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Organic Reactions Catalyzed by Crystalline Aluminosilicates

IV. Beckmann Rearrangement of Ketoximes to Amides

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Acidic crystalline aluminosilicates show catalytic activity for the rearrangement of ketoximes to amides. Optimum conditions include temperatures in the range of 250–350°C, a nonpolar solvent, and an inert carrier gas. Under these conditions, using a hydrogen Y zeolite, 75% to 95% yields of amides have been obtained from the oxime rearrangement.

INTRODUCTION

In 1886 Beckmann (*1*) found that ketoximes were rearranged to acid amides under the action of certain reagents such as phosphorus pentachloride or acetic anhydride. Using sulfuric acid as a catalyst Wallach (*2*) reported the rearrangement of cyclohexanone oxime to ε-caprolactam. This synthesis was improved by Ruzicka (*3*) and later perfected by industrial chemists when caprolactam was developed as a nylon precursor. Experimental and mechanistic details of the homogeneous catalyzed Beckmann rearrangement have been adequately described (*4*).

A heterogeneous catalytic technique for this rearrangement would offer several advantages over a sulfuric acid process. In the latter, 1 mole of concentrated acid is required for the preparation of 1 mole of amide. Subsequently, a mole of base is needed to neutralize the reaction medium. In addition, the rearrangement in sulfuric acid is exothermic and under some conditions can lead to a violent reaction.

There are a number of references directed towards the use of heterogeneous catalysts for rearranging ketoximes. Silica gel, alumina, magnesia, thoria, and heteropoly acids (*5, 6*) are reported to catalyze the cyclohexanone oxime rearrangement which is attended by a competing reaction producing 5-cyano-1-pentene and a trimeric condensation product. Solid phosphoric acid similarly gives caprolactam and 5-cyano-1-pentene, but the catalyst quickly loses activity and regeneration conditions are severe (*7*). Boron phosphate has been proposed as a catalyst but 5-cyano-1-pentene is the predominant product (*8*). Davydoff (*9*) recently reported details of the use of a boric-acid-on-alumina catalyst for the rearrangement of a variety of ketoximes. This was the first demonstration that the rearrangement could be surface-catalyzed in that more than 1 mole of amide could be produced per mole of boric acid incorporated into the catalyst. About 70% yields of amide were obtained.

In earlier papers (*10, 11*) we reported that acidic crystalline aluminosilicates were active catalysts for alkylation. We have now found that such acidic zeolites show a surface catalytic effect in the Beckmann rearrangement, forming amides in variable yields depending upon the structure of the starting ketoxime.

METHODS

Acetone oxime, acetophenone oxime, and cyclohexanone oxime were Eastman Kodak

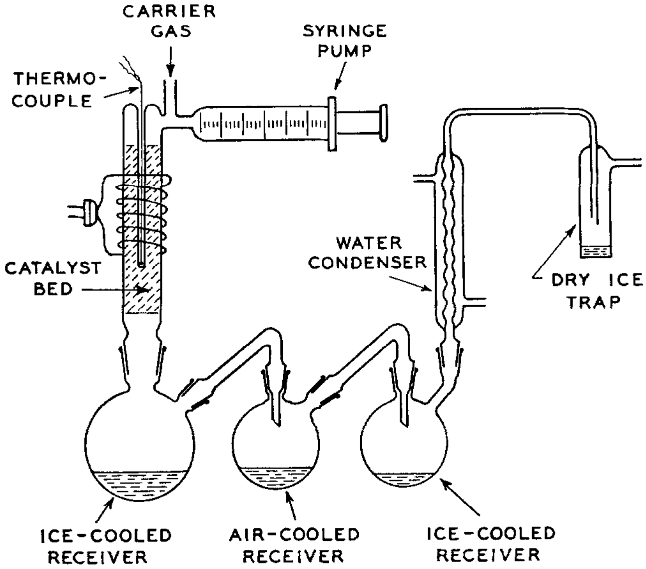


FIG. 1. Apparatus for Beckmann rearrangement reactions.

White Label grade samples which were recrystallized to constant melting point. Purity was 99.5% as determined by GLC analysis. Catalyst preparation, analysis, and activation were described earlier (*10*).

The experimental work was carried out at atmospheric pressure using the apparatus depicted in Fig. 1. A given catalyst, usually 3 g, was placed in the electrically heated Vycor reactor and raised to the reaction temperature over a period of an hour while a carrier gas, such as nitrogen, was passed through the system. Using a syringe pump, a solution of ketoxime in a given solvent (10 to 30 wt% oxime) was continuously passed through the system. At reaction temperatures of 250° to 350°C, 90% of the product was collected in the first ice-cooled receiver. Samples were removed periodically and analyzed by GLC. A programmed F and M chromatography unit was used for the analysis and a column of 20% silicone gum rubber on Diatoport S was used for separations. In all cases, peak areas were corrected by comparison with standard mixtures.

Products were identified by retention times on the chromatograph and by physical separation and identification using melting point and infrared spectral comparisons.

The catalysts used in this work are adequately described in the previous paper of this series (*13*).

RESULTS AND DISCUSSION

The results from passing ketoximes over acidic crystalline aluminosilicates are summarized in Table 1. Of all the catalysts evaluated for the Beckmann rearrangement, hydrogen zeolite Y (HY) proved the most satisfactory.

Beckmann rearrangement catalyzed by HY. When acetone oxime was passed over HY at 325°C (Table 1), conversions of 30% to *N*-methylacetamide were obtained. High selectivity for amide was observed, and there was no appreciable coking observed after several hours on stream. Under similar conditions, but at 450°C, conversion increased to 55%, but selectivity for *N*-methylacetamide was drastically reduced to 30%, as extensive fragmentation was observed.

Acetophenone oxime (I) gave even higher overall conversions (93%) at 300°C, using HY and similar reaction conditions. Selectivity for acetanilide (II) was 95%, with the remaining amide fraction (5%) consisting of *N*-methylbenzamide (III). The high ratio of (II):(III) (19:1) is in accordance with the *anti* position of the

TABLE 1
BECKMANN REARRANGEMENT REACTIONS OVER ACID ZEOLITES[a]

			Highest conversion of oxime[d]		
Catalyst[b]	Oxime reactant (%)[c]	LHSV	Temp. (°C)	Total conversion	% Selectivity for amide
HY	Acetone (20%)	1.5	325	31	100
HY	Acetone (20%)	1.5	450	55	31
HY	Acetophenone (20%)	1.1	300	93	96[e]
HY	Cyclohexanone (30%)	1.2	380	85	76
REX	Cyclohexanone (23%)	1.1	175	2	33
REX	Cyclohexanone (23%)	1.1	250	40	45
REX	Cyclohexanone (23%)	1.0	335	40	58
CuX	Cyclohexanone (5%)	0.9	325	79	0
CoX	Cyclohexanone (23%)	0.9	250	60	30
CoX	Cyclohexanone (23%)	0.9	330	97	51
ZnX	Cyclohexanone (20%)	1.0	325	69	52
NiX	Cyclohexanone (23%)	1.1	250	39	31
NiX	Cyclohexanone (25%)	1.1	300	44	66
H-Mordenite	Cyclohexanone (23%)	1.1	250	8	25
H-Mordenite	Cyclohexanone (5%)	1.0	325	51	47
H-Mordenite	Cyclohexanone (5%)	1.1	400	94	3
NaX	Cyclohexanone (23%)	1.1	300	62	0
NaX	Cyclohexanone (30%)	1.0	500	81	10
CuX	Cyclohexanone (30%)	1.0	500	72	6

[a] All reactions at 1 atm; nitrogen carrier gas (40 ml/min).

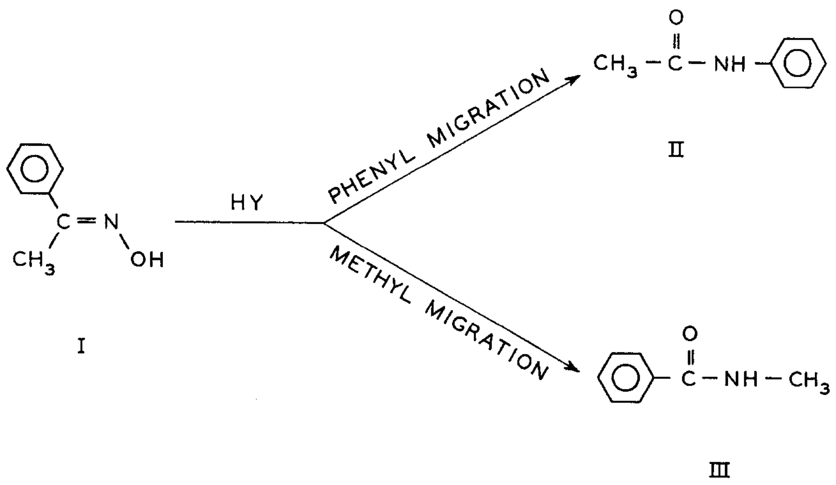
[b] No reaction when cyclohexanone oxime (23% in benzene) or acetone oxime (20% in benzene) passed over quartz at 300°C and LHSV 1.0.

[c] As solutions by weight in benzene.

[d] At time on stream of maximum activity: usually 2 or 3 hr.

[e] 95% acetanilide, 5% *N*-methylbenzamide.

phenyl ring in (I) (m.p. 59–60°C). The small amount of benzamide observed in the rearrangement of (I) may arise from isomerization of small amounts of oxime *prior* to rearrangement, rather than migration of a *syn*-methyl group. The lower temperature for rearrangement of (I) relative to the oximes of acetone and cyclohexanone is in accord with the generally greater migratory aptitude of phenyl,



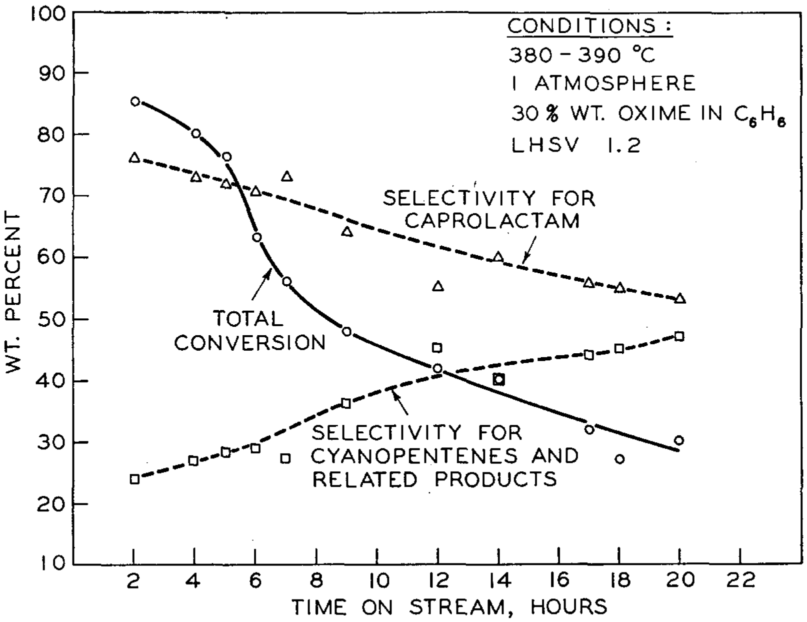
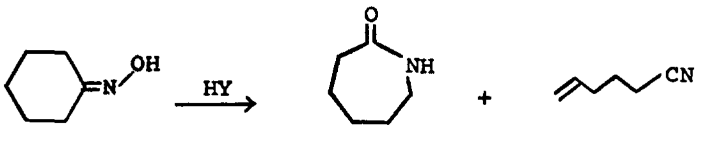


FIG. 2. Conversion of cyclohexanone oxime over HY catalyst.

relative to alkyl, in typical 1,2-shifts to electron-deficient migration centers (*12*).

High initial (2 hr) conversions (85%) of cyclohexanone oxime (IV), with 76% selectivity for caprolactam (V) were observed with HY catalyst at 380–390°C (Table 1 and Fig. 2). Of the 24% of by-products, 5-cyano-1-pentene (VI) constituted the largest proportion, together with small amounts of internal double bond isomers of (VI), cyclohexanone [from hydrolysis of (IV)] and traces of cyclohexanol. Compound (VI) has specifically been reported in the rearrangement of (IV) catalyzed by other acids (*9*), and the formation of ω-olefinic nitriles has generally been observed (*4*) in the Beckmann rearrangement of dialkyl or alicyclic ketoximes.



IV V VI

As the reaction was continued, overall conversion decreased to about 30% after 20 hr, with a drop to 50% selectivity for caprolactam (V).

Reactions of cyclohexanone oxime (IV) over REX catalyst. Initial studies employing stirred mixtures of molten oxime and a rare earth zeolite X (REX) catalyst (at 80–130°C) gave only low conversions, with 5-cyano-1-pentene (VI) as major product. Beckmann rearrangement reactions of (IV) in benzene solution at higher temperatures are shown in Table 1.

Effect of temperature. The effects of an increase in temperature from 250° to 350°C on the product distribution and reaction rates of cyclohexanone oxime over a REX catalyst are shown in Fig. 3. Roughly equal parts of caprolactam (V) and 5-cyano-1-pentene (VI) were noted throughout the middle portion of the run. At the higher conversions, appreciable quantities of by-products, including isomers of (VI) and cyclohexanone were observed.

Of particular interest was the elimination of an induction period and generally higher

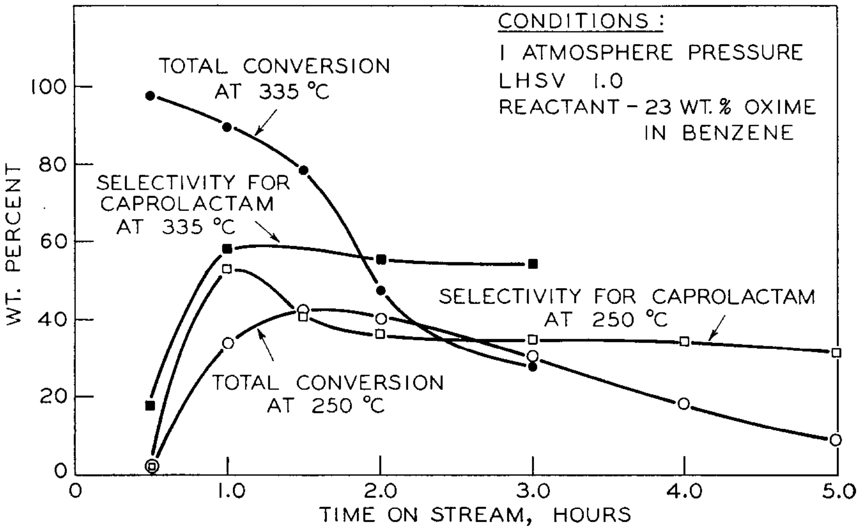


FIG. 3. Effect of temperature on Beckmann rearrangement using REX catalyst.

selectivity for caprolactam formation at the higher temperatures. Cyanopentenes comprise the bulk of side products. Above 400°C caprolactam decomposition was observed.

Effect of pressure. The effect of 300 psig operating pressure on the conversion of cyclohexanone oxime at 200° to 250°C over REX catalyst was to decrease selectivity for caprolactam formation. While total conversions were very high, the principal product at elevated pressures was (VI).

There was no evidence for visible coke formation on the REX catalysts in the runs under pressure, and regeneration could be effected by extraction with hot benzene using a Sohxlet extractor. About 10% wt of a viscous yellow oil was separated from the catalyst in this manner.

Effect of solvents. The nature of the solvent had important effects on the rearrangement of cyclohexanone oxime (IV) over REX catalyst (Table 2). Moderate conversions (30–40%), with fair selectivity for caprolactam [(V), 60–45%] were obtained with nonpolar solvents such as cyclohexane and benzene. A more polar solvent, methanol, markedly decreased selectivity for (V), while still showing about 38% conversion. Acetic acid, however, completely inhibited the rearrangement reaction under these conditions.

This direction in solvent effects is opposite to that in many homogeneous rearrangement systems (*4*), where reaction rate is enhanced in solvents with high dielectric constant or ionizing power. The cause is probably competitive adsorption of the polar solvents at catalyst acidic sites, where they may undergo subsequent decomposition. This would effectively block reactants from sites active for rearrangement.

TABLE 2
EFFECT OF SOLVENT ON CONVERSION OF CYCLOHEXANONE OXIME OVER REX CATALYST AT 250°C

Solvent[a]	LHSV	Highest total conversion of oxime[b]	% Selectivity for caprolactam
Cyclohexane	1.0	30	60
Benzene	1.1	40	45
Methanol	1.1	38	26
Acetic acid	1.0	2	0

[a] 20% wt solutions of oxime; 1 atm; N_2 carrier.
[b] Usually at 2–3 hr on stream.

Reaction of cyclohexanone oxime over other catalysts. As shown in Table 1, CoX, ZnX, NiX, and H-mordenite all demonstrated appreciable catalytic activity for rearrangement to caprolactam (V) at temperatures near 325°C, while CuX and NaX were inactive under similar condi-

TABLE 3

EFFECT OF CARRIER GASES ON THE CONVERSION OF CYCLOHEXANONE OXIME[a]

Catalyst	Carrier gas (ml/min)	Highest conversion of cyclohexanone oxime: Temp. (°C)	Time (hr)	Total conversion[b]	% Selectivity for caprolactam[c]
REX	CO (23.6)	340	1	44	64
			2	22	23
REX	CO_2 (23.6)	350	1	100	26
			2	76	59
			3	39	64
REX	NH_3 (23.6)	340	1	48	50
			2	21	53
REX	N_2 (142)	330	1	84	61
			3	30	57
NiX	N_2 (47.0)	300	1	99	3
			5	14	72
NiX	H_2 (50.0)	300	1	99	17
			5	99	26
			10	95	55

[a] Solutions (23% wt) in benzene, atmospheric pressure, LHSV 0.9–1.1.

[b] Of oxime to all other products.

[c] Based on converted oxime.

tions. Both catalysts provided low conversions to caprolactam at higher temperatures.

Effect of carrier gas on rearrangement of cyclohexanone oxime. With REX catalyst, the use of carbon dioxide or nitrogen as carrier gases, under otherwise similar conditions, gave high total conversion and relatively high selectivity for caprolactam (V) as shown in Table 3. With the more basic gases, carbon monoxide and ammonia, lower total conversions were observed, although a fairly high selectivity for (V) was observed in the case of ammonia. With NiX, however, a most striking extension of catalyst life was associated with the use of hydrogen as a carrier gas, as contrasted with nitrogen. Here, conversions of 95–99% were maintained for as long as 10 hr, with conversion of as much as 10 g of oxime/g of catalyst. Selectivity for (V) steadily increased with time on stream to 55% at 10 hr.

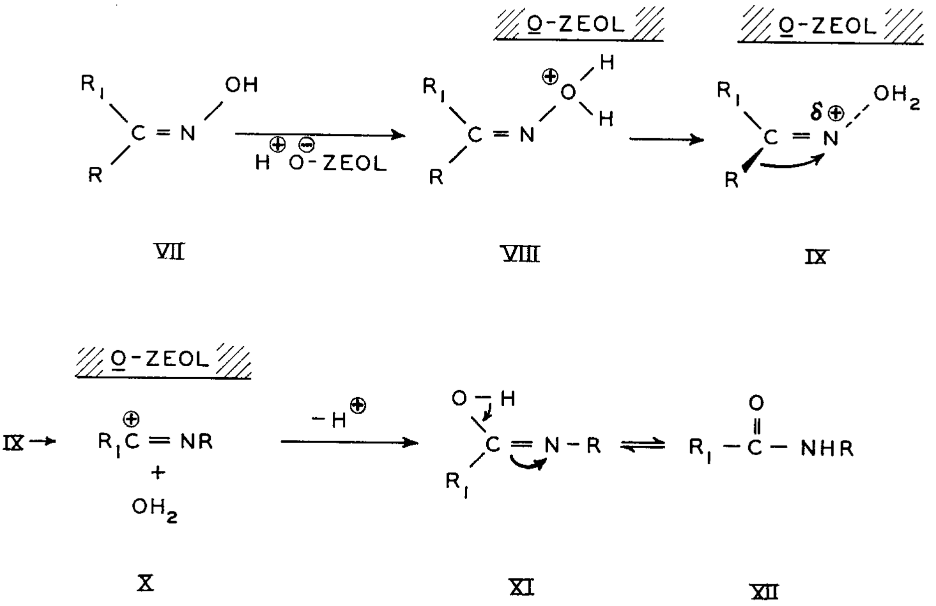
MECHANISTIC CONSIDERATIONS

The rearrangement reactions over acidic crystalline aluminosilicate catalysts probably involve initial adsorption of ketoxime (VII) at a catalyst acid site, forming the conjugate acid, (VIII). The acid site is represented as protonic (*11*), although, other types of polar, electron-withdrawing sites could be involved. In the next stage, intramolecular migration of a group (with its pair of electrons) *anti* to the departing hydroxyl function occurs, (IX), with the electron-deficient nitrogen atom formed by partial ionization of the oxygen–nitrogen bond as migration terminus. The resulting imine derivatives [(X) and (XI)] may then rearrange to the amide (XII).

In the case of cyclohexanone oxime (IV), the formation of 5-cyano-1-pentene (VI) may be visualized as proceeding through a competitive process where the developing positive charge on the nitrogen atom is stabilized by negative charge arising from beta scission (XIII), rather than alkyl migration as in (IX) above. In (XIII), the events are pictured as proceeding via a wholly concerted transition state, although an intermediate such as (XIV), with carbonium ion character, might be involved.

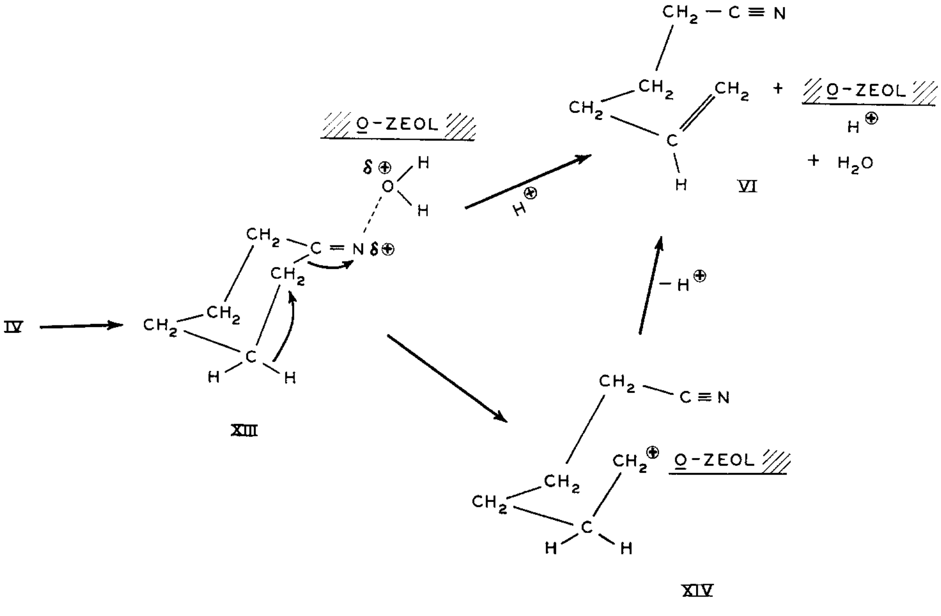
CONCLUSIONS

Thus, the Beckmann rearrangement of simple dialkyl, arylalkyl, and alicyclic ketones has been shown to be catalyzed by acidic, crystalline aluminosilicates. Opti-



mum rearrangement of ketoxime to amide was generally observed at atmospheric pressure, and temperatures of 300–380°C, with dilute solutions of oxime in nonpolar solvents and with nonbasic carrier gases. In one case (NiX), the use of hydrogen as carrier gas had important effects in prolonging catalyst life. Selectivity for amide was critically dependent on temperature, and a carefully controlled balance between conversion and selectivity was necessary.

Based on product distributions, the heterogeneous, aluminosilicate-catalyzed rearrangements appear to be rather similar to those observed in homogeneous acidic systems. Typical Beckmann rearrangements catalyzed by sulfuric acid proceed efficiently at 100–140°C, while those catalyzed by



sulfur trioxide, phosphorus pentachloride, or hydrogen fluoride are carried out near or below room temperature (*4*). The reasons for the higher temperatures required for reaction in the crystalline aluminosilicate systems may be related to those discussed earlier for the analogous phenomenon in alkylation (*11*).

Generally, the greatest limitations in these reaction systems were rapid catalyst aging and low selectivity for amide. Nevertheless, 3 to 5 g of oxime/g of catalyst were commonly converted over several hours on stream, and in one case 10 g of caprolactam/g of catalyst was obtained. This emphasizes the heterogeneous nature of the catalysis and sets it apart from sulfuric or phosphoric acid catalysis, where only one mole of caprolactam can be obtained from one mole of acid.

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