Improvement of selectivity for partial hydrogenation of benzene by rare earth nitride upon NH_3 treatment

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For the liquid-phase partial hydrogenation of benzene at 483 K, the selectivity toward cyclohexene was greatly improved upon treating rare earth nitride with ammonia. For YbN obtained by thermal decomposition of $Yb(NH_2)_2$ at 1173 K, the selectivity of the NH_3-treated YbN was 75%, in contrast to nil for the untreated YbN.

KEY WORDS: partial hydrogenation of benzene; cyclohexene; ytterbium nitride; ammonia; YbN.

1. Introduction

Recently there has been a growing interest in heterogeneous catalysis of rare earth elements and their related compounds [1]. By taking advantage of the solubility of Eu and Yb in liquid ammonia [2a,b], we have developed methods for preparing novel rare earth catalysts and have demonstrated that they exhibit unexpected activity and selectivity for various reactions [3]. The present investigation forms a part of studies on the rare earth catalysts, which are here employed for the partial hydrogenation of benzene [4–6].

Synthetically and industrially, particularly in nylon industry, it is of great importance to hydrogenate selectively benzene to cyclohexene. There have been extensive studies published of ruthenium catalyst systems [7a–g], and not for rare earths. The rare earth amides, $Yb(NH_2)_2$ and $Eu(NH_2)_2$, show the catalytic activity for cyclohexene formation when used for the liquid-phase hydrogenation of benzene at 483 K. However, $Yb(NH_2)_2$ and $Eu(NH_2)_2$ usually decompose to imides from the temperatures near 370 and 500 K, respectively [8,9a–c]; thus it seems quite certain that the thermally decomposed states rather than the amide essentially act as actual catalysts for the partial hydrogenation of benzene. In this paper, the catalytic properties of thermally decomposed products for $Yb(NH_2)_2$ and $Eu(NH_2)_2$ have been studied for the liquid-phase partial hydrogenation of benzene. We also report a novel way to improve the selectivity toward cyclohexene for the rare earth catalysts.

2. Experimental

Yb and Eu metals (99.9%) were obtained from Santoku Co. Ammonia gas (Iwatani Ind. Ltd.) was purified through a calcium oxide column and subsequently through a sodium hydroxide column. Benzene was of research purity and further purified twice by distillation in the presence of sodium wire.

$Yb(NH_2)_2$ and $Eu(NH_2)_2$ were prepared according to the method of Hadenfeldt *et al.* [10] using liquid ammonia. The thermal treatment of rare earth amides thus prepared was carried out by heating under vacuum for 1 h.

The treatment with ammonia was carried out at room temperature by introducing ammonia at varied pressures into a glass reactor with a fixed volume (164 cm^3). NH_3 uptake by the rare earth samples was determined by the drop in pressures in the reactor.

For the liquid-phase hydrogenation was used a 50 cm^3 stainless steel reactor, in which the rare earth catalyst (0.2 g) and benzene (5 cm^3) were placed. The reaction was conducted at 483 K under H_2 pressures of 3 MPa with stirring. All operations were carried out in an atmosphere of dry nitrogen, otherwise the catalysts were totally inactivated.

3. Results and discussion

In the liquid-phase hydrogenation of benzene, the catalytic properties of $Yb(NH_2)_2$ and $Eu(NH_2)_2$ strongly depended upon thermal pretreatment with evacuation. When $Yb(NH_2)_2$ was used for the hydrogenation reaction at 483 K, the conversion of benzene after reaction times of 3 h, as an index of activity, increased from 2% to 16% with increasing evacuation temperatures (673–1173 K) (figure 1). In particular, the evacuation around 750–800 K led to an abrupt increase in activity, and subsequently, the Yb catalysts showed a maximal conversion of 16% when evacuated at 1023–1173 K. On the other hand, the selectivity toward

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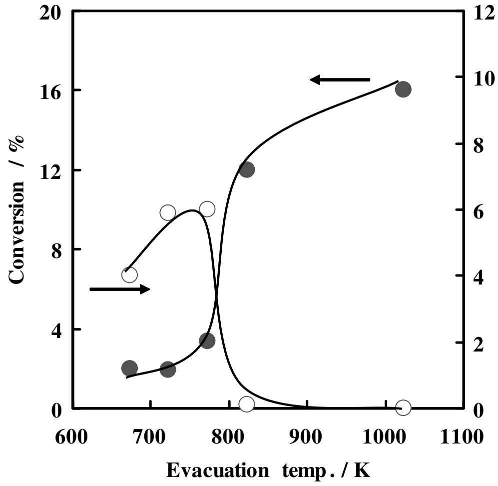

Figure 1. Variation of the conversion and selectivity with evacuation temperatures of $Yb(NH_2)_2$.

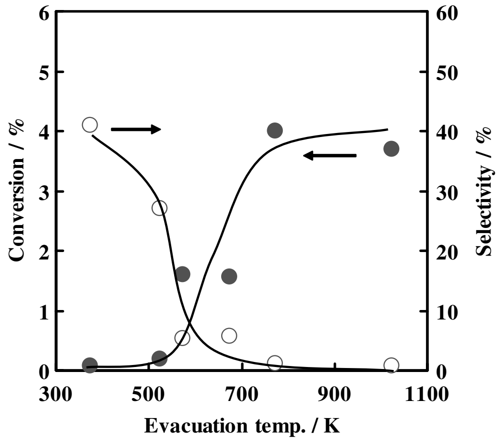

Figure 3. Variation of the conversion and selectivity with evacuation temperatures of $Eu(NH_2)_2$.

cyclohexene was as low as 5–6%, and upon raising the evacuation temperatures above 820 K it steeply dropped to almost 0%. It has been show that $Yb(NH_2)_2$ and $Eu(NH_2)_2$ release ammonia to decompose to the imides (YbNH and EuNH) above ca. 373 and 503 K, which are subsequently transformed into the nitrides above 773 and 573 K, respectively [8,9]. Rare earths introduced into Y-zeolite by impregnation from Yb or Eu metal solutions in liquid ammonia are also converted into the imides and nitrides on heating under vacuum [11]. Judging from XRD (figure 2) recorded with the thermal treatment of $Yb(NH_2)_2$, the hydrogenation activity of benzene reached a maximum when the ytterbium was transformed into the nitrides, YbN, with cubic structures. Since the catalytic activity of imides has proved to be very high for the usual hydrogenation [8,12], the gradual increase in conversion observed from temperatures around 750 K (shown in figure 1) is probably due to the transformation into YbNH.

As shown in figure 3, $Eu(NH_2)_2$ was similar in the dependence of catalytic properties on evacuation temperatures although the activity was lower than that of $Yb(NH_2)_2$. However, the dependence of activity for $Eu(NH_2)_2$ as a function of the evacuation temperatures was shifted about 200 K to lower temperature side compared with that of $Yb(NH_2)_2$. In this connection, similar results have been obtained when $Eu(NH_2)_2$ and $Yb(NH_2)_2$ are examined for the hydrogenation of ethane [8]. Thus, for the liquid-phase hydrogenation of benzene the rare earth nitrides obtained by thermal decomposition of the amides were excellent in catalytic activity, but the selectivity toward cyclohexene stands further improvement.

An interesting feature of rare earth catalysts is that the selectivity was greatly improved upon treating the nitrides with ammonia as shown in figure 4. When YbN

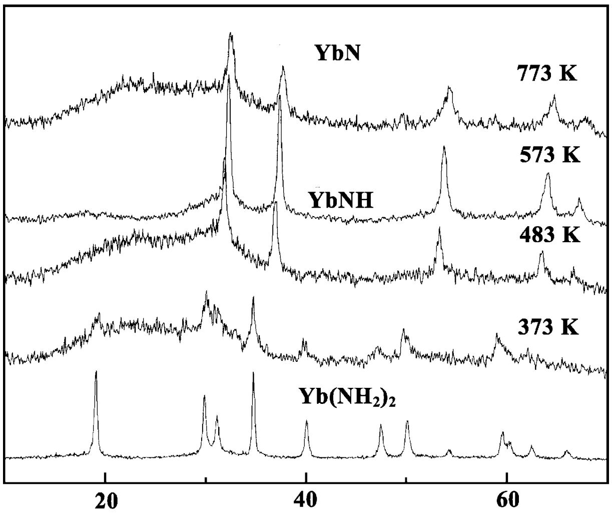

Figure 2. Changes in XRD with evacuation of $Yb(NH_2)_2$ at 373, 483, 573 and 773 K.

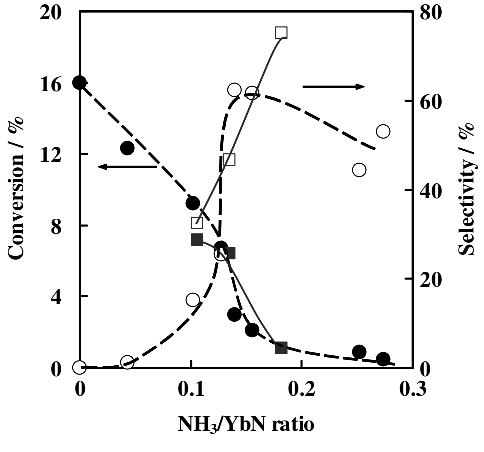

Figure 4. Dependence of the conversion (●, ■) and selectivity (○, □) on the NH_3/YbN ratios. Dotted line: YbN obtained by evacuation at 1023 K; solid line: YbN obtained by evacuation at 1173 K.

obtained by heating $Yb(NH_2)_2$ under vacuum at 1023 K was used as a sample, the selectivity increased with increasing the amounts of ammonia treated and passed through a maximum around $NH_3/YbN = 0.14$, in contrast to nil for the untreated YbN. The ammonia treatment was carried out at room temperature by bringing YbN into contact with ammonia gas at varied pressures. Upon contact with ammonia, YbN immediately took up ammonia, leading changes from dark brown to reddish brown. As shown in figure 4, the selectivity was greatly improved in the NH_3/YbN molar ratios exceeding 0.1, while the conversion of benzene was gradually lowered with an increase in NH_3 uptake by YbN. The NH_3-treated YbN in the ratio of ca. 0.14 showed the selectivity of 62% at the conversion of 3%. YbN was almost inactivated when excessively treated with ammonia.

When YbN previously evacuated at 1173 K was used instead, similar results for the ammonia treatment were obtained as shown in figure 4. A maximum selectivity of 75% was reached, and the yield of cyclohexene product was in excess of that for YbN evacuated at 1023 k. EuN obtained by decomposition of $Eu(NH_2)_2$ at 773 k similarly showed improvement of the selectivity upon NH_3 treatment, but the reaction results were inferior to those of YbN.

As to the ammonia taken up, there was no indication of desorption even if the NH_3-treated YbN was evacuated. Thus such NH_3 uptake by YbN seems to accompany some reactions with ammonia rather than pure adsorption, leading to the improvement of selectivity toward cyclohexene formation. XRD of the NH_3-treated YbN showed diffraction peaks shifted to lower angles. When the NH_3-treated sample was additionally heated under vacuum, the desorption of H_2 and N_2 was observed around 973 K and simultaneously the XRD pattern returned to the one identical with the untreated YbN. In view of the dependence of the conversion and selectivity on the NH_3 uptake (figure 4), at least two effects likely act on the catalytic behavior for the present hydrogenation of benzene; the coverage of catalytic active surfaces with ammonia and the enhanced selectivity for cyclohexene arising from the ammonia uptake. Indeed, it is true that the activity of YbN and EuN decreased with NH_3 uptake, but an important feature of the rare earth nitrides is that such high selectivity with some measure of hydrogenation activity is realized upon treatment with proper amount of ammonia. Further study is under way to understand how the ammonia works to improve the catalytic properties of the rare earth nitrides.

References

[1] The Role of Rare Earths in Catalysis, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol 29, eds. K.A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 2000).

[2] (a) W.J. Peer and J.J. Lagowski, J. Phys. Chem. 84 (1980) 1110; (b) J.C. Thompson, *Electrons in Liquid Ammonia*, (Clarendon Press, Oxford, 1976).

[3] 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.

[4] H. Imamura, T. Kumai, K. Nishimura, T. Nuruyu and Y. Sakata, Catal. Lett. 82 (2002) 69.

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

[6] H. Imamura, T. Konishi, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Chem. Commun. (1993) 1852; J. Chem. Soc. Faraday Trans. 88 (1992) 2251.

[7] (a) H. Nagahara, M. Ono, M. Konishi and Y. Fukuoka, Appl. Surf. Sci. 121/122 (1997) 448; (b) H. Nagahara, M. Ono and Y. Fukuoka, Stud. Surf. Sci. Catal. 92 (1995) 375; (c) F. Doebert and J. Gaube, Catal. Lett. 31 (1995) 431; (d) M. Soede, E.J.A.X. van de Sandt, M. Makkee and J.J.F. Scholten, Stud. Surf. Sci. Catal. 78 (1993) 345; (e) F. Mizukami, S. Niwa, S. Ohkawa and A. Katayama, Stud. Surf. Sci. Catal. 78 (1993) 337; (f) J. Struijk, M. D'Angremond, W.J.M. Lucas-De Regt and J.J.F. Scholten, Appl. Catal. A 83 (1992) 263; (g) Y. Fukuoka and H. Nagahara, Prepr. Am. Chem. Soc., Div. Pet. Chem. 36 (1991) 5481.

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

[9] (a) K. Howell and L.L. Pytlewski, J. Less-Common Met. 19 (1969), 399; (b) S. Salot and J.C. Warf, J. Am. Chem. Soc. 90 (1968) 1932; (c) R. Juza and C. Hadendeldt, Naturwissenschaften 55 (1968) 229.

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

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

[12] H. Imamura, K. Nishimura, T. Yoshimura, H. Yoshimochi, M. Ueno, Y. Sakata and S. Tsuchiya, J. Mol. Catal. A 165 (2001) 189.