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Ammoximation of cyclohexanone over a titanium silicate molecular sieve, TS-2

J. Sudhakar Reddy, S. Sivasanker and **P. Ratnasamy**
National Chemical Laboratory, Pune 411 008 (India)

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Abstract

The catalytic activity and selectivity of the titanium silicate molecular sieve, TS-2 (having ZSM-11 structure), in the ammoximation of cyclohexanone and other carbonyl compounds with H_2O_2 and NH_3 is reported in this paper. The studies were carried out at different temperatures and reactant concentrations and with different catalysts. TS-2 produces cyclohexanone oxime with high selectivities, while silicalite-2 and SiO_2 produce large quantities of the condensation product, peroxydicyclohexylamine. Similarly, when the concentrations of cyclohexanone and H_2O_2 are larger than that of NH_3, the formation of the byproducts is favoured. Based on the above results, mechanisms for the formation of cyclohexanone oxime and peroxydicyclohexylamine are presented.

Introduction

The use of zeolites as catalysts in the manufacture of organic fine chemicals is an important and growing field [1]. The production of cyclohexanone oxime is a major step in the production of nylon-6. The methods presently employed in the manufacture of cyclohexanone oxime are associated with the coproduction of ammonium sulfate and the use of hazardous chemicals such as oleum, halides and nitrogen oxides [2]. There have been many attempts to modify the process to avoid the use of corrosive and environmentally undesirable reactants. Gas phase ammoximation using NH_3 and O_2 has been reported [3], but the yields were low. Recently the titanium silicate molecular sieve, TS-1, was found to catalyze the conversion of cyclohexanone into the oxime in the presence of NH_3 and H_2O_2 with high selectivities without the co-production of any ammonium sulfate [4, 5]. TS-1 is a titanium isomorph of ZSM-5 and has a MFI-type structure.

We have recently reported the synthesis of another titanium silicate, TS-2, having a MEL (ZSM-11) structure [6]. The detailed catalytic properties of this new molecular sieve are yet to be investigated. In this paper, we report the oximation of cyclohexanone using ammonia and hydrogen peroxide over TS-2.

Experimental

The titanium molecular sieve with MEL structure (TS-2) was synthesized by mixing tetrabutyl ammonium hydroxide, tetraethyl orthosilicate and titanium butoxide, and autoclaving the mixture at 443 K for 48 h. The details of the synthesis and characterization of this new titanium silicate have already been reported elsewhere [6, 7]. The as-synthesized TS-2 was filtered, washed, dried and calcined in dry air for 16 h at 823 K. The calcined form of the zeolite was treated with 1 N ammonium acetate solution and calcined at 773 K for 6 h prior to use in the reaction.

The other zeolites used in this study, *viz.* silicalite-2, ZSM-11 and Al-TS-2, were synthesized as per published procedures [8–10] and converted in the H-form by conventional techniques.

The reactions were carried out in a three-necked flask (250 ml); one neck was fitted with a mechanical stirrer, another with a condenser and the third with a rubber septum. The temperature was maintained using an oil bath. The standard reaction conditions were: 1 g catalyst, temperature 353 K, and cyclohexanone:H_2O_2:NH_3 molar ratio 1:1:4. The reaction time was 5 h. Hydrogen peroxide (26 wt.%) was injected dropwise through the septum using a feed pump (Sage Instruments, USA) over a period of 2 h. After the addition of hydrogen peroxide, the reaction was continued for another 3 h. After completion of the reaction, the organic products were extracted with ether and analyzed in a gas chromatograph (Hewlett Packard 5880 A) equipped with a capillary column (50 m × 0.25 mm crosslinked methyl silicone gum).

Results and discussion

Though the ammoximation of cyclohexanone to its oxime over the molecular sieve TS-1 has already been reported [4, 5], no reports on the mechanism of the reaction are available. We have carried out our studies on the ammoximation of cyclohexanone and other carbonyl compounds using TS-2 as a catalyst in an attempt to clarify the reaction mechanism.

Comparison of TS-2 with other catalysts

Silicalite-2, ZSM-11 and TS-2 possess the same MEL framework structure. The differences among them lie in the composition of the framework. While silicalite is a pure silica molecular sieve, ZSM-11 and TS-2 possess additionally Al^{3+} and Ti^{4+} ions respectively in the lattice. While the presence of Al^{3+} lends acidity to the system, Ti^{4+} ions do not. However, they make the molecular sieve active in oxidation reactions, especially those involving hydrogen peroxide. Al-TS-2 possesses both Al^{3+} and Ti^{4+} ions and should hence take part in both acid-catalyzed and oxidation reactions. It is, therefore, interesting to compare the activities and selectivities of the MEL isomorphs silicalite-2, ZSM-11, TS-2 and Al-TS-2 in the oximation of cyclohexanone. The results of the studies using the different catalysts are presented in Table 1. Though the major product over most of the catalysts is the desired cyclohexanone oxime, byproducts are also formed in considerable amounts over the non-Ti-catalysts. The names and structures of the products formed in the reaction are given below.

TABLE 1

Ammoximation of cyclohexanone over different catalysts[a]

	Catalyst						
	ZSM-11	SiO_2[b]	Si-2[c]	TS-2 Si/Ti mol.ratio			Al-TS-2[d]
				27	70	125	
Cyclohexanone conversion (wt.%)	17.7	55.3	44.9	84.5	53.5	35.1	19.1
product distribution (wt.%)							
cyclohexanone oxime	1.3	1.8	3.8	80.2	48.5	28.4	12.3
peroxydicyclohexyl amine	12.0	47.1	34.4	3.2	4.2	4.4	2.2
others[e]	4.4	6.4	6.7	1.1	0.8	2.3	4.5
oxime selectivity (wt.%)	7.4	3.3	8.5	94.9	90.7	80.9	64.6

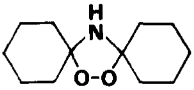
[a] Reaction conditions: temperature = 353 K; feed (moles) = cyclohexanone:NH_3:H_2O_2 = 0.102:0.40:0.102; catalyst = 1 g; reaction duration = 5 h.

[b] Fumed silica, Type S-5005, supplied by Sigma Chemical, USA.

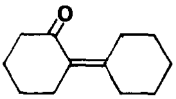
[c] Si-2 = silicalite-2.

[d] Si/Ti = 70; Si/Al = 69.

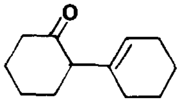
[e] Others: 2-cyclohexylidene cyclohexanone and 2-(1-cyclohexen-1-yl)cyclohexanone.



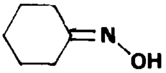
peroxydicyclohexyl amine



2-cyclohexylidene cyclohexanone



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



cyclohexanone oxime

An examination of the data (Table 1) reveals that the catalysts can be arranged in the following orders (increasing) for activity (conversion of cyclohexanone), selectivity for cyclohexanone oxime and its yield (conversion × selectivity).

Activity:	TS-2 > SiO_2 > Si-2 > Al-TS-2 > ZSM-11
Selectivity:	TS-2 > Al-TS-2 > Si-2 > ZSM-11 > SiO_2
Yield:	TS-2 > Al-TS-2 > Si-2 > SiO_2 > ZSM-11

The results show that while Ti increases the activity, Al ions have just the opposite effect. This is clear from the lower activity of Al-TS-2 when compared to SiO_2 and silicalite-2. However, interestingly, the selectivity for oxime is higher in the case of Al-TS-2 (which contains Ti ions also) than silicalite-2 and SiO_2. The net yield of oxime is found to be dependent on the presence of Ti in the sample.

The pure silica materials (SiO_2 and silicalite-2) favour the formation of peroxydicyclohexylamine, PDCA (a condensation product with NH_3 and H_2O_2), while the presence of Ti in the system favours the formation of the oxime, suppressing the formation of PDCA. The reason for the low selectivity of the Al-containing samples (Al-TS-2 and ZSM-11) is the rapid decomposition of the H_2O_2 over the Al^{3+} centers of the zeolite.

Blank experiments carried out in the absence of any catalyst did not yield any oxime, though small amounts ($<3\%$) of PDCA were produced. Thus PDCA formation seems to be catalyzed by Si–OH groups on the surface of SiO_2 and the other catalysts.

The other byproducts found in the experiments, *viz.* 2-cyclohexylidene cyclohexanone and 2-(1-cyclohex-1-en-1-yl)-cyclohexanone, are aldol condensation products and are obtained in much smaller quantities. The yields of these two compounds also are larger in the absence of Ti.

Influence of temperature

The results of the experiments carried out at three different temperatures are presented in Table 2. It is noted that increasing the temperature increases the conversion and at the same time decreases the formation of byproducts. Lower temperatures seem to favour the formation of byproducts. Similar results have also been reported by earlier workers [4] during their study of the reaction over TS-1. The slight decrease in conversion at 373 K, the highest temperature studied, is probably due to the rapid loss of the reactants,

TABLE 2

Influence of temperature on the oximation of cyclohexanone over TS-2[a]

	Temperature, K		
	333	353	373
cyclohexanone conversion (wt.%)	77.6	84.5	82.0
product distribution (wt.%)			
cyclohexanone oxime	24.2	80.2	78.0
peroxydicyclohexyl amine	33.0	3.2	4.0
others[b]	20.5	1.1	–
oxime selectivity (wt.%)	31.2	94.9	95.1

[a] Reaction conditions: catalyst = 1 g (Si/Ti = 27); feed (mol) = cyclohexanone:NH_3:H_2O_2 = 0.102:0.40:0.102; reaction duration = 5 h.

[b] Others: 2-cyclohexylidene cyclohexanone and 2-(1-cyclohexen-1-yl)cyclohexanone.

NH_3 and H_2O_2, at the higher temperature and thus their nonavailability for the reaction.

Influence of catalyst amount

Increasing the catalyst concentration (Table 3) to 10 g catalyst/mole of cyclohexanone increases the conversion and also decreases the formation of byproducts, thereby increasing the selectivity for oxime formation. However, beyond the 10 g level, the conversion did not increase, but the selectivity improved further. In Table 1, the influence of increasing Ti content of TS-2 on the reaction was reported. It was observed that increasing the Ti content increased both conversion and selectivity. The influence of increasing Ti content and catalyst amount are similar.

Influence of solvent

The results reported in Tables 1 to 3 were carried out in the absence of a solvent in a 3 phase system, *viz.* a solid catalyst phase, and two liquid phases, an organic and an aqueous phase. The addition of solvents such as methanol and t-butanol converts the two liquid phases into a single one. The influence of adding solvents on the conversion and selectivity are presented in Table 4. Surprisingly, the addition of solvents decreased the conversion, but the selectivity for oxime was not affected to any significant amount.

Influence of duration of run

The influence of duration of the run on product formation was studied by analyzing samples of the reaction mixture at different intervals of time over a period of 5 h. The results are presented in Fig. 1. The experiment was carried out in t-butanol with a small amount of catalyst (5 g per mol

TABLE 3

Influence of catalyst concentration on the oximation of cyclohexanone over TS-2[a]

	Catalyst concentration (g per mol ketone)			
	0	5	10	15
cyclohexanone conversion (wt.%)	<3.0	38.0	84.5	83.9
product distribution (wt.%)				
cyclohexanone oxime	0.0	29.7	80.2	80.7
peroxydicyclohexyl amine	<3.0	5.8	3.2	2.8
others[b]	0.0	2.5	1.1	0.4
Oxime selectivity (wt.%)	0.0	78.2	94.9	96.2

[a] Reaction conditions: catalyst = 1 g (Si/Ti = 27); temperature = 353 K; feed (mol) = cyclohexanone:NH_3:H_2O_2 = 0.102:0.204:0.102; reaction duration = 5 h.

[b] Others: 2-cyclohexylidene cyclohexanone and 2-(1-cyclohexen-1-yl)cyclohexanone.

TABLE 4

Influence of solvents on the oximation of cyclohexanone over TS-2[a]

	Solvent		
	none	methanol	t-butanol
cyclohexanone conversion (wt.%)	84.5	39.2	74.6
product distribution (wt.%)			
cyclohexanone oxime	80.2	37.2	69.1
peroxydicyclohexyl amine	3.2	1.4	5.3
others[b]	1.1	0.6	0.2
oxime selectivity (wt.%)	94.9	94.8	92.6

[a] Reaction conditions: catalyst = 1 g (Si/Ti = 27); temperature = 353 K; feed (mol) = cyclohexanone:NH_3:H_2O_2 = 0.102:0.40:0.102; reaction duration = 5 h; solvent used = 20 ml.
[b] Others: 2-cyclohexylidene cyclohexanone and 2-(1-cyclohexen-1-yl)cyclohexanone.

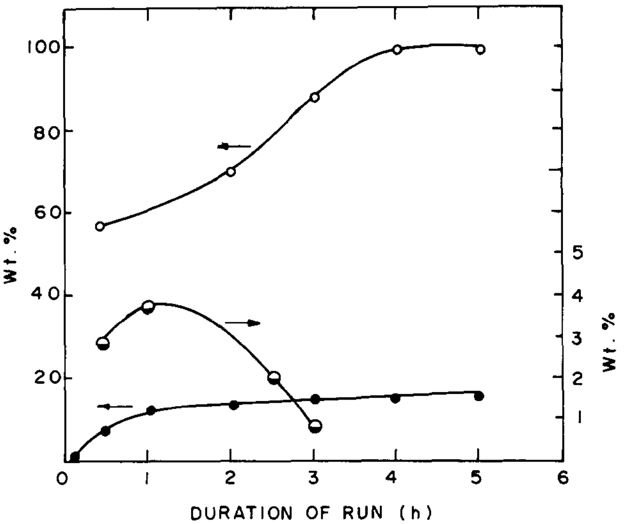


Fig. 1. Influence of duration of run on product yield in the ammoximation of cyclohexanone; (●) conversion of cyclohexanone, (○) selectivity for oxime, (⊖) yield of byproducts.

cyclohexanone) to keep the conversion low. It is observed (Fig. 1) that conversion and selectivity for oxime increase steadily with time. The yield of byproducts goes through a maximum. Initially, when the concentration of the reactants, especially cyclohexanone and H_2O_2, is large, the condensation products are formed rapidly. After a certain time their rate of formation decreases, with simultaneous breakdown and transformation into the desired cyclohexanone oxime.

Influence of concentration of reactants

The results of the experiments carried out at different concentrations of the reactants are presented in Table 5. The results indicate that when cyclohexanone and hydrogen peroxide are in excess, the byproducts are formed in significant quantities, and when ammonia is in excess when compared to either of the other two reactants, or when all the reactants are in equal quantities, the selectivity for oxime is maximum.

Ammoximation of other carbonyl compounds

The ammoximation of a number of compounds with carbonyl groups was carried out under typical conditions. The results of the studies are presented in Table 6. The activity of the compounds followed the decreasing

TABLE 5

Effect of concentration of reactants[a]

Reactants (mol)			Cyclohexanone conversion	Oxime selectivity	Product distribution (wt.%)		
cyclohexanone	H_2O_2	NH_3			CH	oxime	others
0.01	0.02	0.02	38.2	100.0	61.8	38.2	0.0
0.02	0.02	0.02	25.4	100.0	74.6	25.4	0.0
0.04	0.02	0.02	22.1	63.7	77.9	14.1	8.0
0.02	0.01	0.02	22.0	100.0	88.0	12.0	0.0
0.02	0.04	0.02	27.4	89.4	72.6	24.5	2.9
0.02	0.02	0.01	37.8	94.0	62.0	35.5	2.5
0.02	0.02	0.04	26.8	100.0	73.2	26.8	0.0

[a] Reaction conditions: catalyst wt = 1 g; temperature = 353 K; reaction time = 2 h; solvent = t-butanol; amount of solvent varied to keep total moles including solvent at 0.2; CH = cyclohexanone.

TABLE 6

Ammoximation of different carbonyl compounds over TS-2[a]

Reactant	Conversion (wt.%)	Selectivity to oxime (wt.%)	Product distribution (wt.%)	
			oxime	byproducts
cyclohexanone	84.5	94.9	80.2	4.3
benzaldehyde	100.0	96.0	96.0	4.0
acetophenone	54.3	98.2	53.3	1.0
benzophenone	0.4	50.0	0.2	0.2
2-butanone	85.0	98.2	83.5	1.5

[a] Reaction conditions: catalyst = 1 g (Si/Ti = 27); temperature = 353 K; feed (mol) = ketone:NH_3:H_2O_2 = 0.102:0.40:0.102; reaction duration = 5 h.

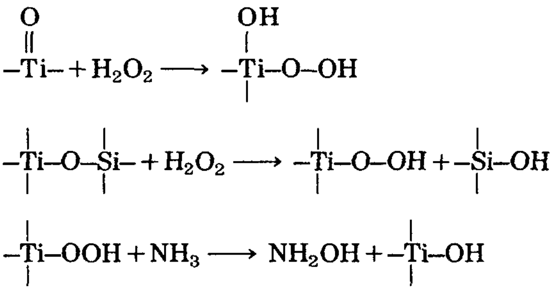
order: benzaldehyde > 2-butanone > cyclohexanone > acetophenone > benzophenone.

The high activity of benzaldehyde may be attributed to its more active carbonyl group, the activity of the carbonyl group increasing with increasing positive charge of the carbonyl carbon. The low activity of benzophenone could also be due to steric effects, and its difficulty to diffuse into the MEL pore system. The byproducts obtained in the case of the different compounds were not condensation products in all cases.

Mechanism of ammoximation over titanium silicate molecular sieves

Based on the results reported earlier, two possible mechanisms for the ammoximation of cyclohexanone can be proposed:

(1)



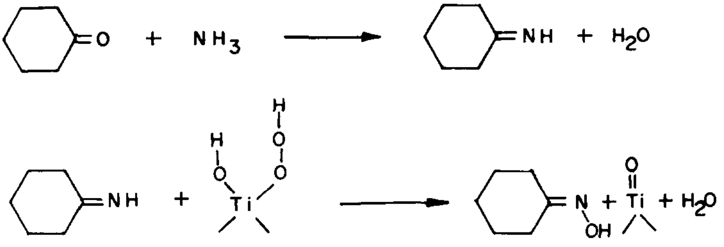
$$-\overset{\overset{O}{\|}}{Ti}- + H_2O_2 \longrightarrow -\underset{|}{\overset{\overset{OH}{|}}{Ti}}-O-OH$$

$$-\underset{|}{\overset{|}{Ti}}-O-\underset{|}{\overset{|}{Si}}- + H_2O_2 \longrightarrow -\underset{|}{\overset{|}{Ti}}-O-OH + -\underset{|}{\overset{|}{Si}}-OH$$

$$-\underset{|}{\overset{|}{Ti}}-OOH + NH_3 \longrightarrow NH_2OH + -\underset{|}{\overset{|}{Ti}}-OH$$

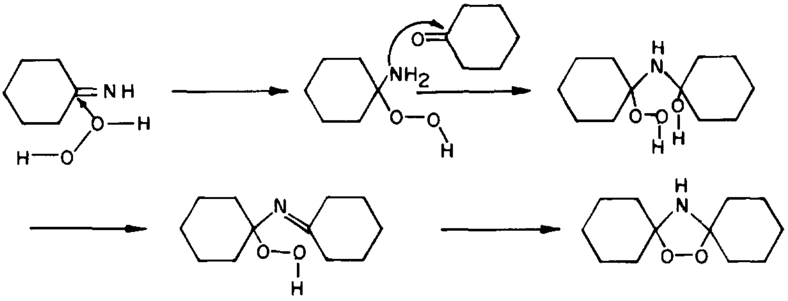
NH_2OH + cyclohexanone ⟶ cyclohexanone oxime + H_2O

(2)



Evidence for the presence of $-Ti{=}O$, $-Ti-OH$ and $-Ti-O-Si-$ groups in titanium silicates has already been reported by earlier workers [11–13]. Similarly, the transformation of $-Ti{=}O$ or $-Ti-O-Si-$ groups in the presence of H_2O_2 has also been reported [13, 14]. $-Ti-O-Si-$ groups have been shown to possess an IR absorption at 960 cm^{-1} [11]. On addition of H_2O_2, the 960 cm^{-1} band disappears and a new $-Ti-OOH$ species with absorption in the visible region at 425 nm appears [14]. The 960 cm^{-1} band has, however, been attributed by some workers [15] to $Ti{=}O$ species. In any case, the formation of the peroxytitano complex $-Ti-OOH$ is beyond doubt.

Though both mechanisms can be operative, the latter mechanism also explains the formation of the major byproduct, peroxy-dicyclohexyl amine. A possible mechanism for its formation could be:



Evidence supporting the above mechanism is that:

(1) Ti is not necessary to produce the byproduct;

(2) byproduct yield is greater when cyclohexanone and H_2O_2 concentrations are higher;

(3) when Ti is present, byproduct formation is suppressed, due to the rapid insertion of an oxygen atom from the peroxytitanium complex into the intermediate cyclohexylimine to produce the oxime.

If we assume that the formation of cyclohexylimine is catalyzed by surface silanol groups, the reason for the greater formation of PDCA in the case of silica and silicalite is evident.

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