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Ammoximation

I. A Direct Route to Cyclohexanone Oxime and Caprolactam from NH_3, O_2, and Cyclohexanone

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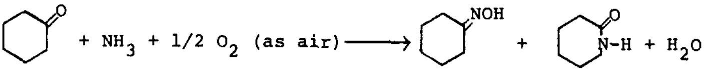
This report describes the first direct synthesis of cyclohexanone oxime and caprolactam from ammonia, air, and cyclohexanone. Most routes to caprolactam employ circuitous routes involving the oxidation of ammonia to oxides of nitrogen followed by a separate step for the reduction of these oxides to hydroxylamine, reaction with cyclohexanone, and then rearrangement of the resulting oxime with H_2SO_4. By using the novel chemistry described herein, it is possible to selectively react cyclohexanone, ammonia, and air to produce the oxime and/or caprolactam in one step:



To date, the best selectivity for oxime is 68%. The reaction is catalyzed heterogeneously over a variety of silicas and aluminas at temperatures ranging from 120 to 250°C. By using a dual-bed catalyst, we can convert some of the oxime to caprolactam as it emerges from the first bed of catalyst.

INTRODUCTION

In the conventional process for the manufacture of caprolactam, the amide nitrogen is derived from NH_2OH by an indirect route. First, N_2O_3 is prepared by the aerial oxidation of NH_3 at 800°C. The N_2O_3 is converted to NH_4NO_2, and this is reduced with SO_2 at low temperatures to produce hydroxylamine disulfonate [which is then hydrolyzed to form hydroxylammonium sulfate $(NH_2OH)_2$–H_2SO_4]. Two-thirds of the ammonia consumed ends up as ammonium sulfate. Thus, the profitability of the process would also vary depending on the demand for this by-product.

There are several alternative synthetic routes to the NH_2OH used in the synthesis of caprolactam (*1*, *2*). Dutch State Mines (*3*) has a patented process wherein the synthesis of hydroxylamine is carried out in buffered phosphoric acid (DSM-HPO process). Other processes which also use H_2 as the reductant include one by DuPont and another by BASF/Inventa (*4*, *5*). In the DSM and Inventa processes, nitric oxide is produced via high-temperature, aerial oxidation of ammonia over a Pt/Rh catalyst. The NO is then reduced by H_2 to hydroxylamine over a 10% Pt on carbon catalyst with some $(NH_4)_2SO_4$ being produced [with the DSM-HPO process, no $(NH_4)_2SO_4$ is produced]. Hydroxylamine is then reacted with cyclohexanone to prepare the oxime. The oxime is then rearranged with H_2SO_4 to caprolactam. Toyo Rayon Company employs a photochemical route (via NOCl and cyclohexane) to prepare cyclohexanone oxime. All these processes to caprolactam involve a large number of steps and/or are very energy intensive. Further, most of these processes incorporate an overoxidation of the NH_3 which is then followed by a selective reduc-

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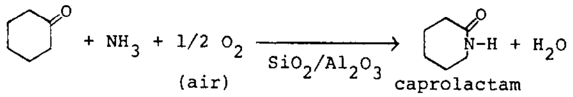
tion to hydroxylamine. Recently, we reported a unique heterogeneously catalyzed reaction for converting ketones to oximes (*6, 7*). We have termed the reaction described by Eq. (1) ammoximation.

$$\text{ketone} + NH_3 + \tfrac{1}{2}O_2 \rightarrow \text{oxime} + H_2O. \quad (1)$$

The ammoximation process described by Eq. (1) avoids the production of any $(NH_4)_2SO_4$ as a by-product. Further, the direct oxidation of NH_3 to the oxime eliminated the need for the reductant now used in the synthesis of hydroxylamine. At the time of the discovery of the ammoximation reaction, it also seemed possible to carry out the direct synthesis of caprolactam (*8*) via Eq. (2) using catalysts which are effective for the rearrangement of oximes to lactams (*9, 10*).



(2)

The significance of this latter process lies in its potential simplicity with respect to the direct generation of caprolactam. The practice of the process described by Eq. (1) would still require the use of H_2SO_4 for the rearrangement of the oxime to the lactam and thus entails the production of some $(NH_4)_2SO_4$. However, the process described by Eq. (2) provides a way of completely avoiding $(NH_4)_2SO_4$ as a by-product. Thus, the direct production of caprolactam from NH_3, O_2, and cyclohexanone offered a new route to caprolactam without the production of any $(NH_4)_2SO_4$. The elimination of a number of process steps as compared to current processes would seem to offer an economically attractive route to caprolactam.

The term "ammoximation" has some parallel to the well-established term "ammoxidation" (*11, 12*) for the complete oxyamination of propylene to acrylonitrile. Here, the term ammoximation is meant to designate a selective oxidation of NH_3 and ketone to the oxime. To our knowledge, this new process represents the first such aerial oxidation of a mixture of ketone and NH_3 to the oxime. Recent reports on the ammoxidation of ketones with NH_3 and O_2 at 450°C over Bi/Mo oxides indicate that nitriles (*13*) of reduced *C* number are formed at these high temperatures. However, by going to much lower temperatures (180–250°C), we observe substantial amounts of the oxime. The catalyst for this selective oxyamination of ketones is a material which is certainly not a significant oxidation catalyst, silica gel. A particular silica–alumina (*14*) is an even better catalyst for Eq. (1) [$S = 68\%$; S, selectivity = (moles oxime produced/total moles of ketone consumed) × 100]. The only previous description of SiO_2/Al_2O_3 as an oxidation catalyst is by Chapman and Hair (*15*). They report ir evidence for the oxidative properties of SiO_2/Al_2O_3 surfaces for the oxidation of benzaldehyde to the corresponding adsorbed benzoate ion. The work we describe herein represents the first substantial oxidation reaction catalyzed by SiO_2/Al_2O_3 or silica gel.

EXPERIMENTAL

Analysis of Products

In the early stages of this work, gas chromatography (gc), mass spectrometry, and wet chemical analyses were employed to confirm the presence of the oxime and to obtain the conversion of cyclohexanone and/or NH_3 during the course of the reaction. The gc method of analysis was the prime method of analysis because it was already available. The automated reactor systems used throughout this study are capable of a sophisticated analysis of all the reactants and products—provided that discrete peaks for these materials can be separately eluted on a gas chromatograph. Columns of Carbowax 20M and KOH on Chromosorb WAW either by themselves or mounted in series with molecular sieve, Porapak, or Chromosorb columns were satisfactory for separating cyclohexanone, the oxime, and caprolactam ("high boilers"). In order to separate these "high boilers" from the low boilers (O_2, N_2, NH_3, H_2O, CO, CO_2, etc.), an alternative method using two columns in parallel with equal back pressures was devised (*16*). The first column was a 6-ft, ¼-in.-o.d. glass column containing 5% Carbowax 20M on Chromosorb T. By use of a 4-port valve, the low boilers which exit the first column as one peak can be exclusively crossed over to an 8-ft, ⅛-in.-o.d., stainless-steel column of molecular sieve 5A (60–70 mesh) in parallel with an 8-ft, ⅛-in.-o.d., stainless-steel column containing Chromosorb 104 (60–80 mesh).

The areas of the peaks emerging from the gc were calculated using a Hewlett–Packard 3353A computer, and the raw data were normalized to read out the volume percentage of each product.

A specific analysis for the oxime was employed to confirm the presence of cyclohexanone oxime (*17*). Further proof that oximes were being generated was obtained from the gc/ms data (*18*). Fractions of the condensable products exiting the reactor were collected and submitted for mass spectrographic analysis. Injection of the products into a gc/ms indicated that the product attributed to cyclohexanone oxime did indeed have a molecular weight of 113 g. The oximes can be further verified since they readily lose water and a secondary peak is observed at 95 amu.

Configuration of the Automated Reactor

In order to facilitate the analysis of the components of the product stream, an automated sampling system was used to monitor the inlet (reactants) and exit (products) gases over the catalyst under study (Fig. 1). Two high-temperature, 6-port valves were used to direct the inlet or exit gases to the gc through stainless-steel lines maintained at ~190°C. The valves were heated at 200°C independent of the cyclohexanone vaporizer (at 95–130°C), the catalyst oven, and the oven at the exit of the catalyst bed. A Data-Trak micro-processor-based process controller was used to control the sampling of the gases as well as the operation of the gc program. The analytical procedure cannot detect very high boiling byproducts. Since some tar is deposited on the catalyst during reaction, the weight of the catalyst tube (~50 g) was recorded before and after the experiment. Also a glass trap (in a separate oven situated between the catalyst oven and the valve-box oven) was mounted at the bottom of the catalyst tube in order to collect any tars or oils produced as by-products (see Fig. 1).

The catalyst was contained in a quartz reaction tube designed in such a way that the reactant gases passed through an outer tube (to preheat them), after which they passed downward through layers of quartz wool, coarse quartz chips (2 cm^3), fine quartz powder ($<0.2\ cm^3$), the catalyst (0.5 to 6 cm^3), and quartz wool. All gas flows were controlled using Tylan flow controllers (Torrance, Calif.). The cyclohexanone flow was controlled by passing a known rate of N_2 through a glass vessel (containing the cyclohexanone) contained in an oven maintained at ~90°C.

Catalysts

Porasil A can be purchased directly from Waters Associates (Framingham, Mass.) or most gc supply houses. This material is a very pure form of silica gel (see Analysis—Table 1). It has a surface area of ~450 m^2/g and a pore volume of 1.0 cm^3/g. The average pore diameter is calculated to be 8.4 nm.

SiO_2/Al_2O_3 catalyst. In the following paper we have described a variety of catalysts

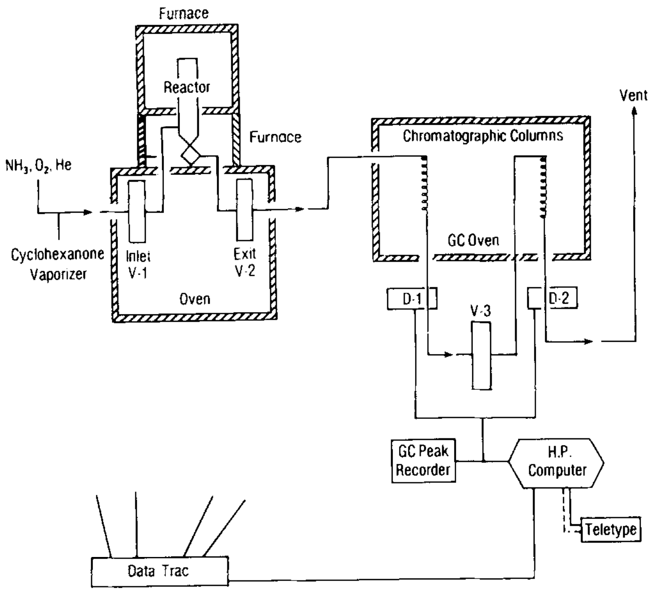


FIG. 1. Schematic of automated sampling system. (D-1 and D-2 are heated detectors; V-1, 2, and 3 are gas sampling valves.)

effective for the ammoximation of cyclohexanone. Among the best catalysts is one prepared as follows from the hydrolysis of TMOS (tetramethyl-orthosilicate) and ASB (aluminum *sec.*-butoxide). Tetramethylorthosilicate (liquid, 3.0 g) and aluminum *sec.*-butoxide (viscous liquid, 1.95–2.0 g) were mixed. With stirring, about 0.75–2.00

TABLE 1

Analysis of Porasil A Emission Analysis

Al	tH	Mg	<.01%	Ti	tH
As	ND	Mn	Trace	W	ND
Sb	ND	Hg	X	U	X
Ba	ND	Mo	ND	V	ND
B	ND	Nb	ND	Zn	ND
Bi	ND	Ni	ND	Zr	ND
Cd	ND	P	X		
Ca	tH	K	X		
C	X	Na	ND		
Cr	ND	S	X		
Co	ND	Si	10–100%		
Cu	<0.01%	Ag	ND		
Fe	0.01–0.1%	Ta	ND		
Pb	ND	Te	X		
Li	ND	Sn	ND		

Note. ND—not detected, ⩽ 100 ppm; t—0.01 to 0.1%; H—upper half of range shown; X—not tested. Atomic absorption: Ca, 220 ppm; Mg, 48 ppm; Ti, 420 ppm; Cu, 1 ppm; Na, 1 ppt; Al, 580 ppm; K, 13 ppm; S, 330 ppm; Fe, 310 ppm; C = 1.15%, H = 1.15%. Detailed emission: B, 20 ppm; Pb, 70 ppm; Mn, 20 ppm; Ni, 50 ppm; Cr, 40 ppm; Sn, 30 ppm.

TABLE 2

Emission Analysis of SiO_2/Al_2O_3 Catalyst[a]

Aluminum	P	Molybdenum	ND
Arsenic	ND	Niobium	ND
Antimony	ND	Nickel	ND
Barium	ND	Phosphorus	X
Beryllium	ND	Potassium	X
Boron	ND	Sodium	ND
Bismuth	ND	Sulfur	X
Cadmium	ND	Silicon	P
Calcium	ND	Silver	ND
Chromium	ND	Tantalum	ND
Cobalt	ND	Tellurium	X
Copper	vft	Tin	ND
Iron	vft	Titanium	ft
Lead	ND	Tungsten	ND
Lithium	ND	Uranium	X
Magnesium	ft	Vanadium	ND
Manganese	ND	Zinc	ND
Mercury	X	Zirconium	ND

Note. P—10 to 100%; ft—less than 0.01%; ND—not detected; X—not tested; vft—very faint trace. Atomic absorption: Cu, 37 ppm; Fe, 124 ppm; Ti, 37 ppm; Mg, 12 ppm.

[a] Schwartzkopf Microanalytical Lab.

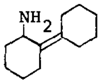
ml (typically 1.25 ml) of water was added all at once to the nearly clear liquid. Within 10 to 60 sec the liquid suddenly set to a wet gel. The gel was allowed to stand to ensure completion of the hydrolysis of the esters and then dried at temperatures ranging from 60 to 200°C in order to evaporate the by-product alcohols (methanol and butanol).

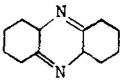
The surface area was as high as 450 m^2/g, and the average pore diameter was about 15 nm. This material had a PV of 1.64 cm^3/g. The plot of $DV(r)$ versus pressure displayed no distinct maximum; however, a weak band appeared to be centered at 9.1 nm. The product was found to be amorphous by X-ray analysis. The percentage of carbon in the product was less than 2% by weight. The bulk density was about 0.35 g/cm^3. Emission analysis on this catalyst indicated that no substantial impurities were present (Table 2).

RESULTS

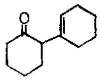
Products

Our initial discovery of cyclohexanone oxime from the reaction of NH_3, O_2, and ketone over silica was verified by three independent analytical methods: gc, mass spectrographic, and wet chemical analysis. Early in this work, we saw a large amount of water produced as well as unreacted ketone and a number of products which could be attributed to condensation and/or dehydration products of the ketone. These latter products included dodecahydrotriphenylene ($C_{18}H_{24}$), phenol, aniline, cyclohexylamine,

$C_{12}H_{21}N$: 

, $C_{12}H_{18}N_2$: 

, and

2-(1-cyclohexen-1-yl)-cyclohexanone 

However, as the selectivity (S) for the reaction rose from 1 to 68%, a marked decrease in the number of volatile products resulted. Instead, the major by-product has remained as a black residue which deposits on the catalyst. Attempts to remove and fully characterize this residue by conventional analytical techniques have failed.

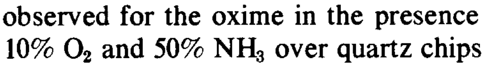
Early in the course of this work, we sought to determine the extent of cyclohexanone being converted to by-products and being deposited on the catalyst. Using 2 cm^3 of Porasil A (0.80 g) under conditions which give a peak S of ~50% to the oxime, cyclohexanone (0.15 cm^3 liquid/hour), NH_3 (9.5 cm^3/minute), and air (4.0 cm^3/minute) were passed over the catalyst at 185°C. All the liquid and gaseous products were collected by passing these products through two traps of ethanol emersed in an ethylene glycol/CO_2 bath. The weight gain on 0.8 g of Porasil A on the catalyst over 7.5 hr amounted to 0.50 g. Microanalysis of the black, free-flowing, spent catalyst gave 30.2% C, 2.94% H, and 4.3% N which corresponds to an empirical formula of $(C_8H_9N_1O_x)_n$. (It was too difficult to get an accurate value for the percentage of O present, if any. Typically, the ratio for C/N varies between 6/1 and 8/1.) Therefore, the spent catalyst contained 29% of the carbon originally fed in as cyclohexanone. Approximately 37% of the cyclohexanone was recovered unreacted in the traps. The amount of oxime produced amounted to 21% of the ketone originally added to the reactor (total C recovered = 87 ± 8%). CO, CO_2, NO, or NO_2 were not detected by gc analysis.

Stability of Cyclohexanone Oxime or Caprolactam under Reaction Conditions

Cyclohexanone oxime. Several reports

(*19, 20*) in the literature have discussed the instability of the oxime in the presence of Cu^{2+}, Cu^{+}, Cr^{VI}, or V^{V} salts. However, no data was available with respect to the stability of the oxime over solid surfaces. In order to determine the stability of cyclohexanone oxime in the gas phase, a variety of experiments were performed with ~0.5–4.0% oxime in the gas phase. No conversion of the oxime was detected over quartz chips at 200°C. Neither was any conversion observed for the oxime in the presence of 10% O_2 and 50% NH_3 over quartz chips at 200°C. Using 2 cm^3 of Porasil A at 200°C, <6% of the oxime was unaccounted for when compared with the control run in the absence of the catalyst. Mixtures of cyclohexanone, its oxime, and N_2 indicated <8% conversion of the oxime. Therefore, there is no evidence to suggest that cyclohexanone is substantially unstable or reactive under the same reaction conditions employed for ammoximation.

Caprolactam. Caprolactam is known to react with NH_3 when this mixture is passed over a SiO_2/Al_2O_3 catalyst at 350–400°C to give ϵ-aminocapronitrile. Further, at 125–250°C without a catalyst, polyamides are formed.



(3)

For this reason, we decided to determine the stability of caprolactam under our reaction conditions. This was especially important because many of the catalysts which were effective for ammoximation also produced small amounts of caprolactam. The potential reactivity of caprolactam with our reactants was tested in the following manner. With ~1–2% caprolactam (gas phase), NH_3 (50%), and O_2 at 10% over a 2-cm^3 bed of quartz chips at 200°C, no conversion of the caprolactam was detected (1 sec contact time). Mixtures of caprolactam with (1) N_2; (2) N_2, O_2; (3) O_2, N_2, and cyclohexanone; or (4) NH_3, cyclohexanone, gave no conversion of caprolactam over Porasil A. Further, addition of caprolactam to the actual feed mixture (NH_3, O_2, cyclohexanone, diluent) over Porasil A at 195°C gave no detectable conversion of caprolactam. Therefore, under our reaction conditions, the decomposition of caprolactam cannot be a significant factor. However, these control experiments with cyclohexanone oxime or caprolactam did not rule out the possibility that surface-generated precursors of these valuable products might undergo decomposition with NH_3 and/or oxidation by O_2 to yield a highly crosslinked, unidentifiable, and intractable form of Nylon-6.

Control Experiments

Using the automated reactor system, gaseous reactants and products were monitored by periodically sampling the inlet and exit streams of the volatile materials both before and after they reached the catalyst bed. In order to determine whether any reactions occurred in the gas phase, several control experiments were performed and are summarized in Table 3.

An important point in Table 3 is that cyclohexanone is not oxidized by O_2 over Porasil A and that NH_3 reacts with cyclohexanone to give undesirable by-products. Thus, the combination of NH_3 plus oxygen yields a selective oxidation of the ketone and NH_3 to the oxime.

If O_2 (8%) was turned on after Experiment 8 (in Table 3) was run for ~14 hr, the conversion of cyclohexanone increased by 10% with the immediate production of the oxime (yield = 20%).

Catalyst Life

The following paper (*14*) indicates in detail the catalysts which were active for the ammoximation of cyclohexanone. Very early in our work we discovered that a pure form of silica gel (which was commercially available) was an effective catalyst. It was with this sample of Porasil A that most of our initial testing of the ammoximation process was performed.

Figure 2 indicates that for a 0.4-g (1-cm^3)

TABLE 3

Control Experiments

Expt. No.	Feed composition as volume %[a]			Contents of reactor	Conversion[c]	Additional comments
	NH_3	O_2	CH[b]			
1	57	5	4	Empty	Little if any at 500°C	
2	57	5	4	1 cm^3 Q chips[d]	Little if any at 200°C; C = ~48% at 475°C	
3	57	8	8	~5 cm^3 Q chips	Little if any at 195°C	Trace of water
4	—	—	8	~5 cm^3 Q chips	None at 195°C	
5	57	20	—	0.4 g Porasil A	Little if any at 195°C	*Perhaps* a trace of water and N_2
6	—	—	3	0.4 g Porasil A	None at 195°C	
7	—	20	3	0.4 g Porasil A	Little if any at 195°C	
8	57	—	3	0.4 g Porasil A	~79% initially; after 8 hr, levels off to ~50%; no volatile product detected by gc; product(s) end up as residue on catalyst	

[a] Balance as helium (total flow 21 cm^3/min).

[b] CH = cyclohexanone.

[c] C = Conversion = (total number of moles of cyclohexanone used/total moles of cyclohexanone fed into the reactor) × 100.

[d] Q chips = quartz chips.

sample of Porasil A there is an induction period of approximately 1–2 hr during which the yield, Y [(moles of oxime produced/total number of moles of cyclohexanone fed into the reactor) × 100] rises rapidly and the conversion, C = (Y/S) × 100, drops from >90 to 60% within 2 hr. The selectivity [(moles of oxime produced/total number of moles of cyclohexanone consumed) × 100] shows a gradual increase over a period of 2–14 hr with a drop in S after ~16 hr. If one monitors the increase in weight of the catalyst during this period, one observes a gradual increase in the weight of the residue deposited on the catalyst, which follows the rate at which the conversion drops off (*21*).

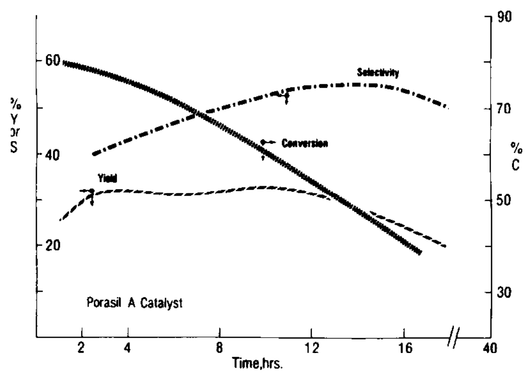


FIG. 2. Variation in the yield of oxime, the selectivity to oxime, and the conversion of cyclohexanone over 0.4 g (1 cm^3) of Porasil A catalyst at 195°C; NH_3 (51%); O_2 (10%); cyclohexanone (2%).

Increasing the amount of Porasil A increases the conversion and extends the apparent life of the catalyst. Further, the yield increases with the amount of catalyst as demonstrated in Fig. 3 for the plot of the Y versus reaction time (with different amounts of Porasil A).

With our automated reactor system and

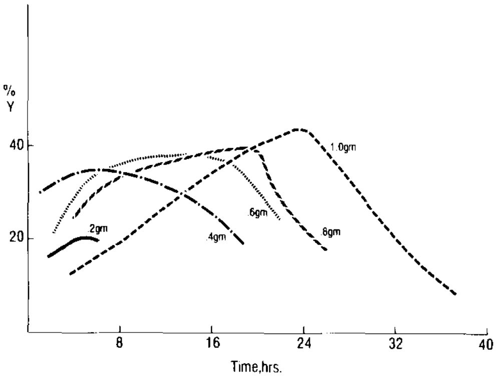


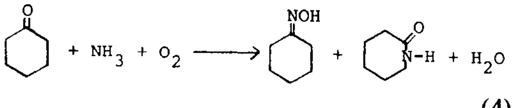
FIG. 3. Variation in yield for various amounts of Porasil A (in grams) at 195°C with 50% NH_3, 10% O_2, and 2% cyclohexanone (vapor).

the clean analysis of all our volatile reactants and products obtained by gc, we were able to plot the relative changes in volume percentage of all reactants and products versus time. The only species really changing during the reaction was that in least amount, the cyclohexanone (*22*) (Fig. 4). Further, it is clear that the high conversion apparent in the first phase of the reaction (<4 hr) is accompanied by a large increase in the production of water. The excess O_2 consumed and H_2O produced during this reaction was consistent with oxidative dehydrogenation as well as aldolization of the cyclohexanone in addition to the ammoximation of the ketone. Remarkably, very little NH_3 is consumed during the reaction, and it would appear that the S for oxime formation with respect to NH_3 consumption exceeds 60%.

Recently, we discovered that a particular type of SiO_2/Al_2O_3 catalyst was more effective than Porasil A as a catalyst. With this catalyst, selectivities of 68 ± 3% to the oxime were achieved. Variations in Y, C, and S over a 0.25-g sample of this catalyst are illustrated in Fig. 5. Not only did one observe a much higher S with this material, but also the catalyst life doubled using only one-half the weight of catalyst as described in Fig. 2 for Porasil A.

Direct Production of Caprolactam

Since acidic catalysts (*9, 10*) are known to catalyze the rearrangement of cyclohexanone oxime to caprolactam, we felt that it might be possible to produce caprolactam directly in one step, according to:



(4)

Very early in the course of our work we studied the ammoximation of cyclohexanone over Porasil A at 200°C. A bed of Linde SK-500 (La-coated SiO_2/Al_2O_3) was placed below the bed of Porasil A. The temperature of this coated SiO_2/Al_2O_3 catalyst (8-mm reaction tube, downward, plugged flow reactor) was maintained at 250°C. Small amounts of caprolactam (S =

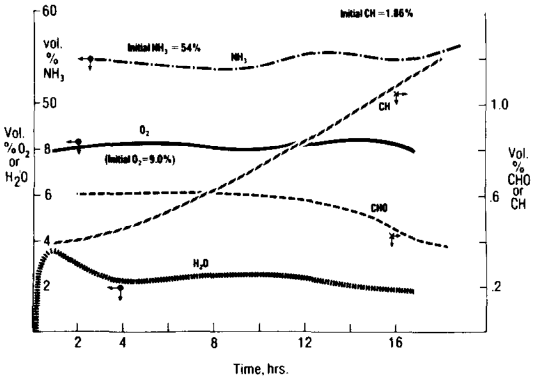


FIG. 4. Variation in the volume percentages of reactants and products during the experiment described in Fig. 3. (CH = cyclohexanone; CHO = cyclohexanone-oxime)

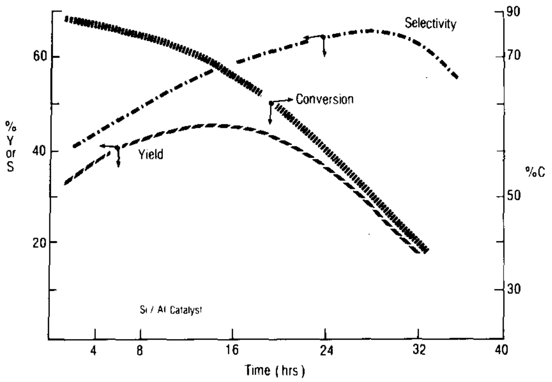


FIG. 5. Variation in the yield of oxime, the selectivity to oxime, and the conversion of cyclohexanone over 0.25 g (1 cm^3) of SiO_2/Al_2O_3 catalyst at 220°C; NH_3 (51%); O_2 (10%); cyclohexanone (2%).

14%) as well as the oxime (S = 45% at 93% C) were observed. If the second bed was maintained at 200°C, only trace amounts of lactam were observed. As a control, the isomerization of the oxime to caprolactam was studied.

With only the SK-500 catalyst at 240°C, one observed a 62% S for converting the oxime to caprolactam (fed in through a vaporizer, similar to that used for cyclohexanone) at 37% C. With O_2 (10%) and NH_3 (50%) added to the feed stream of oxime, the S for oxime to lactam fell to 23%. However, by lowering the level of NH_3 to 5%, the S for lactam rose to 45%.

Returning to a feed stream of cyclohexanone (2%), NH_3 (5%), and O_2 (10%) over a layer of SiO_2/Al_2O_3 (via our preparation from TMOS/ASB) at 220°C followed by another layer of this same catalyst at 260°C, we obtained a S of 25% for cyclohexanone directly to caprolactam and a S of 24% for cyclohexanone directly to the oxime (at ~53% conversion).

Assessment of the Heat of Reaction

Several experiments were performed using a modified reactor containing a concentric glass thermocouple well down the middle of the reaction tube (the latter was either 11 or 5.5 mm in diameter). The temperature of the catalyst (Porasil A) rose markedly if only cyclohexanone was allowed to pass over the catalyst at 185°C. If both the NH_3 and air were then turned on, the temperature of the catalyst rose a few degrees. The discontinuation of the NH_3 and air flows resulted in a drop in the temperature of the catalyst. The initial temperature rise of ~10°C with just the ketone alone could be due to the dehydration of any aldol by-product over the catalyst. The second temperature rise of ~3–5°C should be due primarily to the ammoximation reaction. It would appear that we are not encountering any serious exotherm on the surface of the catalyst. These small temperature changes would be consistent with the earlier observation that increasing the diameter of the catalyst bed did not substantially improve the S of the reaction (*22*).

DISCUSSION

We have described a novel, selective oxidation (by air) of mixtures of cyclohexanone and NH_3 to yield cyclohexanone oxime. The gas-phase or liquid-phase rearrangement of this oxime to caprolactam has been well established (*9, 10*). The ammoximation process represents a reduction in the number of steps to caprolactam by at least two major process steps. By avoiding the overoxidation of NH_3 to NO_x and the following reduction of NO_x with H_2 or SO_2, much of the complexity and high capital costs associated with most of the current routes to caprolactam has been eliminated. Further, when a solid, acidic catalyst was added immediately after the ammoximation catalyst, a direct one-pass synthesis of caprolactam was achieved. For the rearrangement of oxime to caprolactam, there was some reaction of the oxime with NH_3 and O_2 especially at very high levels of NH_3. This was circumvented to some extent by running at lower levels of NH_3. One should recall that the rearrangement of oxime to lactam is highly exothermic and the gas-phase rearrangement is usually run in a fluid-bed reactor. (Perhaps by altering the reactor system, one might observe much higher selectivities to the lactam.) At this early stage, our goal was to demonstrate that it was possible to proceed directly to the lactam in one pass over the appropriate catalyst(s).

By contrasting Figs. 2 and 5, it is apparent that the higher S obtained with SiO_2/Al_2O_3 may be attributed to the higher yield of oxime (at approximately the same conversion). What this implies is that the SiO_2/Al_2O_3 catalyst diverts more ketone to oxime than does Porasil A. By the addition of a small amount of alumina to the silica, we generate a much more active and productive catalyst.

The current S is ~68% for the production of the oxime from ketone. Our experience with the development of catalysts for this reaction indicates that improvements in selectivity are tied to eliminating secondary reactions which result in a black deposit on the catalyst. With time this deposit completely destroys the activity of the current catalysts after a buildup of more than two times the initial weight of the catalyst. However, while the catalyst has a significant deposit on its surface, it remains fairly active for an extended period of time.

Since one can account for almost all of the ketone fed into the reactor, the carbon mass balance experiments with Porasil A indicated that the residue is the primary by-product of ammoximation. These results have to be carefully considered since they were obtained using the less accurate reactor system which employed a syringe pump to feed the ketone and required hand calculations of the gc data. Further, the yield and amount of ketone recovered include the ketone originally required to activate the catalyst (see Fig. 2). Thus a yield, conversion, and selectivity calculated from the above data represented the worst possible case. In later studies with Porasil A, we observed higher selectivities with longer catalyst life and relatively less residue deposited on the catalyst. The longer life and higher S observed with SiO_2/Al_2O_3 catalysts correspond to an even smaller amount of residue deposited on the catalyst (versus Porasil A) over the same period of time. The residue on the catalyst accounted for almost all the ketone which was not converted to the oxime.

Catalysts which are effective for Eq. (1) (*14*) tend to be traditional nonoxidation catalysts (e.g., Al_2O_3, SiO_2, and SiO_2/Al_2O_3). These catalysts are also known to catalyze the aldolization (*23*) of ketones. Some elegant work by Scheidt (*24*) is summarized in Table 4. His work demonstrated that catalysts such as Li_3PO_4, Al_2O_3 (*25*), and calcium *o*-phosphate were very effective in converting cyclohexanone to the aldol condensate: 2-(1-cyclohexen-1-yl)-cyclohexanone. Indeed many of the catalysts which are effective for the ammoximation of cyclohexanone are also catalysts which are known to effect the condensation of the ketone. Further, in the presence of excess ammonia, the condensation is expected to occur quite readily.

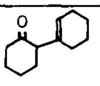
Many of the by-products which were observed in our early studies on the ammoximation of cyclohexanone (in low yields) could be viewed as simple condensation products of cyclohexanone and/or its imine. Even the residue has an empirical formula of $C_{6-8}/H_9/N_1$ and could represent an unsaturated organonitrogen product. Alternatively, the oxime in the presence of

TABLE 4

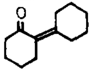
Vapor-Phase Aldol Condensations[a]

Ketone	Catalyst	Temp(°C)	S.V.	Conv.	Product	S
Acetone	Li_3PO_4	281–290	2.4	23	Mesityl oxide	43
					Isophorone	21
Cyclopentanone	Li_3PO_4	233–242	2.2	44	(C_5)1-yl;ylidene[a]	10;83
Cyclohexanone	Li_3PO_4	237–250	0.74	39	2-(1-Cyclohexen-1-yl)-Cyclohexanone[a]	90
	Al_2O_3	238–258	.76	37	"	80
	$Ca(OH)_2$	264–285	.34	48	"	84
	Ca-o-phosphate	276–284	.23	38	"	60
Cycloheptanone	Li_3PO_4	260–285	.77	23	(C_7)1-yl;ylidene[a]	45;45

a



2-(1-Cyclohexen-1-yl)-Cyclohexanone

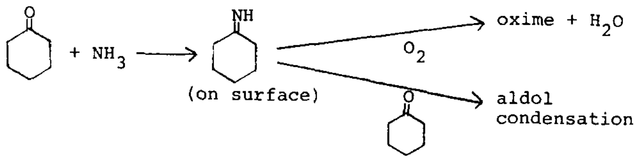


2-Cyclohexylidenecyclohexanone

[a] Scheidt, F. M., *J. Catal.* 3, 372 (1964).

NH_3 can undergo decomposition to polylactam. In the presence of air, these polylactams could associate to form a highly stable, crosslinked caprolactam.

In a later report, we will demonstrate a detailed mechanism for the ammoximation of ketone (based on surface studies). For the moment, we believe that the following simplified sequence of reactions best represents what is occurring during the process.



(5)

(6)

The facts that support this reaction scheme include: (1) aldolization seems to be a competitive process; (2) NH_3 and cyclohexanones alone give very high conversion (50–80%); however, when O_2 is added to this feed, the conversion actually increases, producing more oxime than can be accounted for by the increase in the conversion of the ketone; (3) the best catalysts are materials which are known to form transient imines (*26*) with NH_3; and (4) for silica to be an oxidation catalyst, the oxidation must be occurring after the ketone is activated (i.e., to an imine-like species). While our original thought was to prepare transient hydroxylamine on the surface of the catalyst, it would appear quite unlikely that hydroxylamine could be generated over silica at 200°C. Catalysts for ammonia oxidation often comprise a metal center (such as Pt or Co) and operate at temperatures far in excess of 200°C. [However, there is evidence to indicate that hydroxylamine precursors are formed from NH_3 and O_2 at >1100°C over glowing platinum (*27*).]

In succeeding papers, we will describe the application of reaction (1) to a wide variety of ketones (*28*) and discuss our efforts to optimize the reaction by variations in the concentration of the substrates as well as the dependence of reaction (1) upon temperature (*22*).

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