

Selective Hydrogenation of Benzene to Cyclohexadiene and Cyclohexene by Lanthanide Precipitates Obtained from Eu or Yb Metal Solutions in Liquid Ammonia

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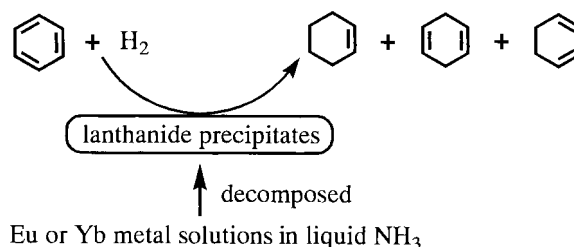
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Lanthanide precipitates obtained by decomposition of Eu or Yb metal solutions in liquid ammonia were active at 393 K for the partial liquid-phase hydrogenation of benzene to cyclohexene with high selectivity ($\geq 90\%$). When the reaction temperature decreased to 323 K, cyclohexadienes were preferentially formed. The reducing behavior was markedly enhanced by the addition of ammonia to the reaction system.

Synthetically and industrially it is of great interest to partially hydrogenate benzene. With benzene rings it is usually difficult to stop the reaction after only one or two bonds have been reduced, since olefins are more easily reduced than aromatic rings. A number of reagents and catalysts have been reported for the partial hydrogenation of benzene.¹⁻³ However, scarcely any studies have been reported with the hydrogenation of benzene using lanthanides. Recently we have developed methods for the preparation of new catalytic materials containing lanthanides and have demonstrated that they exhibit specific catalytic behavior.⁴ In this paper, we report unexpected and interesting properties of lanthanide precipitates obtained upon decomposition of liquid ammonia solutions of Eu or Yb metal for the partial liquid-phase hydrogenation of benzene to cyclohexadiene and cyclohexene.

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. In a typical preparation of lanthanide precipitates, in a 30-cm³ stainless steel reactor were placed measured amounts of Eu or Yb metals (0.5 g;

99.9%; Santoku Co.) under an atmosphere of dry nitrogen. The reactor was briefly evacuated, cooled by a dry ice/methanol bath, and then, about 1350 cm³ of purified ammonia gas was liquefied. The Eu and Yb metal readily dissolve in liquid ammonia to yield a blue homogeneous solution containing the divalent metal cations and ammoniated electrons.⁵ On standing at 273 K for 1 or 12 h, the solutions of Eu and Yb decomposed with the formation of a precipitate. Ammonia was subsequently removed from the reactor leaving powdery lanthanide precipitates.



Following the preparation of the lanthanide precipitates in the stainless steel reactor, benzene (2 cm³; 22.5 mmol) was immediately placed in this reactor, subsequently hydrogen was introduced. The liquid-phase hydrogenation was usually carried out for 3 h under a hydrogen pressure of 3 MPa. The lanthanide precipitates thus obtained were active at 393 K for the partial hydrogenation of benzene to cyclohexene, simultaneously yielding trace amounts of cyclohexadiene (Table 1). The selectivity toward cyclohexene was more than ca. 90%; the lanthanides were more selective than reported previously.^{6,7} When the reaction tempera-

Table 1. Liquid-phase hydrogenation of benzene using lanthanide precipitates^a

No.	Lanthanide precipitate ^b	Reaction temp./K	Reaction time/h	Conversion %	Products ^c
1	Yb (1 h)	393	3	8.5	C ₆ H ₈ (2), C ₆ H ₁₀ (95), C ₆ H ₁₂ (3)
2	Yb (12 h)	393	6	4.5	C ₆ H ₁₀ (89), C ₆ H ₁₂ (11)
3	Yb ^d (1 h)	393	3	0.2	C ₆ H ₁₀ (91), C ₆ H ₁₂ (9)
4	Eu (1 h)	393	3	1.7	C ₆ H ₁₀ (96), C ₆ H ₁₂ (4)
5	Eu (12 h)	393	3	0.8	C ₆ H ₁₀ (92), C ₆ H ₁₂ (8)
6	Eu ^d (1 h)	393	3	trace	
7	Yb (1 h)	323	3	13.6	C ₆ H ₈ (67), C ₆ H ₁₀ (33), C ₆ H ₁₂ (<1)
8	Yb ^d (1 h)	323	3	<0.1	
9	Eu (1 h)	323	3	1.8	C ₆ H ₈ (38), C ₆ H ₁₀ (62), C ₆ H ₁₂ (<1)

^aThe reaction between benzene (2 cm³) and hydrogen (3 MPa) was carried out. ^bThe time in the parentheses indicates the reaction time of Eu or Yb (0.5 g) and NH₃ (1350 cm³) at 273 K for the preparation of precipitates. ^cThe parentheses indicates the selectivity (%) of products. ^dThe precipitates after the preparation were kept in an atmosphere of dry N₂ for some time, subsequently being subjected to the reaction.

Table 2. Effects of NH₃ addition on the hydrogenation of benzene^a

No.	Lanthanide precipitate ^b	H ₂ MPa	NH ₃ gas cm ³	Reaction temp./K	Conversion %	Products ^c
10	Yb	3	1000	393	16.6	C ₆ H ₈ (14), C ₆ H ₁₀ (85), C ₆ H ₁₂ (1)
11	Yb ^d	4	500	393	2.7	C ₆ H ₈ (35), C ₆ H ₁₀ (64), C ₆ H ₁₂ (1)
12	Eu	3	1000	393	4.0	C ₆ H ₁₀ (97), C ₆ H ₁₂ (3)
13	Eu ^d	3	1000	393	<0.1	C ₆ H ₈ (17), C ₆ H ₁₀ (83)
14	Yb	0	1500	323	8.1	C ₆ H ₈ (79), C ₆ H ₁₀ (21), C ₆ H ₁₂ (<1)
15	Yb	3	1500	323	13.3	C ₆ H ₈ (79), C ₆ H ₁₀ (21), C ₆ H ₁₂ (<1)
16	Eu ^d	3	1500	323	0.2	C ₆ H ₈ (47), C ₆ H ₁₀ (53), C ₆ H ₁₂ (<1)

^aThe hydrogenation of benzene (2 cm³) was carried out in the presence of ammonia. ^bThe lanthanide precipitates were obtained by the reaction of Eu (0.5 g) or Yb (0.5 g) with NH₃ (1350 cm³) at 273 K for 1 h. ^cThe parentheses indicates the selectivity (%) of products. ^dSee the footnote in Table 1.

tures decreased to 323 K, the formation of cyclohexadiene rather than cyclohexene were predominant. Cyclohexadiene was formed with a 1,4-/1,3-isomer ratio of 1–4, depending on the reaction conditions applied. Cyclohexane was scarcely formed at 323 K.

The reaction times were prolonged, but the benzene conversion was not so raised. This is partly due to that the precipitates changed in quality during the reaction and that the hydrogenation consists of processes proceeding stoichiometrically and catalytically. The europium and ytterbium exhibited similar reducing properties, but the ytterbium was superior to the europium in activity.

The reducing behavior of the lanthanide precipitates markedly depended upon the conditions separating out from the Eu or Yb metal solutions in liquid ammonia during the preparation process. It has been reported that the liquid ammonia solutions of lanthanide metals decompose through metal, amide or imide to finally convert into nitride.⁸ To obtain information as to the structural changes of precipitates, XRD powder patterns were measured without exposure to air. XRD of precipitates obtained when the Yb metal in liquid ammonia was permitted to stand for 1 h, showed the existence of metallic Yb with additional diffraction peaks at $2\theta = 29.8, 34.5, 49.7$ and 59.0° , while on standing for 12 h, the Yb precipitates (No. 2) consisted primarily of diamide and triamide. The crystallite sizes for the Yb metallic phase were estimated as ca. 12–15 nm from XRD.

The lanthanide precipitates acted more effectively in the presence of ammonia, although the mechanism of its action in the reducing process was not appreciably proved yet. As shown in Table 2, the benzene conversion and the selectivity were enhanced in the presence of ammonia. Upon addition of ammonia gas of 1000 cm³ to the reaction system, the benzene conversion increased by a factor of about 2 (Nos. 1 and 10).

Moreover, the reaction results of the lanthanide precipitates as prepared and otherwise were quite different (Tables 1 and 2). The precipitates (Nos. 1, 4, 7 and 12) were used more efficiently when subjected to the reaction immediately after the preparation, in contrast to the precipitates (Nos. 3, 6, 8 and 13) kept once in an atmosphere of dry nitrogen after preparation, respectively. The "stale" lanthanides (Nos. 3, 6 and 8) exhibited very low activity for the hydrogenation of benzene with hydrogen. A very important characteristic of such precipitates is that upon addition of ammonia the reducing power was restored to some extent. Even

if hydrogen was not used, benzene was reduced with ammonia (No. 14); the transfer hydrogenation of benzene with ammonia occurred. It has been shown that the lanthanides promote the catalytic transfer hydrogenation with ammonia as a hydrogen source.⁹ That the ammonia directly participates in the hydrogenation is likely responsible for the selective formation of cyclohexene or cyclohexadiene. For the hydrogenation of benzene using both hydrogen and ammonia, the conversion of benzene was naturally higher than that for the hydrogenation with ammonia.

The hydrogenation of benzene to cyclohexadiene is known as the Birch reaction: when benzene is reduced by sodium in liquid ammonia, usually in the presence of alcohol, 1,4-addition of hydrogen takes place to yield cyclohexadiene.¹⁰ The reduction is known as homogeneously dissolving metal reductions in which direct electron transfer from the Na metal to the benzene ring with subsequent protonation by alcohol is involved. Unlike the Birch reduction, the present system was heterogeneous, and besides, no alcohol was added to the reaction system. As described above, the addition of ammonia to the reaction system led to the increased conversion of benzene, in which ammonia acted as a promoter, as well as a hydrogen donor. Thus, it is understandable on the basis of the comparison of Nos. 14 and 15 that the ammonia promotes the lanthanide precipitates, resulting in an increase in the benzene conversion for the hydrogenation by hydrogen.

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