Catalytic transfer hydrogenation over bimetallic lanthanide (Eu or Yb)-containing catalysts using NH_3 as a hydrogen donor

Hayao Imamura,* Koji Fujita, Yukihisa Miura, Katsuhiko Mizuno, Yoshihisa Sakata and Susumu Tsuchiya

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

Catalytic transfer hydrogenation of ethene and buta-1,3-diene with the aid of ammonia as a hydrogen donor is greatly enhanced by lanthanide (Ln)-promoted catalysts (Ln–Ni/SiO_2, Ln–Ru/C, Ln–Cu/SiO_2 and Ln–Ag/ZrO_2), prepared by the reaction with Eu or Yb metal dissolved in liquid ammonia.

Catalytic transfer hydrogenation using hydrogen donors shows some interesting features which are of potential synthetic importance and use.[1–4] We now report that lanthanide (Ln)-promoted catalysts obtained by the reaction of Ni/SiO_2, Ru/C, Cu/SiO_2 or Ag/ZrO_2 with Eu or Yb metal solutions in liquid ammonia are active for catalytic hydrogen transfer from ammonia molecules to organic acceptors (ethene and buta-1,3-diene). Scarcely any studies have been reported on the remarkable promoting effects of lanthanides in bimetallic catalysts on the transfer hydrogenation in which ammonia is a preferred hydrogen donor. Recently there has been also a growing interest in the catalytic properties of lanthanides and their related compounds.

20 mass% Ni/SiO_2, 30 mass% Cu/SiO_2 and 20 mass% Ag/ZrO_2 were prepared by impregnating SiO_2 (or ZrO_2) with an aqueous metal nitrate solution. 5 mass% Ru/C was obtained from N. E. Chemcat Co. In a typical preparation of Ln-promoted Ni/SiO_2, 20 mass% Ni/SiO_2, which had previously been reduced with hydrogen, was placed in a Schlenk tube (50 cm^3) flushed thoroughly with dry nitrogen. Ammonia (Iwatani Ind. Ltd.), which had been dried through a calcium oxide column and subsequently through a sodium hydroxide column, was liquefied in the tube at 198 K. Eu or Yb metal (99.9%; Shin-Etsu Chemical Co. Ltd.) was added in varying amounts to Ni/SiO_2 suspended in liquid ammonia (*ca.* 15 cm^3) with stirring. The lanthanide metal immediately dissolved in liquid ammonia to yield an intense blue homogeneous solution containing solvated electrons,[5] which gradually faded as a result of reaction of Ni/SiO_2 with the lanthanide metal dissolved in liquid ammonia. The excess ammonia was then removed leaving Eu–Ni/SiO_2 and Yb–Ni/SiO_2. Other Ln-promoted catalysts were similarly prepared.

The catalytic transfer hydrogenation reactions were carried out in the gas phase using a Pyrex gas-recirculation reactor. After the catalysts were evacuated, a mixture of ethene (or buta-1,3-diene) and ammonia was introduced into the reactor to initiate the reaction. The results using various Ln-promoted catalysts are summarized in Table 1. Time courses of the reaction on Eu–Ni/SiO_2 (Eu/Ni = 0.72) are shown in Fig. 1, where the hydrogenation of ethene occurred effectively with ammonia as the source of hydrogen. As ammonia was consumed during the hydrogenation, nitrogen was stoichiometrically released and hydrogen was scarcely detected in the gas-phase. Thus, the present reaction followed the stoichiometrical relationship: $3C_2H_4 + 2NH_3 \rightarrow 3C_2H_6 + N_2$. Ni/$SiO_2$ alone showed some activity (shown by the dotted line in Fig. 1), while Eu (or Yb)/SiO_2† exhibited only negligible activity. The hydrogenation activity varied markedly with lanthanide content in Ln–Ni/SiO_2 (Fig. 2). Particularly at high levels of europium, Eu–Ni/SiO_2 was activated and its activity increased ⩾ 10-fold relative to Ni/SiO_2. Ln–Ru/C showed behaviour similar to Ln–Ni/SiO_2.

Substrate selectivity by catalysts was also observed for the transfer hydrogenation. Ln–Ni/SiO_2, Ln–Ru/C and Ln–Cu/SiO_2 showed activity for the hydrogenation of ethene and buta-

Table 1 Transfer hydrogenation from ammonia over Eu- and Yb-promoted catalysts[a]

Catalyst	Reactant	*T*/K	Activity/ mmol min^{-1} g^{-1}
20 mass% Ni/SiO_2	Ethene	403	2.0×10^{-4}
Eu–Ni/SiO_2 (Eu/Ni = 0.75)	Ethene	403	2.1×10^{-3}
Eu–Ni/SiO_2 (Eu/Ni = 0.61)	Buta-1,3-diene	403	1.2×10^{-3}
Yb–Ni/SiO_2 (Yb/Ni = 0.47)	Ethene	403	2.4×10^{-4}
5 mass% Ru/C	Ethene	453	1.4×10^{-4}
Eu–Ru/C (Eu/Ru = 4.0)	Ethene	453	6.4×10^{-4}
30 mass% Cu/SiO_2	Buta-1,3-diene	453	—[b]
Eu–Cu/SiO_2 (Eu/Cu = 0.67)	Buta-1,3-diene	453	3.8×10^{-3}
20 mass% Ag/ZrO_2	Buta-1,3-diene	453	—[b]
Eu–Ag/ZrO_2 (Eu/Ag = 0.67)	Buta-1,3-diene	453	1.2×10^{-4}
Yb–Ag/ZrO_2 (Yb/Ag = 0.67)	Buta-1,3-diene	453	1.5×10^{-5}
Eu–Ag/ZrO_2 (Eu/Ag = 1.5)	Ethene	453	—[b]

[a] The reaction was conducted by admitting reactant (21 Torr) and NH_3 (40 Torr). [b] The activity was zero within the detection limits.

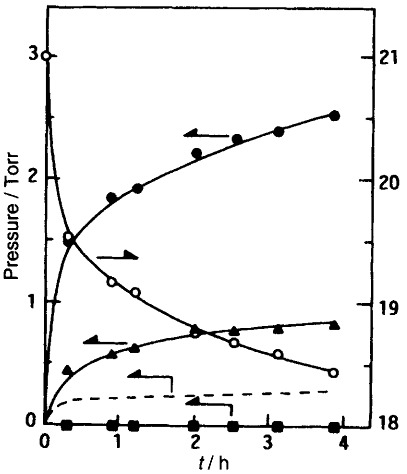

Fig. 1 Time courses of the transfer hydrogenation of ethene over Eu–Ni/SiO_2 (Eu/Ni = 0.72) at 403 K; (○) C_2H_4, (●) C_2H_6, (■) H_2, (▲) N_2. The dotted line represents the time course of C_2H_6 formation, carried out at 403 K using the unpromoted Ni catalyst for comparison. *Reaction conditions*: Eu–Ni/SiO_2 = 0.4 g, Ni/SiO_2 = 0.4 g, C_2H_4 = 21 Torr, NH_3 = 40 Torr.

1,3-diene, while Ln–Ag/ZrO_2 showed activity towards buta-1,3-diene but not for ethene. Cu/SiO_2 or Ag/ZrO_2 alone showed no activity for this type of hydrogenation. Upon addition of small amounts of lanthanides, the catalytic activity of Ln–Ag/ZrO_2 and Ln–Cu/SiO_2 was apparent and increased abruptly by > 2–3 orders of magnitude with increasing europium content. In most catalyst systems, the activity of Eu-containing catalysts was much higher than that of Yb-containing ones, the reason for which is presently unknown. Such enhanced activities in the transfer hydrogenation evidently reflect synergetic action between europium and the transition metals. We have shown that Ln–Co[6] and Ln–Ni[7] exhibit enhanced activities for normal hydrogenation with hydrogen. It has been reported that lanthanide (La, Ce or Sm)-promoted Ru/Al_2O_3 exhibits a higher activity for ammonia syntheses.[8]

The synergetic effect also exhibited selectivity for buta-1,3-diene hydrogenation. The Eu–Ni/SiO_2 (Eu/Ni = 0.61)-catalysed hydrogenation yielded preferential butene formation with high selectivity (*ca.* 100%). The yield of but-2-ene was relatively high compared with but-1-ene and the *trans* : *cis* ratio in the but-2-ene isomer was low (*ca.* 2). This was strikingly different from the results with Ni/SiO_2 or Ln/SiO_2 alone. Moreover, the product composition was observed to differ from normal hydrogenation using molecular hydrogen over Ln–Ni catalyst.[9]

For the transfer hydrogenation on Eu–Ni/SiO_2 (Fig. 1), hydrogen was scarcely detected in the gas phase throughout the reaction; therefore, the preferential addition processes of hydrogen to the acceptor molecules seem to occur immediately before coupling with subsequent liberation of hydrogen gas. It was found that in the absence of acceptors, ammonia remained unchanged at 403 K and that upon introduction of ethene into the reaction system, transfer hydrogenation from ammonia was initiated at similar reaction rates to the above systems. For Eu–Ni/SiO_2 and Yb–Ni/SiO_2, normal hydrogenation of ethene with molecular hydrogen readily occurred under similar conditions.[7] Therefore, it is likely that the participation of the donor in the hydrogen transfer step rather than the dehydrogenation of the donor and hydrogen addition to the acceptor is an important factor in determining the activity of the present transfer hydrogenation over the Eu–Ni/SiO_2 catalyst. Isotopic effects in Eu–Ni/SiO_2-catalysed reaction kinetics observed when ND_3–C_2H_4 or NH_3–C_2D_4 were used were r_H/r_D = 1.5 or 3.0, respectively, where r_H/r_D is the ratio for the reaction rate (r_H) using NH_3–C_2H_4 relative to ND_3–C_2H_4 or NH_3–C_2D_4. These results are consistent with the reaction mechanism described above in which transfer hydrogenation proceeds by concerted hydrogen transfer between ethene and ammonia over the catalysts. Further study is under way to understand characteristics about the transfer hydrogenation using ammonia over bimetallic lanthanide-containing catalysts.

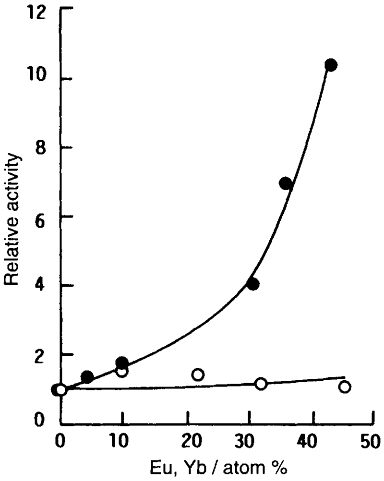

Fig. 2 Relative activities of the transfer hydrogenation (403 K) *vs.* lanthanide content in Ln–Ni/SiO_2; (●) Eu–Ni/SiO_2, (○) Yb–Ni/SiO_2. *Reaction conditions*: C_2H_4 = 21 Torr; NH_3 = 40 Torr.

The authors are grateful to The Ministry of Education, Science and Culture for financial support on Priority Areas 'New Development of Rare Earth Complexes' (No. 08220248).

Footnote

† Eu/SiO_2 and Yb/SiO_2 were prepared by the reaction of SiO_2 (1.0 g) with liquid ammonia solutions of Eu (0.45 g) or Yb (0.64 g), respectively.

References

1 R. A. W. Johnstone and A. H. Wilby, *Chem. Rev.*, 1985, **85**, 129.
2 H. Hartner, *Kontakte*, 1980, **1**, 3.
3 G. Brieger and T. J. Nestrick, *Chem. Rev.*, 1974, **74**, 567.
4 A. Furst, R. C. Berlo and S. Hooton, *Chem. Rev.*, 1965, **65**, 51.
5 J. C. Thompson, *Electrons in Liquid Ammonia*, Clarendon Press, Oxford, 1976.
6 H. Imamura, S. Hiranaka, M. Takamoto, Y. Sakata and S. Tsuchiya, *J. Mol. Catal.*, 1992, **77**, 333.
7 H. Imamura, K. Yoshimura, Y. Sakata and S. Tsuchiya, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2805.
8 S. Murata and K. Aika, *J. Catal.*, 1992, **136**, 118; S. Murata, K. Aika and T. Onishi, *Chem. Lett.*, 1990, 1067.
9 H. Imamura, M. Y. Yoshinobu and T. Mihara, in *Catalytic Science and Technology*, ed. S. Yoshida and T. Ono, Kodansha, Tokyo, 1991, vol. 1, p. 279.

Received, 20th May 1996; Com. 6/03469A