JOURNAL OF CATALYSIS **131**, 394–400 (1991)

Catalytic Properties of Crystalline Titanium Silicalites

III. Ammoximation of Cyclohexanone

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Received January 29, 1991; revised May 7, 1991

The ammoximation of cyclohexanone to cyclohexanone oxime over the titanium silicalite TS-1 with NH_3 and H_2O_2 is reported. The ammoximation takes place at conversions exceeding 90% with selectivities greater than 99%. The influence of various catalyst and process parameters on the oximation reaction is reported. By-products from condensation reactions become significant at low concentrations of H_2O_2 and NH_3. Possible mechanisms for the formation of the oxime and by-products are reported. © 1991 Academic Press, Inc.

INTRODUCTION

The titanium silicalite molecular sieve, TS-1, has been reported (*1–3*) to catalyze many oxidation reactions in the presence of dilute hydrogen peroxide. In an earlier paper of this series (*4*), we reported the TS-1 catalyzed hydroxylation of phenol to hydroquinone and catechol using hydrogen peroxide. The present paper deals with the ammoximation of cyclohexanone to cyclohexanone oxime in high yields over TS-1 in the presence of hydrogen peroxide and ammonia.

Cyclohexanone oxime is the key intermediate in the manufacture of ε-caprolactam. The conventional routes to its (oxime) production involve numerous steps and the use of hazardous chemicals like oleum, halides, and oxides of nitrogen. In addition, large quantities of the low value by-product ammonium sulfate are often co-produced. The direct formation of cyclohexanone oxime by reacting cyclohexanone with NH_3 and O_2 in the gas phase has also been reported (*5*). The yields, however, were found to be low (*5*). Recently, details of the ammoximation of cyclohexanone in good yields over TS-1 without the coproduction of ammonium sulfate has been reported (*6, 7*).

We now present additional information on ammoximation of cyclohexanone by TS-1. Possible mechanisms of the ammoximation reaction and reasons for the formation of the by-products are also discussed.

EXPERIMENTAL

Details regarding the synthesis and characerization of the TS-1 samples used in this study have already been described in part I (*8*) of this series. The catalysts (TS-1) used in this study were pretreated by refluxing with 0.1 *N* H_2SO_4 (15 ml/g of catalyst) and 26 wt% H_2O_2 (1 ml/g of catalyst) at 358 K for 2 h, then were washed, dried, and calcined at 773 K for 6 h. The amorphous SiO_2–TiO_2 mixture used in this study was obtained by co-gelling tetraethylorthosilicate and titanium tetrabutoxide with tetrapropylammonium hydroxide (gel precursor used in TS-1 synthesis (*4*)). The gel was washed, dried, and calcined at 773 K. Its Si/Ti ratio was 45. Powder XRD revealed the SiO_2–TiO_2 to be fully amorphous.

The catalytic runs were carried out in a three-necked glass flask (200 ml capacity) fitted with a mechanical stirrer, a condenser, and a rubber septum through which aqueous H_2O_2 could be injected using a feed pump (Sage instruments, USA). The temperature of the reaction vessel was maintained using an oil bath. In a standard run, 10 g of cyclohexanone, 12 g (22 wt%) of

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TABLE 1

Influence of Titanium Content of TS-1 on the Oximation of Cyclohexanone

Catalyst:	ZSM-5[a]	SiO_2–TiO_2	TS-1				
x = [Ti/Si + Ti]:	0	0.022	0[b]	0.010	0.021	0.042	0.091
cyclohexanone conversion (wt%):	1.9	13.5	7.4	82.5	92.9	90.1	87.7
Product distribution (wt%)							
Cyclohexanone	98.1	86.5	92.6	17.5	7.1	9.9	12.3
Cyclohexanone oxime	1.8	12.9	7.1	82.4	92.6	88.4	83.3
ε-caprolactam	—	—	0.1	0.2	0.2	0.2	0.2
Others[c] (I)	0.1	0.6	0.3	—	0.1	1.5	4.2
	(I)	**(I)**	**(I)**		**(I)**	**(I)**	**(I, II)**
Oxime selectivity (wt.%)	94.7	95.5	94.6	99.9	99.7	98.1	95.9

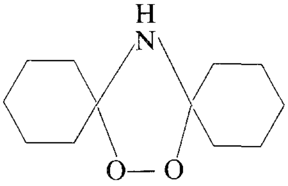
Note. Reaction conditions: Temperature = 333 K; Feed = cyclohexanone : NH_3 : H_2O_2 (1 : 1.5 : 1 molar ratio); duration of run = 6 h.

[a] Si/Al = 43.

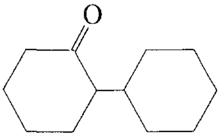
[b] Silicalite-1.

[c] Compound I was always the major by-product; for example, in the case of TS-1 with x = 0.091, the breakdown of the 4.2% (others) is **I**, 3.8% and **II**, 0.4%.

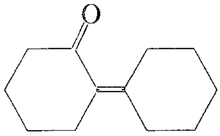
(I)
Peroxy dicyclohexylamine



(IIa)
2-cyclohexylidenecyclohexanone



(IIb)
2-(1-cyclohex-1-en-1-yl)-cyclohexanone



ammonia solution, and 1 g of the catalyst (particle size 300–400 mesh) were taken in the reaction vessel and warmed to the desired temperature. An aqueous solution of H_2O_2 (26 wt%, 13.3 g) was injected dropwise by a feed pump over a period of 4 h. The reactions were carried out in a three-phase system, viz., a solid catalyst phase, an aqueous phase, and an organic phase. At the end of the reaction (6 h), the reaction mixture was extracted with diethyl ether and analyzed using a gas chromatograph (Hewlett–Packard 5880 A; capillary column HP1, cross-linked methyl silicone gum, 50 m × 0.5 mm; FID detector). In view of the large differences in the response factors for the different components of the products, standard calibration mixtures were used to estimate their response factors accurately.

RESULTS AND DISCUSSION

The ammoximation of cyclohexanone was found to proceed with good yields over the titanium silicalite TS-1. A number of process and catalytic variables were found to affect the reaction. These are discussed below.

1. *Influence of titanium content.* Table 1 presents the results of the ammoximation of cyclohexanone with ammonia and dilute hydrogen peroxide over ZSM-5, amor-

phous SiO_2–TiO_2, Silicalite-1, and crystalline titanium silicalite (TS-1) with varying amounts of titanium. The major product of the reaction is found to be cyclohexanone oxime, while small amounts of ε-caprolactam and some dimeric compounds are also produced (Table 1, footnote). It is noted from the table that the relative activities of various catalysts increase in the order ZSM-5 < Silicalite < SiO_2–TiO_2 < TS-1. The much larger activities of SiO_2–TiO_2 (Si/Ti = 45) and TS-1 suggest that the active centres are Ti-related species. This is further confirmed by the increase in conversion observed with increasing Ti content of TS-1. Interestingly, however, while Silicalite (*9*) is found to possess some catalytic activity, ZSM-5 possesses very little activity (7.4% for Silicalite and 1.9% for ZSM-5). Both ketone conversion and selectivity to oxime increase on increasing the Ti content up to an atom fraction of 0.021. However, beyond $x = 0.021$, the activity decreases. In the case of zeolites, similar maxima in activities observed with variations in SiO_2/Al_2O_3 ratios have often been related to "efficiency maxima" (a combination of number and strength) of the acid centres (*10, 11*). Likewise, it is possible that maxima efficiency for TS-1 exists at an intermediate Ti content. Oxime selectivity is greater than 95% in all the cases, though a maximum selectivity (>99%) for the oxime is obtained over TS-1 with $x = 0.021$. Amorphous SiO_2–TiO_2 was found to be less active than crystalline TS-1 in terms of conversion of the ketone and selectivity to H_2O_2 and oxime. These results also suggest that the Ti^{4+} present in TS-1 is different from that present in SiO_2–TiO_2. Amorphous TiO_2 and SiO_2 were also examined as catalysts and were found to be inactive for the oximation of cyclohexanone. A small amount of ε-caprolactam formed by the rearrangement of the oxime over TS-1 was invariably found in most of the reaction products. The ε-caprolactam yield was independent of the Ti content of the sample.

TABLE 2

Influence of Reaction Temperature on the Oximation of Cyclohexanone over TS-1

	Temperature (K)				
	298	313	333	353	373
Cyclohexanone conversion, (wt%):	60.5	81.3	92.9	74.4	57.5
Product distribution (wt%)					
Cyclohexanone	39.5	18.7	7.1	25.6	42.5
Cyclohexanone oxime	60.5	81.3	92.6	65.8	47.5
ε-Caprolactam	—	—	0.21	0.3	0.3
Others	—	—	0.09	8.3[a] (**I, II**)	9.8[a] (**I, II**)
Oxime selectivity: (wt%)	100	100	99.7	88.5	82.3

Note. Reaction conditions: Catalyst = 1 g ($x = 0.021$); Feed = cyclohexanone : NH_3 : H_2O_2 (1 : 1.5 : 1 molar ratio); duration of run = 6h.

[a] **I** = 7.8, 8.2%; **II** = 0.5, 1.6%, at 353 and 373 K, respectively. (see footnote, Table 1 for **I** and **II**).

2. *Influence of the reaction temperature.* Both the conversion of cyclohexanone and the selectivity to oxime are dependent on the reaction temperature (Table 2). Conversion of cyclohexanone increases with increasing temperatures up to 333 K, beyond which it decreases. The decrease in conversion at higher temperatures (above 333 K) is probably due to the lower availability of NH_3 and H_2O_2 in the reaction mixture due to their more rapid loss at higher temperatures. The formation of high boiling compounds (>8 wt%) is observed at temperatures greater than 333 K. Again, in contrast to the light yellow color of the reaction mixture below 333 K, the color of the final product was dark red (–brown) above 340 K, which suggests the formation of large molecular conjugated products. The composition of the by-products (dimeric species) is also reported in Table 2 in the case of the high temperature experiments. The formation of compounds II(a) and II(b) has been reported in the literature at temperature above 473 K over SiO_2 and SiO_2–Al_2O_3 during ammoximation of cyclohexanone in the vapour phase with NH_3 and O_2 (*5*), and during aldol condensation over Al_2O_3 (*12, 13*) and Ni–Sn–SiO_2 (*14*). The formation of

compound I has also been reported over TS-1 by earlier workers (*6*). The identification of the various compounds was carried out by matching gas chromotograph retention times with pure compounds and also by isolating (in the case of I) and matching the IR and mass spectra with those of the known compound. The formation of peroxydicyclohexylamine (PDCA, I) consumes $\frac{1}{2}$ mole of H_2O_2 and $\frac{1}{2}$ mole of NH_3 for every mole of cyclohexanone consumed. 2-cyclohexylidenecyclohexanone (II a) and 2-(1-cyclohex-1-en-1-yl)-cyclohexanone (II b) do not require any H_2O_2 or NH_3 for their formation. Oxime formation needs 1 mole of H_2O_2 and 1 mole of NH_3 per mole of cyclohexanone. Thus at higher temperatures, as the NH_3 and H_2O_2 get depleted, the formation of these by-products sets in.

3. *Influence of NH_3/H_2O_2 molar ratio.* Although the ammoximation reaction requires equal moles of cyclohexanone, ammonia, and hydrogen peroxide, the observed results (Table 3) indicate that an excess of ammonia has to be taken initally to produce high yields of the oxime. Very high selectivities to cyclohexanone oxime (>99%) are obtained when the NH_3/H_2O_2 molar ratio is >1.5. Under these conditions, the formation of high boiling compounds is reduced. When the NH_3/H_2O_2 mole ratio is less than 1, the conversion of the ketone and the selectivity to the oxime decrease. Further, higher boiling compounds like peroxydicyclohexylamine (I), 2-cyclohexylidenecyclohexanone (IIa), and 2-(1-cyclohex-1-en-1-yl)-cyclohexanone (II b) are formed as by-products. The formation of ε-caprolactam (formed in small quantities in all cases) is independent of the reactant concentrations.

TABLE 3

Oximation of Cyclohexnone to Oxime—Influence of NH_3/H_2O_2 Molar Ratios

	NH_3/H_2O_2 molar ratio			
	0.5	1.0	1.5	2.0
Cyclohexanone conversion (wt%):	70.9	80.6	92.9	94.3
Product distribution (wt%)				
Cyclohexanone	29.0	19.4	7.1	5.7
Cyclohexanone oxime	58.6	78.1	92.6	94.1
ε-Caprolactam	0.3	0.2	0.2	0.2
Others	12.1[a] **(I, II)**	2.3[a] **(I, II)**	0.1 **(I)**	—
Oxime selectivity: (wt%)	82.7	96.9	99.7	99.8

Note. Reaction conditions: Temperature = 333 K; catalyst = 1 g (x = 0.021); duration of run = 6h.

[a] **I** = 10.7, 2.0%; **II** = 1.4, 0.3%, at NH_3/H_2O_2 = 0.5 and 1.0, respectively (see footnote, Table 1 for **I** and **II**).

TABLE 4

Influence of Catalyst Concentration on Cyclohexanone Oximation

	Catalyst concentration (g cat./mole ketone)				
	0	2	5	10	20
Cyclohexanone conversion (wt%):	0	35.9	88.1	92.9	96.7
Product selectivity (wt%)					
Cyclohexanone	100	64.1	11.9	7.1	3.3
Cyclohexanone oxime	—	34.8	87.2	92.6	96.4
ε-Caprolactam	—	0.3	0.2	0.2	0.2
Others[a]	—	0.8	0.1	0.1	0.1
Oxime selectivity (wt.%):	—	96.9	99.0	99.7	99.7

Note. Reaction conditions: catalyst = 1 g (x = 0.021); Feed = cyclohexanone : NH_3 : H_2O_2 (1 : 1.5 : 1 molar ratio); Temperature = 333 K; duration of run = 6h.

[a] Peroxy dicyclohexylamine, **I**.

At lower molar ratios of ammonia (<1.5), the reaction mixture was deep red in colour, probably due to the presence of the above by-products, especially those arising from the aldol condensation.

4. *The influence of catalyst concentration.* As the catalyst concentration is increased, both the conversion and the selectivity for the oxime increase (Table 4). At the catalyst loading of 20 g catalyst/mole ketone, the selectivity for the oxime is more than 99% and the yield of the high boiling products is small.

TABLE 5

Influence of the Method of Hydrogen Peroxide Addition on Cyclohexanone Oximation

	Method of H_2O_2 addition			
	A[a]	B[b]	C[c]	D[d]
Cyclohexanone conversion (wt%):	65.4	86.4	92.9	29.2
Product distribution (wt%)				
Cyclohexanone	34.6	13.6	7.1	70.8
Cyclohexanone oxime	64.3	85.7	92.6	27.3
ε-Caprolactam	0.1	0.2	0.2	—
Others[e]	1.0	0.5	0.1	1.9
Oxime selectivity (wt%):	98.3	99.2	99.7	93.5

Note. Reaction conditions: catalyst = 1 g (x = 0.021); Feed = cyclohexanone : NH_3 : H_2O_2 (1 : 1.5 : 1 molar ratio); Temperature = 333 K; duration of run = 6h.

[a] Method A: The entire quantity of the requisite H_2O_2 was added to the reaction mixture containing cyclohexanone and ammonia solution at 298 K and the temperature slowly raised to 333 K.

[b] Method B: H_2O_2 was added dropwise at 333 K for 1h to the reaction mixture containing cyclohexanone and ammonia solution, (reaction continued to 6 h).

[c] Method C: H_2O_2 was diluted with distilled water to 5% and was added dropwise for 4h at 333 K to the reaction mixture containing cyclohexanone and ammonia solution (reaction continued to 6 h).

[d] Method D: NH_3 solution was added dropwise for about 2h at 333 K to the reaction mixture containing cyclohexanone and hydrogen peroxide, (reaction continued to 6h).

[e] Peroxy dicyclohexylamine, **I**.

5. *Influence of the mode of hydrogen peroxide addition.* As both H_2O_2 and NH_4OH are decomposed and lost during the reaction, the amounts of the two reactants available for reaction with cyclohexanone will depend on the rate of decomposition of the above compounds at the different process parameters. Therefore, a slow continous addition of the two reactants will not only enhance conversion and selectivity but also increase the useful utilization of the two chemicals.

Table 5 illustrates the influence of the mode of addition of reactants. The different modes adopted are detailed in the table. Method C, in which cylcohexanone and ammonia are taken first along with the catalyst and dilute hydrogen peroxide (5 wt% in water) is added dropwise at 333 K for 4h, is found to be the most efficient. This mode of addition reduces the decomposition of the peroxide and the formation of other byproducts. On the other hand, method D, in which the ketone and peroxide are taken first and the ammonia solution added dropwise later on for about 2h, produces smaller quantities of the oxime. Higher boiling compounds are also formed. In method A, the entire quantity of the requistite amount of H_2O_2 is added to the reaction mixture containing the ketone and ammonia solution at 298 K, the system is slowly warmed to the reaction temperature (333 K), and the reaction is continued for 6 h. In this case the ketone conversion is moderate and the selectivity to oxime is good. It is to be noted that all the studies reported in the other sections in this paper were carried out according to method C (see experimental), which leads to maximum conversion and oxime selectivity.

6. *Influence of solvents.* All the studies reported so far have been carried out in a three-phase (one solid and two liquid phases) mixture. The obvious question is: will the conversion of the two liquid phases (organic and inorganic) into a single phase improve the efficiency of the process? Roffia *et al.* (*7*) have reported the influence of various solvents on the reaction. Though they have reported a mixture of water and *t*-butanol to be the best solvent at 353 K (conversion 89.7% and oxime selectivity 99.5%), we have found that at a lower temperature (333 K) the absence of solvents leads to good results (conversion 92.9% and selectivity 99.7%, Table 6). However, both conversion and selectivity are lower in the absence of solvents at the higher temperature of 353 K (see Table 2).

Mechanism of Ammoximation over TS-1

The presence of —Ti═O and —Ti—O—Si— in TS-1 have been reported by earlier workers (*15–17*). Similarly, the transformation of —Ti═O or —Ti—O—Si— groups in the presence of H_2O_2 into a hydroxy peroxy (or peroxy) titanium species has also been reported (*3, 15*):

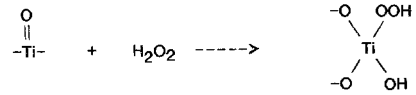
TABLE 6

Influence of Solvent on the Oximation of Cyclohexanone

	Solvent			
	Methanol	2-propanol	*t*-butanol	no solvent
Cyclohexanone conversion (wt%):	66.0	42.3	57.0	92.9
Product distribution (wt%)				
Cyclohexanone	34.0	57.7	43.0	7.1
Cyclohexanone oxime	36.0	42.3	56.8	92.6
ε-Caprolactam	—	—	—	0.2
Others[a]	30.0 **(I, III)**	—	0.2 **(I)**	0.1 **(I)**
Oxime selectivity (wt%):	54.5	100	99.6	99.7

Note. Reaction conditions: Catalyst = 1 g (x = 0.21); Feed = cyclohexanone : NH_3 : H_2O_2 (1 : 1.5 : 1 molar ratio); duration of run = 6h, Temperature = 333 K.

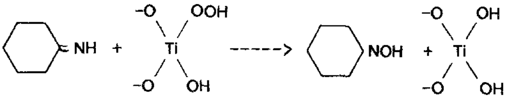
[a] **I** = 18%; **III** = methylamines, 12% (see Table 1, footnote).



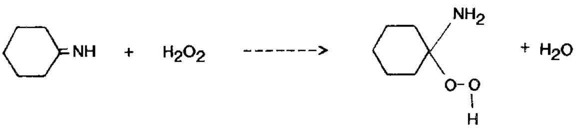
Caro's acid, H_2SO_5, a hydroxy peroxy acid, converts secondary amines to oximes (*18*):

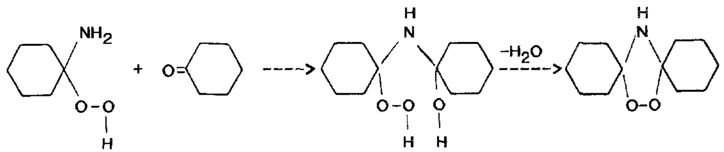
By analogy, a mechanism can be written for the ammoximation of ketones with H_2O_2 and NH_3 in the presence of TS-1. First, we can visualize the formation of an unstable imine as follows:

The imine ("an internal secondary amine") can react with the peroxy titanium catalyst to yield the oxime,



when the amount of catalyst (or Ti/(Si + Ti) ratio of the catalyst) is small, i.e., when there are not enough peroxy titanium complexes to insert an "O" rapidly into the imine, the formation of peroxydicyclohexylamine (PDCA) is favoured (Tables 1 and 4):





(PDCA)

CONCLUSIONS

The oximation of cyclohexanone at high conversions (>94%) and excellent selectivities (>99%) is possilbe using the titanium silicate molecular sieve, TS-1, at temperatures as low as 333 K. The yield is maximum at NH_3/H_2O_2 (mole) ratios >1.5 and a temperature of 333 K in the absence of solvents. Similarly, a moderate Ti content (Ti/Si + Ti = 0.021) favours increased yields of the oxime.

ACKNOWLEDGMENTS

This work was partly funded by UNDP. A. Thangaraj thanks CSIR for a research fellowship.

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