JOURNAL OF CATALYSIS **161,** 373–376 (1996)
ARTICLE NO. 0194

Ammoximation of Cyclohexanone by Nitric Oxide and Ammonia: A One-Step Process for Synthesis of Polycaprolactam

R. Prasad and Seema Vashisht

Institute of Chemical Sciences, University of Indore, Khandwa Road, Vighyan Bhawan, Indore 452001, India

Received July 11, 1995; revised January 24, 1996; accepted February 19, 1996

Catalytic transformation of cyclohexanone by nitric oxide and ammonia to cyclohexanone oxime, its rearrangement to caprolactam, and its polymerization to polycaprolactam has been studied in the liquid phase over solid catalysts. The influence of various catalysts and process parameters on the oximation reaction is reported. A maximum yield of 37.78% with a selectivity of 80.95% for caprolactam could be achieved, over a synthetically prepared Al_2O_3–SiO_2 catalyst, at a cyclohexanone : NO : NH_3 molar ratio of 1 : 2.9 : 1.7 and a temperature of 348 K. In this process the production of oxime and its rearrangement to caprolactam occur simultaneously. The resulting caprolactam polymerises later to give a molecular weight ranging from 500 to 5000. A tentative mechanism for the reactions is suggested. © 1996 Academic Press, Inc.

INTRODUCTION

Catalytic transformation of ketones to oximes by ammonia and an oxidizing agent such as hydrogen peroxide, oxygen, air, or nitric oxide over a solid catalyst is termed ammoximation. The process is similar to that of ammoxidation (1) and nitroxidation (2). In ammoxidation an alkyl organic compound and ammonia are simultaneously oxidized by air over a solid catalyst while in nitroxidation the alkyl aromatic is oxidized by nitric oxide. The end products in both the cases are nitriles. Ammoximation of cyclohexanone (3–11) gives rise to cyclohexanone oxime which can be easily converted to caprolactam. Caprolactam is the basic raw material for manufacture of nylon-6. At present, caprolactam is manufactured mainly by the reaction of cyclohexanone with hydroxylamine hydrochloride and rearrangement of the resulting cyclohexanone oxime to caprolactam via a Beckmann rearrangement with sulfuric acid. This process of manufacturing caprolactam by reaction of cyclohexanone and hydroxylamine involves a large number of steps and is energy intensive. Ammoximation provides a direct one-step process for manufacture of cyclohexanone oxime.

Ammoximation of cyclohexanone has been studied in the vapor phase (3–5) mostly over SiO_2 and SiO_2–Al_2O_3 catalyst, as well as in the liquid phase, where high yield and selectivity to oxime are reported over titanium silicate catalyst using hydrogen peroxide and ammonia as oximation reagents (6–11). Recently, some patents have reported that supported SiO_2 catalysts show better performance for the process (12–14). Although there are a few reports on ammoximation of cyclohexanone by air and ammonia over Al_2O_3–SiO_2 catalysts, there is no report on oximation of cyclohexanone using nitric oxide and ammonia as the oximation agents. The present study of the ammoximation of cyclohexanone by nitric oxide and ammonia was undertaken with a view to examining the superiority of the process over earlier processes in which either air and ammonia or hydrogen peroxide and ammonia are used as oximation agents, optimizing the process for maximum yield and selectivity of caprolactam, and suggesting a tentative mechanism.

EXPERIMENTAL

Catalyst Preparation and Experimental Procedure

TiO_2 of commercial grade was used to prepare a titanium peroxo catalyst by treating the oxide with 0.05 *M* sulfuric acid and 26 wt% H_2O_2. The mixture was allowed to stand overnight, filtered, washed and calcined at 673 K for 4 h. The amorphous Al_2O_3–SiO_2 catalyst used in this study was obtained by cogelling aluminum sec-butoxide and tetraethyl orthosilicate with ammonium hydroxide. The gel was washed, dried, and calcined at 773 K. The $SiO_2 : Al_2O_3$ molar ratio was kept at 5 : 1. This is based on the findings by Armor (3) in the ammoximation of cyclohexanone by air and ammonia. The fireclay catalyst was obtained by powdering fireclay bricks. Its approximate composition was $SiO_2 : Al_2O_3 : Fe_2O_3 : TiO_2 :$ CaO : MgO : Alkalis (68.1 : 27.2 : 1.95 : 1.1 : 0.72 : 0.35 : 1.28, respectively).

The catalytic runs were performed in a 200-ml capacity three-necked glass flask fitted with a mechanical stirrer and a condenser, the third neck being used for feeding metered amounts of nitric oxide and ammonia. Both the gases were metered by calibrated flow meters. Ammonia was fed via an ammonia gas cylinder. Nitric oxide was produced by dropping 50% sulfuric acid on to an aqueous solution of sodium nitrite. The NO generator was stirred continuously to ensure constant generation of gas. The temperature of the reaction vessel was maintained using an oil bath. For a

0021-9517/96 $18.00

TABLE 1

Effect of Various Catalysts on the Oximation of Cyclohexanone

Catalyst	Cyclohexanone conversion (wt%)	Product distribution (wt%)			Caprolactam selectivity (%)
		Cyclohexanone	Caprolactam	Others[a]	
TiO_2	22.30	77.70	10.30	12.00	46.18
Ti peroxo catalyst	2.63	97.37	0.63	2.00	23.95
Fireclay	18.17	81.83	14.00	4.17	77.05
Al_2O_3–SiO_2	46.67	53.33	37.78	8.89	80.95

Note. Reaction conditions: catalyst, 2 g; NH_3 : cyclohexanone = 1.7 (molar ratio); NO : cyclohexanone = 2.9 (molar ratio); reaction temperature, 348 K; duration of run, 1 h.

[a] In this and other tables "others" are assumed to be compounds I and II shown in Scheme I.

standard run 14 g of cyclohexanone and 2 g of catalyst were loaded in the reactor and heated to the required temperature. Purified ammonia and nitric oxide were then passed into the system for 1 h. At the end of the reaction, the reaction mixture was cooled to room temperature and the catalyst was filtered.

Identification and Analysis

The identification of the various products formed was carried out by matching gas chromatograph retention times with those of pure compounds. The IR spectrum of the reaction mixture was recorded as a thin film on a Shimadzu IR-460 infrared spectrophotometer in a KBr cell. A band which appeared near 3400 cm^{-1} can be assigned to the N–H stretching mode, and a band appearing at 1700 cm^{-1} is characteristic of C=O stretching. A band at 1680 cm^{-1} can be ascribed to the C=N stretching of oxime. These bands confirm the presence of oxime and caprolactam.

On standing, the reaction mixture polymerizes with molecular weight ranging from 500 to 5000. Degradation of the polymer with sulfuric acid confirmed the presence of caprolactam. For quantitative analysis, the product mixture was extracted with carbon tetrachloride and the organic layer was injected into a gas chromatograph and analyzed using a diethylene glycol adipate column and FID detector. Since polycaprolactam is insoluble in carbon tetrachloride, it is not included in the product distribution.

RESULTS AND DISCUSSION

When oximation is carried out by air and ammonia over this catalyst in the vapor phase, ketone ammonia adduct becomes a major product which is inorganic in nature and is easily separated when extracted with organic solvents such as carbon tetrachloride. However, in the present reaction no such adduct was detected. There was no inorganic product (i.e., ionic in nature). This is perhaps due to the easy availability of oxygen in the present reaction. When hydrogen peroxide and ammonia are used as oximation reagents, oxime is the end product. However, in the present case caprolactam was the end product which slowly polymerized to polycaprolactam on standing.

The performance of various catalysts used in the process is listed in Table 1. The catalytic activity was found to vary in the order Al_2O_3–SiO_2 > fireclay > TiO_2 > titanium peroxo catalyst. Although the Al_2O_3–SiO_2 catalyst system is effective for the process, the low activity of fireclay catalyst is perhaps due to low surface area. Poor performance of TiO_2 and the peroxy titanium compound in the present process when oximation reagents are NO and ammonia is worth nothing. This latter catalyst was found to be very effective when the oximation reagents were hydrogen peroxide and ammonia. This aspect will be reviewed again when discussing mechanisms of the reaction.

Influence of Reaction Temperature

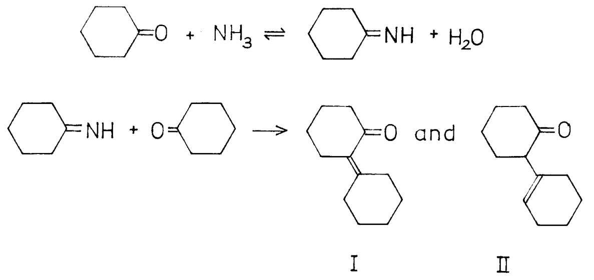
Conversion of cyclohexanone as well as yield and selectivity to caprolactam were found to be affected by temperature (Table 2). A maximum conversion of 46.67% was obtained at 348 K. The decrease in conversion at temperature higher than 348 K can be attributed to lower availability of NO and NH_3 in the reaction mixture due to more rapid

TABLE 2

Influence of Reaction Temperature on the Oximation of Cyclohexanone over Al_2O_3–SiO_2 Catalyst [$SiO_2 : Al_2O_3 = 5 : 1$ (Molar Ratio)]

	Temperature (K)		
	323	348	373
Cyclohexanone conversion (wt%)	14.10	46.67	19.11
Product distribution (wt%)			
Cyclohexanone	85.898	53.33	80.89
Caprolactam	13.42	37.78	16.00
Others	0.678	8.89	3.11
Caprolactam selectivity (wt%)	95.18	80.95	83.73

Note. Reaction conditions: wt. of catalyst, 2 g; NH_3 : cyclohexanone = 1.7 (molar ratio); NO : cyclohexanone = 2.9 (molar ratio); duration of run, 1 h.



SCHEME I. Reactions showing possible route for formation of large molecular weight conjugated products.

losses at higher temperature. The yellow to reddish brown color of the reaction mixture can be attributed to the possible formation of large-molecular-weight conjugated products such as 2-cyclohexylidenecyclohexanone (I) or its isomer 2-(1-cyclohexen-1-yl)-cyclohexanone (II) (Scheme I).

Influence of Catalyst Concentration

A maximum yield of 37.78% with a selectivity of 80.95% to caprolactam was obtained at an Al_2O_3–SiO_2 catalyst concentration of 14 g/mol cyclohexanone (Table 3). Beyond this catalyst concentration the conversion of cyclohexanone as well as the yield and selectivity to caprolactam decreased.

Influence of NH_3 : Cyclohexanone and NO : Cyclohexanone Molar Ratios

Although the ammoximation reaction requires an equal number of moles of cyclohexanone and NH_3 or NO, Tables 4 and 5 indicate that excesses of NH_3 and NO have to be taken to obtain a maximum yield of caprolactam. The maximum yield of caprolactam was found at NH_3 : cyclohexanone and NO : cyclohexanone molar ratios of 1.7 and 2.9, respectively. However, the maximum conversion was found at NH_3 : cyclohexanone molar ratio of 3.6 and NO : cyclohexanone molar ratio of 4.8. An increase in the molar ratios in the case of both NO and NH_3 leads to a decrease in the selectivity to caprolactam, perhaps due to higher production of side-products.

TABLE 4

Influence of NH_3 : Cyclohexanone Molar Ratio

	NH_3 : cyclohexanone molar ratio			
	1.7	2.4	3.6	4.8
Cyclohexanone conversion (wt%)	46.67	49.86	60.14	57.24
Product distribution (wt%)				
Cyclohexanone	53.33	50.14	39.86	42.76
Caprolactam	37.78	24.29	24.54	27.41
Others	8.89	25.57	35.60	29.82
Caprolactam selectivity (wt%)	80.95	48.72	40.80	47.89

Note. Reaction conditions: catalyst concentration, 14 g/mol cyclohexanone; NO : cyclohexanone = 2.9 (molar ratio); reaction temperature, 348 K; duration of run, 1 h.

Mechanism of the Reaction

In the ammoximation of cyclohexanone by ammonia and hydrogen peroxide, it is assumed that cyclohexanone first reacts with ammonia and forms cyclohexanone imine, which then reacts with titanium peroxocompound and produces oxime (6).

The poor performance of TiO_2 and titanium peroxo catalyst in the present study using nitric oxide in place of hydrogen peroxide is perhaps due to the inability of these catalysts to maintain the concentration of peroxo species.

The major product of reaction was found to be caprolactam. The product undergoes polymerization on standing. Since SiO_2 is not an oxidation catalyst, the oxidation must proceed through formation of some activated species. One mechanism could be the formation of imine-like species on the surface (Eqs. [1], [2], and [3] of Scheme II).

The oxidizing nature of NO in reducing atmosphere (23) and in the presence of catalyst (24) is reported.

TABLE 3

Influence of Catalyst Concentration on the Oximation of Cyclohexanone

	Catalyst concentration (g cat/mol ketone)			
	8	11	14	21
Cyclohexanone conversion (wt%)	18.66	18.87	46.67	18.57
Product distribution (wt%)				
Cyclohexanone	81.34	81.13	53.33	81.43
Caprolactam	14.66	11.32	37.78	8.32
Others	4.00	7.55	8.89	10.25
Caprolactam selectivity (wt%)	78.56	59.99	80.95	44.80

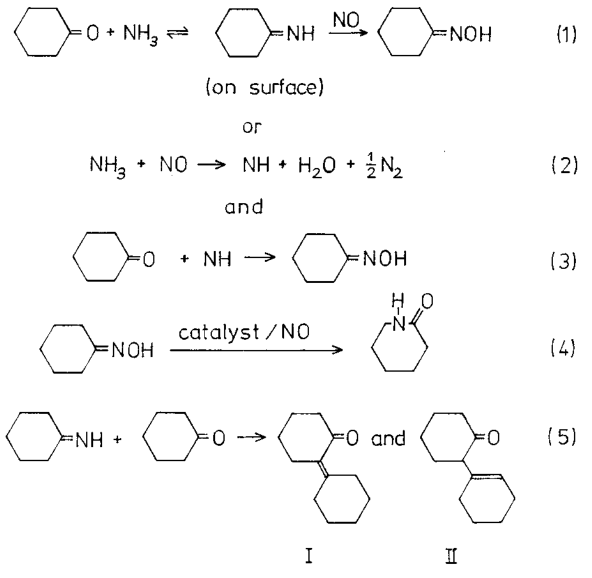
Note. Reaction conditions: NO : NH_3 = 1.7 : 1 (molar ratio); reaction temperature, 348 K; duration of run, 1 h.

TABLE 5

Influence of NO : Cyclohexanone Molar Ratio

	NO : cyclohexanone molar ratio			
	2.9	3.6	4.8	6.1
Cyclohexanone conversion (wt%)	46.67	52.39	68.88	57.73
Product distribution (wt%)				
Cyclohexanone	53.33	47.61	31.12	42.27
Caprolactam	37.78	27.80	25.30	24.08
Others	8.89	24.60	43.57	33.65
Caprolactam selectivity (wt%)	80.95	53.06	36.73	41.71

Note. Reaction conditions: catalyst concentration, 14 g/mol cyclohexanone; NH_3 : cyclohexanone = 1.7 (molar ratio); reaction temperature, 348 K; duration of run, 1 h.



SCHEME II. Mechanism of ammoximation of cyclohexanone by nitric oxide and ammonia.

Formation of cyclohexylimine as the precursor of cyclohexanone oxime in the ammoximation of cyclohexanone by H_2O_2 over titanium–silicate catalyst has been demonstrated by Tvarůzková *et al.* (8) employing IR spectroscopy.

Imine can react with cyclohexanone to give condensation products (Eq. [5] of Scheme II).

Vapor phase Beckmann rearrangement of cyclohexanone oxime to caprolactam has been studied over many acidic catalysts (15–21). Since our catalyst is also acidic in nature, the direct rearrangement of oxime to caprolactam is possible.

Armor (3) has also reported direct production of caprolactam in vapor phase from cyclohexanone, ammonia, and air by placing a further bed of SiO_2–Al_2O_3 catalyst below the oximation catalyst (Porasil A) at a temperature of 523 K. Our study, however, was in the liquid phase and we did not need a separate bed of catalyst: the temperature requirement was also quite low (323–373 K) compared to 523 K used by Armor. It is worth mentioning that Armor was able to obtain only traces of caprolactam below 473 K.

The resulting caprolactam reacts with ammonia to produce polyamide via anionic polymerization (3). The degree of polymerization of the reaction mixture increased with time until it became fully polymerized. The viscosity average molecular weight, M, of the resulting polymer was determine using m-cresol as the solvent and employing the relation $[\eta] = KM^a$, where K and a are constants and $[\eta]$ is the intrinsic viscosity. The values of K and a were taken to be 3.2×10^{-3} and 0.62, respectively (22). Molecular weights were determined for random runs and were always found to be in the range 500–5000.

CONCLUSIONS

A one-step process for production of caprolactam and polycaprolactam by liquid phase ammoximation of cyclohexanone by nitric oxide and ammonia over a Al_2O_3–SiO_2 catalyst is demonstrated. Although ammoximation of cyclohexanone by hydrogen peroxide and ammonia results in high selectivity and yield of cyclohexanone oxime, the present process is better in the sense that it produces polycaprolactam directly. A maximum conversion of 46.67% with a maximum yield of 37.78% and selectivity of 80.95% for caprolactam, at a cyclohexanone : NO : NH_3 molar ratio of 1 : 2.9 : 1.7 and a temperature of 348 K, is achieved.

REFERENCES

1. Shanshal, M., Alghatta, H., and Tahir, S. F., *React. Kinet. Catal. Lett.* **43**, 335 (1991).
2. Prasad, R., Garg, A., and Matthews, S., *Can. J. Chem. Eng.* **72**, 164 (1994).
3. Armor, J. N., *J. Catal.* **70**, 72 (1981).
4. Armor, J. N., Carlson, E. J., Soled, S., Conner, W. C., Laverick, A., DeRites, B., and Gates, W., *J. Catal.* **70**, 91 (1981).
5. Armor, J. N., Zambri, P. M., and Leming, R., *J. Catal.* **72**, 66 (1981).
6. Thangaraj, A., Sivasanker, S., and Ratnasamy, P., *J. Catal.* **131**, 394 (1991).
7. Sudhakar Reddy, J., Sivasanker, S., and Ratnasamy, P., *J. Mol. Catal.* **69**, 383 (1991).
8. Tvarůzková, Z., Habersberger, K., Zilková, N., and Jírů, P., *Appl. Catal.* **79**, 105 (1991).
9. Roffia, P., Padovan, M., Moretti, E., and De Alberti, G., E.P. 301 486 (1989), *Chem. Abstr.* **111**, 9251a.
10. Roffia, P., Leofanti, G., Cesana, A., Mantegazza, M., Padovan, M., Petrini, G., Tonti, S., and Gervasutti, P., *Stud. Surf. Sci. Catal.* **55**, 43 (1990).
11. Dreoni, D. P., Pinelli, D., and Trifirò, F., *J. Mol. Catal.* **71**, 111 (1992).
12. Rainer, S., Rolf, P., Willibald, M., Reinhard, G., Peter, B., Ger. Offen. DE 4,240,698, 9th June, 1994, *Chem. Abstr.* **121**, (1994) 82136 C.
13. Rainer, S., Rolf, P., Willibald, M., Reinhard, G., Peter, K., Peter, B., Ger. Offen. DE 4,240,961, 9th June, 1994, *Chem. Abstr.* 121 (1994) 82137 D.
14. Rainer, S., Peter, K., Peter, B., Fritz, V., Peter, W. K., Ger. Offen. DE 4,240,692, *Chem. Abstr.* 121 (1994) 118706C.
15. Izumi, Y., Sato, S., and Urabe, K., *Chem. Lett.* 1649 (1983).
16. Sato, H., Ishii, N., Hirose, K., and Nakamura, S., *Stud. Surf. Sci. Catal.* **28**, 755 (1986).
17. Aucejo, A., Burguet, M. C., Corma, A., and Fornes, V., *Appl. Catal.* **22**, 187 (1986).
18. Sato, S., Hasebe, S., Sakurai, H., Urabe, K., and Izumi, Y., *Appl. Catal.* **29**, 107 (1987).
19. Sakurai, H., Sato, S., Urabe, K., and Izumi, Y., *Chem. Lett.* 1783 (1985).
20. Sato, S., Urabe, K., and Izumi, Y., *J. Catal.* **102**, 99 (1986).
21. Sato, S., Sakurai, H., Urabe, K., and Izumi, Y., *Chem. Lett.* 277 (1985).
22. Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd edition, p. 32, Vol. 16, John Wiley & Sons, New York, 1968.
23. Bailar, J. C., Emeleus, H. J., Nyholm, R., and Trotman-Dickenson, A. F., *Comprehensive Inorgan. Chem.* **2**, 334 (1973).
24. Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *J. Catal.* **52**, 133 (1978).