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PRIORITY COMMUNICATION

Synthesis of 1,4-Diaminocyclohexane in Supercritical Ammonia

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The amination of 1,4-cyclohexanediol in supercritical ammonia has been studied in a continuous fixed-bed reactor at 135 bar. An unsupported cobalt catalyst stabilized by 5 wt% Fe afforded the main reaction products 4-aminocyclohexanol and 1,4-diaminocyclohexane with a cumulative selectivity of 97% at 76% conversion. Excess of ammonia and short contact time favored the desired reactions. At low and high conversions the amination selectivity decreased due to the formation of dimers and oligomers and degradation products. Recycling of the unreacted diol and amino alcohol intermediate can provide an alternative economic process for the synthesis of 1,4-diaminocyclohexane. © 1999 Academic Press

Key Words: **amination; cobalt–iron; 1,4-cyclohexanediol; 1,4-diaminocyclohexane; supercritical ammonia.**

INTRODUCTION

Amination of aliphatic alcohols on a metal catalyst provides economic access to a multitude of amines (1–4). However, the yields and selectivities are usually rather low in the synthesis of aliphatic diamines from the corresponding diols and ammonia.

The metal-catalyzed synthesis of aliphatic amines from the corresponding alcohol includes dehydrogenation of the alcohol to a carbonyl compound, condensation with ammonia to form an imine or enamine, and hydrogenation to the amine (5, 6). Each intermediate and the product amine can take part in condensation, decarbonylation, disproportionation, and hydrogenolysis side reactions (7–10). The synthesis of a diamine from the corresponding diol requires the repetition of all three steps which increases the by-product formation. In addition, the bifunctional intermediates have the tendency to undergo oligomerization reactions (6, 11, 12). A further difficulty is that the intermediate and product amines are significantly more reactive than ammonia. Application of supercritical fluids provides interesting opportunities for improving the efficiency (conversion, selectivity, catalyst lifetime, and separation) of heterogeneous catalytic processes. Advances made in this field have been discussed in a recent review (13).

In a previous study we found that the application of supercritical ammonia (scNH_3) as a solvent and reactant affords remarkable selectivity improvement in the amination of 1,3-propanediol, compared with the subcritical pressure procedure (14). The selectivity improvement could be traced to the suppression of hydrogenolysis (degradation)-type side reactions. In the present study we describe the amination of 1,4-cyclohexanediol (Scheme 1) under supercritical conditions, using an iron-stabilized cobalt catalyst in a continuous high-pressure reactor.

At present, diaminocyclohexanes are manufactured by the catalytic hydrogenation of aromatic amines such as *p*-phenylenediamine (15, 16). Considering the availability, oxidation stability, and toxicology of the reactant, the amination of cyclohexanediol is an attractive alternative. 1,4-Diaminocyclohexane is an important chemical applied as chain extender in polyurea elastomers (17), ingredient in lubricants (18), agent in the synthesis of ZSM-35 (19), and component of antitumor agent platinum complexes (20). To our knowledge direct amination starting from 1,4-cyclohexanediol has not been reported so far.

EXPERIMENTAL

For the preparation of the 95 wt% Co–5 wt% Fe catalyst, the metal nitrates (molar ratio of 20/1; total metal nitrates: 0.18 mol) were dissolved in 500 ml water. One hundred grams of an aqueous solution containing 20 wt% $(NH_4)_2CO_3$ was added at room temperature over a 1-h period until a pH of 7 was reached. The suspension was stirred for 2 h and filtered. After careful washing, the precipitate was dried at 100°C, calcined at 400°C for 2 h, and activated by hydrogen reduction at 335°C for 4 h. Structural properties of the reduced catalyst were BET surface area of 12 $m^2\ g^{-1}$, specific pore volume of 0.1 $cm^3\ g^{-1}$, and mean pore diameter of 43 nm. A detailed characterization of the catalyst will be presented elsewhere (21).

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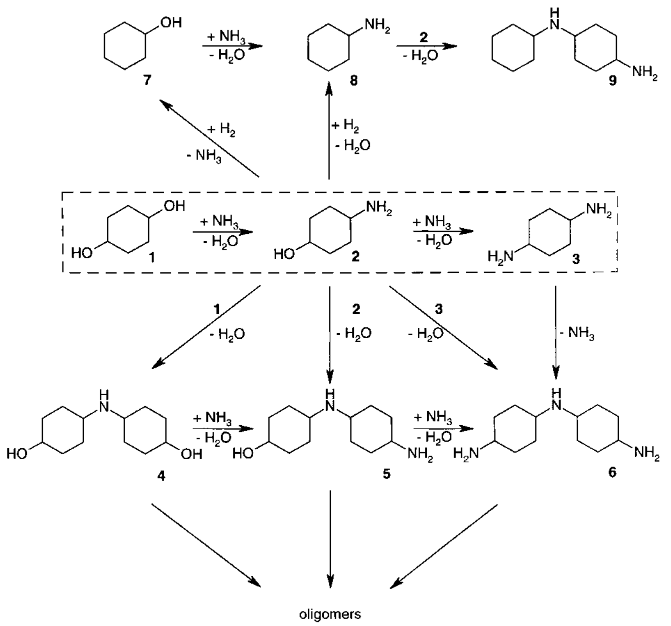

SCHEME 1. Important reactions occurring during the amination of 1,4-cyclohexanediol with ammonia. The intermediates and products shown were identified by GC–MS.

The apparatus comprised the dosing system for the ammonia–alcohol mixture (ISCO D500 syringe pump) and hydrogen (mass flow meter), the high-pressure continuous fixed-bed reactor, and a gas/liquid separator. The reactor was constructed of Inconel-718 tubing of 13-mm inner diameter and 38-ml volume. The temperature in the reaction zone was measured with a thermocouple located in the center of the tube and was regulated by a PID cascade controller. The total pressure in the reactor system was set by a Tescom backpressure regulator. Standard reaction conditions were 8.0 g catalyst, 165°C, 135 bar, 40,000 gs mol^{-1} contact time (WHSV: 1.63 g g^{-1} h^{-1}), and molar ratio of the reactants R-OH/NH_3/H_2 = 1/60/2.

The liquid products were analyzed using a gas chromatograph (HP-5890A with FID detector and HP-1701 column) and were identified by GC–MS analysis.

The following reactant purities were quoted by the manufacturer: 1,4-cyclohexanediol > 98% (Fluka), ammonia 99.98% (Pan-Gas), hydrogen 99.999% (Pan-Gas), and nitrogen 99.995% (Pan-Gas).

The existence of a single fluid phase under the experimental conditions used (130 bar, 200°C) has been corroborated by independent visual tests with two diols in similarly diluted mixtures (1.5 mol% diol). The critical data for ammonia are $T_C = 132.4°C$ and $P_c = 114.8$ bar (22).

RESULTS AND DISCUSSION

As stated in the Introduction, the activity of ammonia is usually lower than that of the intermediate and product amines. To compensate this reactivity difference, a relatively large NH_3/R-OH molar ratio is necessary to obtain acceptable selectivities to primary amines. Accordingly, all reactions were carried out at 165°C and 135 bar with a molar ratio NH_3/R-OH = 60/1. A small amount of hydrogen in the feed (1–5 mol%) was sufficient to prevent the undesired dehydrogenation reactions and the formation of nitriles and carbonaceous deposits.

Figure 1 illustrates the influence of temperature on the amination of 1,4-cyclohexanediol (**1**) in supercritical ammonia over a 95% Co–5% Fe catalyst. The conversion indicates the consumption of **1** via dehydrogenation to 4-hydroxycyclohexanone or acid–base catalyzed side reactions. This metal-catalyzed step has been found to be rate determining in the amination of simple aliphatic alcohols (23).

The formation of the amination products 4-aminocyclohexanol (**2**, Scheme 1) and 1,4-diaminocyclohexane (**3**) shows the typical course of a consecutive reaction series. A maximum yield of 32% for the amino alcohol (**2**) was achieved at 165°C, and a maximum yield of 54% for the diamine (**3**) at 185°C.

The selectivity to the diamine (**3**) could be further improved by varying the contact time. Some examples are shown in Table 1. The two sets of experiments at 165 and 195°C depict the same tendency: at higher contact times the by-products formed by hydrogenolysis dehydration and dimerization/oligomerization became dominant. At 165°C the catalyst was rather selective and the amount of by-products did not exceed 3% up to 40,000 gs mol^{-1}. Contrary to the expectation, there was only a small change in

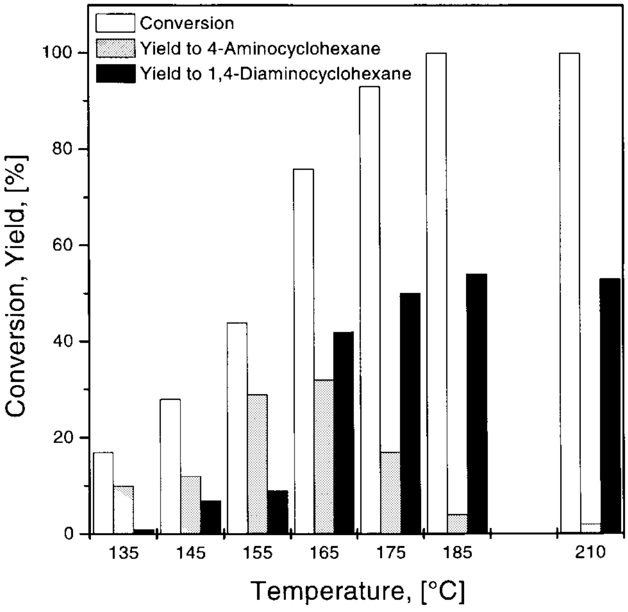

FIG. 1. Influence of conversion on the amination of 1,4-cyclohexanediol over a 95% Co–5% Fe catalyst; standard conditions.

TABLE 1

Influence of the Contact Time on the Amination of 1,4-Cyclohexanediol (1, in Scheme 1) over a 95% Co–5% Fe Catalyst under Otherwise Standard Conditions

Contact time [gs mol^{-1}]	Temperature (°C)	Conversion (%)	Yield (%)		
			2	**3**	By-products
30,000	165	70	21	46	3
40,000	165	76	32	42	2
60,000	165	93	9	29	55
20,000	195	99	6	67	26
30,000	195	100	3	55	42
40,000	195	100	3	54	43
60,000	195	100	1	52	47

the diamine yield at 195°C, despite of the complete conversion of diol. The amount of by-products barely changed when doubling the contact time from 30,000 to 60,000 gs mol^{-1}. Beside dimers and oligomers, degradation products such as **7** and **8** (Scheme 1) could be identified in the product mixture. Figure 2 illustrates the cumulative selectivity to the amino alcohol (**2**) and diamine (**3**) as a function of conversion, on the basis of the data in Fig. 1. The amination selectivity has an optimum of 97% at 76% diol conversion. The lower selectivity at low and high conversion is due to the formation of dimers (**4**–**6**), oligomers, and degradation products. At low conversion the dimer (**5**) was the main by-product. At high conversion (and longer contact times) **2** and **3** were transformed to dimers (mainly **6**) and insoluble oligomers, and the generation of degradation products, e.g., aminocyclohexane (**8**), was also favored. The degradation products were partly further aminated (with ammonia or some amines).

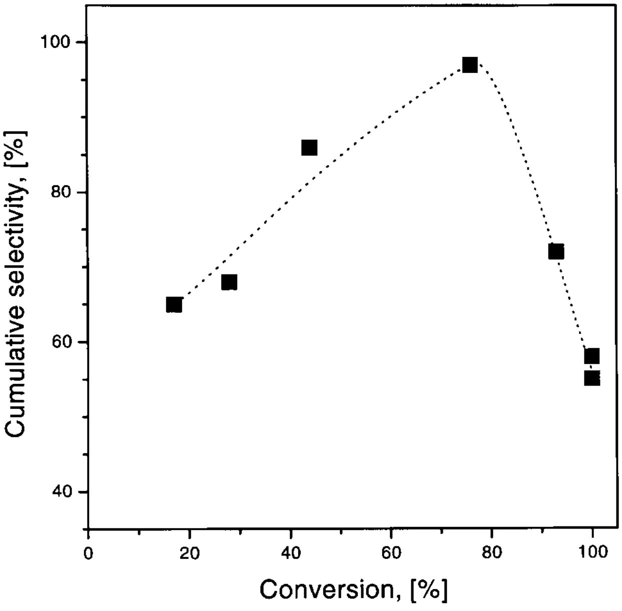

FIG. 2. Influence of temperature on the cumulative selectivity to 4-aminocyclohexanol (**2**) and 1,4-diaminocyclohexane (**3**) over a 95% Co–5% Fe catalyst; standard conditions.

CONCLUSIONS

An alternative catalytic route for the synthesis of 1,4-diaminocyclohexane has been shown that is based on the amination of 1,4-cyclohexanediol over a Co–Fe catalyst in scNH$_3$. The amination affords 67% yield at almost complete conversion. The efficiency of the reaction can be further improved by recycling the unreacted diol and amino alcohol intermediate, reducing the amount of by-products to ca. 3%. The high chemical efficiency combined with the engineering advantages of continuous operation and easy separation from the supercritical solvent and reactant ammonia provides a good basis for industrial application of the process.

ACKNOWLEDGMENT

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REFERENCES

1. Roundhill, D. M., *Chem. Rev.* **92**, 1 (1992).
2. Turcotte, M. G., and Johnson, T. A., *in* "Kirk–Othmer Encyclopedia of Chemical Technology" (F. M. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Eds.), Vol. 2, p. 369. Wiley, New York, 1992.
3. Mallat, T., and Baiker, A., *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 5, p. 2334. VCH, Weinheim, 1997.
4. Fischer, A., Mallat, T., and Baiker, A., *Catal. Today* **37**, 167 (1997).
5. Vultier, R. E., Baiker, A., and Wokaun, A., *Appl. Catal.* **30**, 167 (1987).
6. Kijenski, J., Niedzielski, P. J., and Baiker, A., *Appl. Catal.* **53**, 107 (1989).
7. Baiker, A., *in* "Catalysis of Organic Reactions" (J. R. Kosak and T. A. Johnson, Eds.), Vol. 53, p. 91. Dekker, New York, 1994.
8. Baiker, A., and Kijenski, J., *Catal. Rev. Sci. Eng.* **27**, 653 (1985).
9. Kijenski, J., Burger, J., and Baiker, A., *Appl. Catal.* **11**, 295 (1984).
10. Card, R. J., and Schmitt, J. L., *J. Org. Chem.* **46**, 754 (1981).
11. Sirokmán, G., Molnár, Á., and Bartók, M., *J. Mol. Catal.* **19**, 35 (1983).
12. Molnár, Á., Sirokmán, G., and Bartók, M., *J. Mol. Catal.* **19**, 25 (1983).
13. Baiker, A., *Chem. Rev.* **99**, 453 (1999).
14. Fischer, A., Mallat, T., and Baiker, A., *Angew. Chem. Int. Ed.* **38**, 351 (1999).
15. Brake, L., U.S. Patent 3,636,108 (1977).
16. Rutter, H., Ruhl, T., Breitscheidel, B., Henkelmann, J., Henne, A., and Wettling, T., U.S. Patent 5,773,657 (1998).
17. Primeaux, I., and Dudley, J., U.S. Patent 5,162,388 (1992).
18. Cheng, V. M., Farng, L. O., Horodysky, A. G., and Poole, R. J., U.S. Patent 5,407,592 (1995).
19. Hellring, S. D., Chang, C. D., and Lutner, J. D., U.S. Patent 5,190,736 (1993).
20. Khokhar, A., and Siddik, Z. H., U.S. Patent 5,393,909 (1995).
21. Fischer, A., Maciejewski, M., Bürgi, T., Mallat, T., and Baiker, A., submitted for publication.
22. Allamagny, P. (Ed.), "Encyclopedie de Gaz," p. 951. L'Air Liquide, Elsevier, Amsterdam, 1976.
23. Bassili, V., and Baiker, A., *Appl. Catal.* **70**, 325 (1991).