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Partial liquid-phase hydrogenation of benzene to cylohexene on SiO_2-immobilized lanthanide (Eu and Yb) catalysts

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SiO_2-immobilized Eu and Yb catalysts ($\equiv Si-O-Ln-NH_2$) obtained by the reaction of surface hydroxyl groups on SiO_2 with lanthanide metals dissolved in liquid ammonia are active for the partial liquid-phase hydrogenation of benzene to cyclohexene when the reaction was carried out at 423–483 K with hydrogen pressures of 1–5 MPa. Interestingly, only divalent amides are catalytically effective for the partial hydrogenation of benzene.

KEY WORDS: partial hydrogenation of benzene; cyclohexene; lanthanide catalysts; europium; ytterbium.

1. Introduction

The partial hydrogenation of benzene to cyclohexene is of great importance in the nylon industry. There have been a number of studies published of catalyst systems, and especially of heterogeneous catalysts, and much attention has been directed toward ruthenium-containing systems [1]. During the catalytic hydrogenation, there are difficulties in stopping at the partially hydrogenated intermediate, cyclohexene, and accordingly further search for catalysts with higher selectivity is desired.

We have devoted a great deal of attention to understanding the catalytic properties of lanthanide materials prepared by utilizing the dissolution of Eu or Yb metals in liquid ammonia [2]. It has been shown that lanthanide precipitates obtained by the decomposition of liquid ammonia solutions of lanthanide metals are active for the selective hydrogenation of benzene to cyclohexadiene and cyclohexene [3]. In this paper, SiO_2-immobilized lanthanide catalysts (Ln/SiO_2) obtained by the reaction of SiO_2 with Eu or Yb dissolved in liquid ammonia have been studied for the partial liquid-phase hydrogenation of benzene. We firmly believe that this provides an important clue to achieving the selective production of cyclohexene apart from the usual studies centering on ruthenium catalysts.

2. Experimental

In a typical preparation of Ln/SiO_2, silica (Degussa Aerosil 380) which had been previously evacuated at 773 K for 10 h was placed in a Schlenk tube, which was cooled by a dry ice/methanol bath and then ammonia gas was liquefied. Eu or Yb metal chips (99.9%; Santoku Co.) were added to a solution of liquid ammonia containing SiO_2 with vigorous stirring. The lanthanide metals readily dissolved in liquid ammonia to yield a blue homogeneous solution [4]. The blue color gradually faded as a result of the reaction of the dissolved lanthanides with SiO_2. After completion of the reaction, the vessel was allowed to warm to room temperature, and excess ammonia was removed, leaving Eu/SiO_2 and Yb/SiO_2.

For the liquid-phase hydrogenation we used a 50 cm^3 stainless steel reactor, in which Ln/SiO_2 and benzene were placed. The reaction was conducted at 423–483 K under H_2 pressures of 1–5 MPa with stirring.

All operations were carried out in an atmosphere of dry nitrogen; otherwise the catalysts were totally inactivated.

3. Results and discussion

For the liquid-phase hydrogenation, the activity of Eu/SiO_2 and Yb/SiO_2 appeared upon raising the reaction temperature over 423 K. Time courses of 12% Eu/SiO_2-catalyzed benzene hydrogenation at 483 K at a hydrogen pressure of 1 MPa are shown in figure 1. Very selective formation of cyclohexene occurred at the start of the reaction, but afterward its formation stopped. There was little change in the amounts of cyclohexene during later reaction. This is consistent with the results that the hydrogenation of cyclohexene was slow when carried out under the same conditions. On the other hand, the hydrogenation to cyclohexane simultaneously occurred, but slowly, followed by steady

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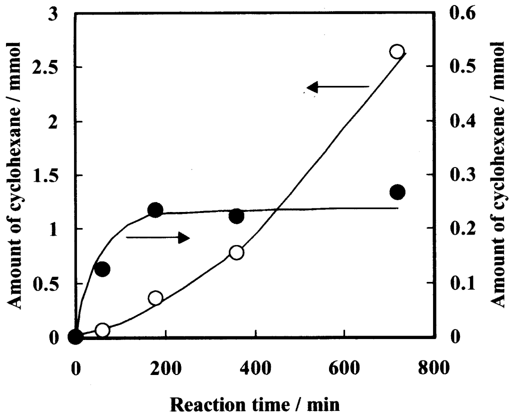

Figure 1. Time courses of the hydrogenation of benzene on 12% Eu/SiO$_2$ at 483 K. The reaction was conducted using 12% Eu/SiO$_2$ (0.1 g) with C_6H_6 (5 cm^3) and H_2 (1 MPa).

reaction. The conversion of benzene linearly increased with reaction times and the catalyst showed a steady activity during the reaction. The selectivity for cyclohexene decreased with an increase in conversion of benzene and reached a value of about 9% after 12 h. 15% Yb/SiO$_2$ exhibited catalytic behavior similar to 12% Eu/SiO$_2$. When the Eu/SiO$_2$ and Yb/SiO$_2$ catalysts were reused after the first run, similar activity and selectivity were reproduced.

An interesting feature of the hydrogenation of benzene using Ln/SiO$_2$ is that the cyclohexene intermediate formed on the catalyst through a series of successive hydrogen-adding processes is hydrogenated to cyclohexane, while the cyclohexene formed once in the liquid phase is hardly consumed to be subsequently hydrogenated during the reaction. The catalytic behavior observed here is derived from the fact that Ln/SiO$_2$ showed negligible reducing power for cyclohexene in the presence of benzene, due to preferential adsorption of benzene on the catalyst with blocking of cyclohexene adsorption.

When the amounts of benzene used varied from 2 to 10 cm^3 in Ln/SiO$_2$-catalyzed hydrogenation at 483 K, the hydrogenation rates (evaluated by the conversion of benzene after 6 h) were almost unchanged, but the selectivity towards cyclohexene increased markedly (table 1). Thus the total amounts of products were approximately constant regardless of the quantity of benzene, while the cyclohexene product increased about five times. An increase in benzene used relatively lowers the concentration of cyclohexene formed in the reaction system, leading to augmentation in amount of the cyclohexene product, as well as a decrease in rates of subsequent hydrogenation to cyclohexane. This is also confirmed by the following run: after the usual hydrogenation (C_6H_6: 5 cm^3; H_2: 1 MPa; 483 K; 3 h) using Ln/SiO$_2$, the reaction was resumed for another 3 h upon further addition of 5 cm^3 benzene. The addition of benzene in the middle of the reaction certainly resulted in an additional increase in cyclohexene product; thus its total amount was nearly equal to that obtained for the hydrogenation with benzene of 10 cm^3 (shown in table 1).

Table 1
Effect of the amounts of benzene on the hydrogenation [a]

Catalyst	Benzene (cm^3)	Conversion (%)	Selectivity [b] (%)
13% Eu/SiO$_2$	2	4.0	10
	5	1.2	30
	10	1.1	42
15% Yb/SiO$_2$	2	4.7	5
	5	1.5	16
	10	1.0	24

[a] The reaction was conducted on Ln/SiO$_2$ (0.1 g) at 483 K with C_6H_6 (2–10 cm^3) and H_2 (1 MPa) for 6 h.

[b] $C_6H_{10}/(C_6H_{10} + C_6H_{12}) \times 100$.

When the hydrogenation on 12% Eu/SiO$_2$ was carried out at 453 K with varying hydrogen pressures (1–5 MPa) under a fixed amount of benzene (5 cm^3), the hydrogenation rates of benzene showed approximately first-order dependence on the hydrogen pressures applied. However, the formation of cyclohexane was proportional to the pressure of hydrogen, while that of cyclohexene was independent. This is also understandable on the basis of the facts that Ln/SiO$_2$ had only low ability to hydrogenate cyclohexene to cyclohexane, and that the formation of cyclohexene was dependent on the concentration of cyclohexene in the reaction system as described previously. An increase in hydrogen pressures applied is considered to lead to the subsequent rapid hydrogenation of the adsorbed cyclohexene intermediate to cyclohexane rather than the formation of the cyclohexene. Consequently, the selectivity decreased from 45% to 14% with increasing H_2 pressures in the range of 1 to 5 MPa.

For the preparation of Ln/SiO$_2$, we have established from extensive Fourier-transform IR studies that when the silica is brought into contact with the solution of Eu or Yb metals dissolved in liquid ammonia, the hydroxyl groups present on the silica surface react preferentially with the dissolved lanthanide to form $\equiv$Si–O–Ln–NH$_2$ [5,6]. The loading of about 13 wt% Eu or 15 wt% Yb roughly corresponds to the total amounts of OH groups present on SiO$_2$ by assuming a lanthanide metal to a OH group ratio of 1 : 1 in the surface complex. This has been also confirmed by using polyvinyl alcohol with uniform and definite hydroxyl groups as a model compound [5]. Thus the lanthanides of Ln/SiO$_2$ are bound in the form of divalent amide to the surface hydroxyl groups on silica. In addition, it has been proved that such SiO$_2$-immobilized lanthanide amides exhibit specific catalysis for the selective hydrogenation, discriminating between conjugated and nonconjugated double bonds [5,7].

Table 2
Hydrogenation on various lanthanide catalysts[a]

Catalyst[b]	Conversion (%)	Selectivity[c] (%)
$Eu(NH_2)_2$	0.2	34
$Yb(NH_2)_2$	0.3	35
$Yb(NH_2)_3$	<0.004	
13% Eu/SiO_2	1.2	30
15% Yb/SiO_2	1.5	16

[a] The reaction was conducted at 483 K with C_6H_6 ($5\,cm^3$) and H_2 (1 MPa) for 6 h.

[b] $Ln/SiO_2 = 0.1$ g; $Ln(NH_2)_2$, $Ln(NH_2)_3 = 0.2$ g.

[c] $C_6H_{10}/(C_6H_{10} + C_6H_{12}) \times 100$.

Interestingly, only divalent amide species are effectively operative for the partial hydrogenation of benzene. It has been shown that the lanthanide metal dissolved in liquid ammonia is readily converted into amides [8]. Europium amide normally exists as diamide, $Eu(NH_2)_2$, while there are di- and triamide for ytterbium, $Yb(NH_2)_2$ and $Yb(NH_2)_3$, respectively. The catalytic properties of $Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$ prepared separately according to the method of Hadenfeldt *et al.* [9] were examined for comparison with those of 13% Eu/SiO_2 and 15% Yb/SiO_2 (table 2). $Yb(NH_2)_3$ was totally inactive, while $Eu(NH_2)_2$ and $Yb(NH_2)_2$ showed catalytic activity. However, their activity was much lower than that of Ln/SiO_2. This is probably due to the difference in degree of dispersion of lanthanide species. These results strongly indicate that the lanthanide diamide of $Eu(NH_2)_2$ and $Yb(NH_2)_2$ undoubtedly show some activity for the partial hydrogenation of benzene but that they are used more efficiently when supported on silica, especially in the form of $\equiv Si-O-Ln-NH_2$.

References

[1] H. Nagahara, M. Ono and Y. Fukuoka, Stud. Surf. Sci. Catal. 92 (1995) 375; F. Doebert and J. Gaube, Catal. Lett. 31 (1995) 431; J. Struijk, M. D'Angremond, W.J.M. Lucas-De Regt and J.J.F. Scholten, Appl. Catal. A 83 (1992) 263.

[2] H. Imamura, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 29, eds. K.A. Gschneidner Jr. and L. Eyring (North-Holland, Amsterdam, 2000), ch. 182.

[3] H. Imamura, K. Nishimura, K. Sumioki, M. Fujimoto and Y. Sakata, Chem. Lett. (2001) 450.

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

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

[6] H. Imamura, T. Konishi, Y. Tokunaga, Y. Sakata and S. Tsuchiya, Bull. Chem. Soc. Jpn. 65 (1992) 244.

[7] H. Imamura, T. Konishi, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Chem. Commun. (1991) 1527.

[8] K. Howell and L.L. Pytlewski, J. Less-Common Met. 19 (1969) 399; S. Salot and J.C. Warf, J. Am. Chem. Soc. 90 (1968) 1932.

[9] C. Hadenfeldt, H. Jacobs and R. Juza, Z. Anorg. Allg. Chem. 144 (1970) 379.