of lanthanide metals dissolved in liquid ammonia, the dissolved lanthanide is found to be deposited on the 3d-transition metal to form novel lantha-

---

[1] To whom correspondence should be addressed.

nide metal overlayers or lanthanide-containing bimetallic catalysts [4–6]. These binary systems exhibit synergetic effects between the lanthanide and 3d-transition metal for the hydrogenation of alkenes and the dehydrogenation of cycloalkanes. It has been shown that the appearance of the synergy is strongly associated with the fraction of coverage with the lanthanide metals. Hence, pronounced effects of sizes of parent Co or Ni metal particles on the catalytic properties as a function of lanthanide content are expected.

We here report catalytic behavior of the lanthanide metal overlayers (Ln–Co and Ln–Ni) obtained when the dissolved lanthanide metal in liquid ammonia reacts with the Co or Ni precursors of different metal sizes (15–28 nm). Much attention has been devoted to defining and understanding the phenomena associated with the synergism of this bimetallic system and its related catalytic consequences.

2. Experimental

2.1. MATERIALS

Eu and Yb ingots (99.9%) were obtained from the Shin-Etsu Chemical Co. Ltd. and used in the form of turnings or granules. Cobalt and nickel fine particles (surface area: 47.9 and 43.8 $m^2 g^{-1}$, respectively) prepared by means of a gas-evaporation method were commercially available from the Vacuum Metallurgical Co. Ltd. Prior to use the fine-particle samples were treated at the reduction temperatures of 453–723 K in an atmosphere of hydrogen to obtain the Co and Ni metals with different particle sizes shown in table 1. Their average particle sizes were varied by changes in the reduction temperatures. Ammonia gas (Iwatani Ind. Ltd.) was dried through a calcium oxide column and subsequently through a sodium hydroxide column before use. Propene was of research purity and further purified by triple distillation.

Table 1
Average particle sizes of Co and Ni metal precursors

Sample [a]	H_2 adsorption ($\mu mol\, g^{-1}$)	CO adsorption ($\mu mol\, g^{-1}$)	Size [b] (nm)
Co (a)		472	15 ± 0.3
Co (b)		159	21 ± 0.4
Co (d)		83	25 ± 0.3
Ni (a)	157	369	19 ± 0.5
Ni (b)	119	290	22 ± 0.4
Ni (c)	83	256	28 ± 0.5

[a] The Co and Ni fine-particle samples were reduced at (a) 453 K, (b) 573 K, (c) 673 K or (d) 723 K.
[b] The metal crystal sizes were deduced from the Scherrer equation.

2.2. PROCEDURES OF CATALYST PREPARATION AND CATALYTIC REACTIONS

In a typical preparation of lanthanide metal overlayers, the Co or Ni metal powder that had been reduced was placed in a Schlenk tube containing a solution of liquid ammonia (15–20 cm^3) at 198 K. Eu or Yb was added to the fine particles suspended in liquid ammonia with vigorous stirring. Upon dissolution of the lanthanide metal in liquid ammonia solvent, a deep blue homogeneous solution was immediately formed, which was characteristic of the solvated electrons [1]. The blue color gradually disappeared as a result of the reaction of the dissolved lanthanides with the Co or Ni metal. Upon disappearance of the blue color, the reaction tube was allowed to warm to room temperature and the excess of ammonia was pumped off leaving the Ln–Co and Ln–Ni overlayers. The content of lanthanides in the samples was represented by the fraction of the atomic %. All sample preparation steps were carried out in an atmosphere of dry nitrogen, otherwise the resulting overlayers became unreactive.

The catalytic reactions were performed in a recirculation reactor constructed of Pyrex glass. Prior to the reaction, the catalyst was subjected to evacuation treatment at 673 K for 2 h, set at the reaction temperature and then the hydrogenation of propene was initiated by admitting a mixture of H_2 and C_3H_6. The reacting gas in the reactor was periodically collected by a gas sampler and analyzed by a Shimazu TCD gas chromatograph to determine the gas composition. The activity was evaluated for the steady-state activity of the catalysts.

The X-ray diffraction (XRD) patterns of the samples were obtained with a Shimazu X-ray diffractometer (VG-107R) using Cu K_α radiation. The mean crystallite sizes of Co and Ni metal precursors were estimated by X-ray line broadening analysis using the (111) peak at 44.2° and at 44.5°, respectively.

3. Results and discussion

The hydrogenation was largely studied by admitting propene (10 Torr) and hydrogen (10 Torr) at 195–273 K. The catalytic behavior of the overlayer catalysts varied markedly with changes in the content of Eu or Yb in Ln–Co and Ln–Ni. The rates of hydrogenation were approximately represented by a first-order rate equation with respect to the hydrogen pressure irrespective of the changes of lanthanide content in the catalysts. The variation of the activity (k: first-order rate constant) as a function of lanthanide addition is shown in fig. 1. Pure Co or Ni alone was normally very active, whereas the lanthanide metal catalysts prepared by the metal vapor technique [7] showed negligible or very low activity under similar reaction conditions. Upon the addition of small amounts of lanthanide metals the hydrogenation activity somewhat decreased but it increased conversely in the region of higher lanthanide content. For Ln–Co and Ln–Ni the dependence of activity on varied levels of lanthanide content revealed a distinct minimum in the

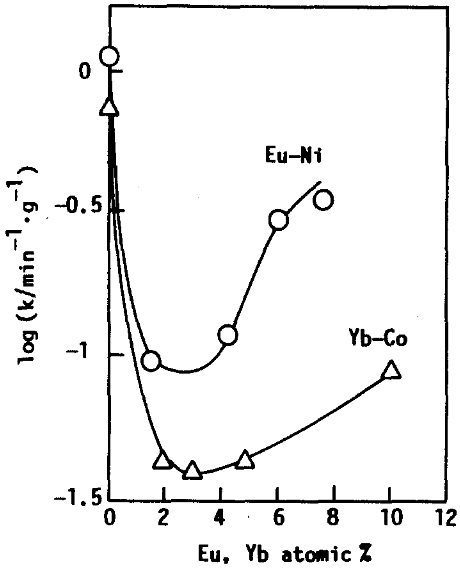

Fig. 1. Hydrogenation activity vs. lanthanide content in Yb–Co (△) and Eu–Ni (○). The catalysts were evacuated at 673 K for 2 h before the reaction. $P(C_3H_6)$ = 10 Torr, $P(H_2)$ = 10 Torr; 273 K for Yb–Co and 195 K for Eu–Ni.

region of 2–4 at% lanthanide. The composition dependence of the activity of Ln–Co and Ln–Ni was reproducible even when the cobalt and nickel catalyst precursors prepared separately were used [5,6]. The influence of lanthanide addition on the catalytic activity was very similar to that observed for the hydrogenation of ethene.

From the results of H_2 chemisorption [5,6], IR spectra of CO [8] and XPS measurements [5,6], deactivation of Ln–Co and Ln–Ni in the low-content region is deemed to be a consequence of lanthanide coverage on the catalytically active 3d-transition metal surface. For Eu–Co [6] and Eu–Ni [5] the Eu_{3d} : Co_{2p} (or Ni_{2p}) peak intensity ratios of XPS spectra increased proportionally with increasing content of Eu in the overlayers. In structure-sensitive reactions, such as alkane rearrangements, the continuous decrease in the rates of hydrogenolysis due to the lanthanide exclusively blocking Co or Ni surface atoms was observed [5,6]. In the higher-content region, it is deduced that some synergetic interactions between the lanthanide and 3d-transition metals appear. This results in a decrease in activation energies of the hydrogenation with simultaneous drastic changes in adsorption characteristics of hydrogen, leading to enhanced activity of Ln–Co [6] and Ln–Ni [5]. The similar synergetic effects have been observed for the isotopic exchange of H_2 and D_2 in which the catalytic activation of hydrogen is important in determining the activity [9].

In this connection the interaction of a lanthanide metal with single-crystal transition metal surfaces has been studied to obtain information about concentration- and structure-dependent surface properties of lanthanide compounds [10,11].

Controlled deposition of Nd, Sm or Yb onto Ni(100), Cu(100) or Cu(111) under UHV condition results in a considerable reaction with the Ni or Cu substrate to form a specific surface intermetallic compound with higher coverages, identified as LnCu and $LnCu_5$. In view of the results just described, at least two effects are in competition for an interpretation of such a variation of hydrogenation activity (fig. 1): the coating of catalytically active cobalt or nickel surfaces with lanthanide metals and enhanced activity arising from combined action of lanthanide and 3d-transition metals. For the hydrogenation, the former effect is pronounced in the low-content region (0–3 at%), while the latter rather than the former for the high-content becomes more prominent.

If the lanthanide exists uniformly in the metallic form on the cobalt and nickel surface, the content of 2–4 at% lanthanide which led to the minimum activity corresponds to roughly one monolayer coverage of the parent metal particles with Eu or Yb. The more activated Ln–Co and Ln–Ni overlayers are those in which the lanthanide exists on the cobalt and nickel surface above the amount equivalent to one monolayer. To provide information as to the factors responsible for the dependence of activity on the lanthanide coverage, the Co and Ni powder samples with different average particle sizes (15–28 nm) were used. Table 1 shows the metal particle sizes evaluated by powder X-ray diffraction for the Co and Ni fine-particle precursors, treated at different temperatures, as described in the experimental section. The average particle sizes increased as the reduction temperature increased, owing to metallic sintering. As shown in the results of the Ln–Ni system in fig. 2, the activities ($k/\text{min}^{-1}\ \text{g}^{-1}$) relative to a value for Ni alone increased with decreas-

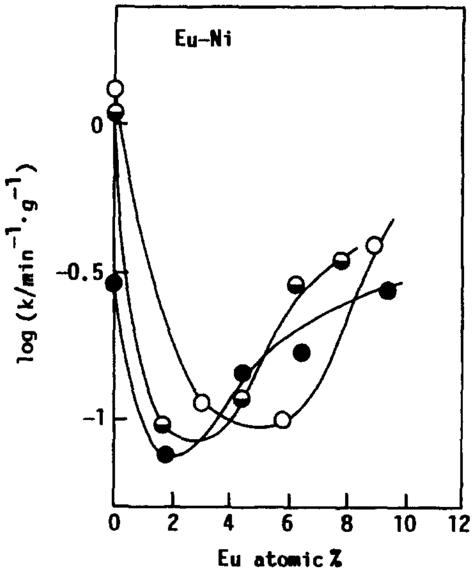

Fig. 2. Effects of particle sizes of Ni precursors on the hydrogenation activity of Eu–Ni. Ni precursor: (○) 19 nm, (◒) 22 nm and (●) 28 nm. The catalysts were evacuated at 673 K for 2 h before the reaction. 195 K; $P(C_3H_6)$ = 10 Torr, $P(H_2)$ = 10 Torr.

ing the average sizes of the parent Ni fine particles used and the level of lanthanide content corresponding to the minimum activity increased with a decrease in the average particle sizes. Eu–Ni with Ni particle size of 19 nm showed promoting effect by introduction of more than ca. 6 at% lanthanide, while for the samples with Ni of 28 nm even introduction above ca. 2 at% was sufficient. For the Ln–Co overlayers prepared with different particle sizes of Co (15, 21 and 25 nm), similar results were obtained (fig. 3). The content of the lanthanide causing the minimum activity also increased with decreasing the average sizes of the Co fine particles as a precursor. An interesting feature is that such a variation of activity as a function of lanthanide contents on the Co and Ni metal particles with different average sizes suggests occurrence of uniform coverages of the parent metal surface with Eu or Yb deposited from a homogeneous solution of lanthanides in liquid ammonia. Furthermore, this indicates that the synergy of the binary Ln–Co and Ln–Ni systems more markedly appears when the lanthanide coverage exceeds certain values. Nix et al. [10] have shown analogous results in the study of controlled deposition of lanthanides onto single-crystal 3d-substrates.

It is well known that the lanthanide metals combine with the 3d-transition metals to yield a large number of alloys and intermetallic compounds, many of which absorb hydrogen copiously [12]. $LaNi_5$ is considered the paradigm among these compounds. The remarkable synergy in the region of high lanthanide content may be involved in the formation of a certain surface-alloy layer in analogy with the cases of the deposition of lanthanide onto single-crystal 3d-substrates reported by Nix et al. [10] or Andersen et al. [11]. To make sure of this, the effect of H_2 pre-

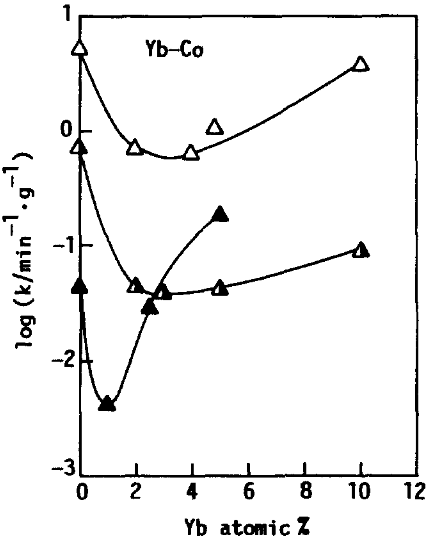

Fig. 3. Effects of particle sizes of Co precursors on the hydrogenation activity of Yb–Co. Co precursor: (△) 15 nm, (◭) 21 nm and (▲) 25 nm. The catalysts were evacuated at 673 K for 2 h before the reaction. 273 K; $P(C_3H_6)$ = 10 Torr, $P(H_2)$ = 10 Torr.

treatment was investigated. It has been shown that for the hydrogenation of ethene over hydrogen-absorbing intermetallics, such as $LnNi_5$ and $LnCo_5$ (Ln = La, Ce, Pr and Sm), the catalytic activity of the hydride is much higher than that in the dehydrided state and that the activity increases with an increase in the concentration of hydrogen in the hydride [13]. Eu–Co and Eu–Ni which had been evacuated at 673 K for 2 h were exposed to hydrogen (200 Torr) at 203 and 195 K for 1 h, respectively and then the reaction system was briefly evacuated to remove hydrogen in the gas phase at the same temperature, followed by admitting a mixed gas of propene (10 Torr) and hydrogen (10 Torr). As shown in table 2, such a pre-treatment with hydrogen resulted in an enhancement of activity (k') of Eu–Co and Eu–Ni. When 10.3% Eu–Co and 9.1% Eu–Ni after the H_2 pre-treatment was subjected to evacuating at 573 K for 1 h prior to the reaction, the activity (k'') nearly returned to the original value (k) obtained for the untreated catalysts. This fact leads to speculations of the formation of hydrogen-absorbing surface intermetallic phases as a result of interactions between the lanthanide and 3d-transition metal, which absorb hydrogen by the H_2 pre-treatment and subsequently the removal of the hydrogen taken up by the evacuation treatment at 573 K. However, the concentrations of hydrogen taken up by the Ln–Co and Ln–Ni surface overlayers were too small to measure. The effect of the H_2 pre-treatment on the activity was more pronounced for the Ln–Co systems than for the Ln–Ni systems (table 2). This is believed to be due to that Ln–Co has usually lower hydrogen-equilibrium pressures compared with Ln–Ni [14] and hence, under conditions of the same H_2 pre-treatment the concentration of hydrogen taken up by Ln–Co is probably higher than that for Ln–Ni.

Table 2
Effects of H_2 pre-treatment on hydrogenation activity of Eu–Co and Eu–Ni [a]

Catalyst	$k/\text{min}^{-1}\,\text{g}^{-1}$	H_2 treatment [b] $k'/\text{min}^{-1}\,\text{g}^{-1}$	k'/k	Evacuation [c] $k''/\text{min}^{-1}\,\text{g}^{-1}$
Co	0.021			
1.3% Eu–Co	0.011	0.45	41	
3.5% Eu–Co	0.0092	0.20	22	
6.5% Eu–Co	0.062	0.78	13	
10.3% Eu–Co	0.078	1.79	23	0.13
Ni	0.13			
3.1% Eu–Ni	0.12	0.25	2.1	
5.9% Eu–Ni	0.090	0.19	2.1	
9.1% Eu–Ni	0.39	3.64	9.3	0.35
12.2% Eu–Ni	0.69	2.65	3.8	

[a] See the text. Reaction temperature: 203 K for Eu–Co and 195 K for Eu–Ni.

[b] Eu–Co and Eu–Ni, previously evacuated at 673 K for 2 h, were exposed to hydrogen (200 Torr) for 1 h at 203 and at 195 K, respectively.

[c] After the H_2 pre-treatment the catalysts were evacuated at 573 K for 1 h.

Acknowledgement

This work was supported by the Asahi Glass Foundation and the Grant-in-Aid for Scientific Research on Priority Area "New Development of Rare Earth Complexes" No. 06241255 from the Ministry of Education, Science and Culture.

References

[1] J.C. Thompson, *Electrons in Liquid Ammonia* (Clarendon Press, Oxford, 1976).

[2] H. Imamura, M. Yoshinobu, T. Mihara, Y. Sakata and S. Tsuchiya, J. Mol. Catal. 69 (1991) 271.

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

[4] H. Imamura, S. Hiranaka, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Faraday Trans. 88 (1992) 1577.

[5] H. Imamura, K. Yoshimura, S. Hiranaka, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Faraday Trans. 87 (1991) 2805.

[6] H. Imamura, S. Hiranaka, M. Takamoto, Y. Sakata and S. Tsuchiya, J. Mol. Catal. 77 (1992) 333.

[7] H. Imamura, K. Kitajima and S. Tsuchiya, J. Chem. Soc. Faraday Trans. I 85 (1989) 1647;
H. Imamura, A. Ohmura and S. Tsuchiya, J. Catal. 96 (1985) 139.

[8] H. Imamura, H. Sugimoto, Y. Sakata and S. Tsuchiya, J. Catal. 136 (1992) 271.

[9] H. Imamura and K. Yoshimura, Z. Phys. Chem. 183 (1994) 407.

[10] R.M. Nix, R.W. Judd and R.M. Lambert, Surf. Sci. 203 (1988) 307.

[11] J.N. Andersen, J. Onsgaard, A. Nilsson, B. Eriksson, E. Zdansky and N. Martensson, Surf. Sci. 189/190 (1987) 399;
J.N. Andersen, J. Onsgaard, A. Nilsson, B. Eriksson and N. Martensson, Surf. Sci. 202 (1988) 183.

[12] A. Percheron-Guégan and J.-M. Welter, in: *Topics in Applied Physics*, Vol. 63, ed. L. Schlapbach (Springer, Berlin, 1988) p. 11;
K.H.J. Buschow, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, eds. K.A. Gschneidner Jr. and L. Eyring (North-Holland, Amsterdam, 1984) p. 1.

[13] K. Soga, H. Imamura and S. Ikeda, J. Phys. Chem. 81 (1977) 1762.; J. Catal. 56 (1979) 119.

[14] F.A. Kuijpers, Philips Res. Repts. Suppl. 2 (1973).