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Ammoximation of Cyclic Ketones on TS-1 and Amorphous SiO_2–TiO_2

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Ammoximation of cyclic ketones on TS-1 and amorphous SiO_2–TiO_2 with H_2O_2 and NH_3 was studied. The reactivity of cyclic ketones over TS-1 and amorphous SiO_2–TiO_2 showed the following order: cycloheptanone > cyclopentanone > cyclohexanone > cyclooctanone. Shape-selective poisoning studies revealed that the active sites of TS-1 for ammoximation of cycloheptanone are mostly inside the molecular sieve. The reactivity of cyclohexanone and methylcyclohexanones over TS-1 followed the order cyclohexanone > 2-methylcyclohexanone ≒ 3-methylcyclohexanone > 2,6-dimethylcyclohexanone, reflecting the difference in the diffusivity among the reactants or products inside TS-1. Besides the diffusivity the reactivity seemed to be affected by the difficulty in access of the carbonyl group to the Ti active site inside the zeolite; from the comparison of reactivity of dimethycyclohexanone isomers, the steric hindrance of the substituent methyl group to the access of carbonyl group was considered to decrease in the following order: *β-equatorial* > *α-equatorial* > *β-axial* > *α-axial*. Diffusion of cyclohexanone or its oxime has been found to play an important role in the ammoximation when the TS-1 crystals larger than 1.5 μm were employed as a catalyst. For the TS-1 crystals smaller than 0.3 μm, the ammoximation activity was independent of the diffusivity factor and was determined by the number of active Ti sites present in the zeolite framework. © 1996 Academic Press, Inc.

INTRODUCTION

The titanium silicalite molecular sieves TS-1 and TS-2 have been reported to catalyze a variety of oxidation reactions in the presence of aqueous hydrogen peroxide (1–9). The production of cyclohexanone oxime is an important step in the production of nylon-6. The methods presently employed in the manufacture of cyclohexanone oxime cannot avoid the production of ammonium sulfate and the use of hazardous chemicals such as oleum, halides and nitrogen oxides (10). There have been many attempts to change the process into environmentally benign ones. Gas-phase ammoximation using NH_3 and O_2 has been reported (11–15), but the yields were relatively low. The titanium silicate molecular sieves, TS-1 and TS-2, are titanium isomorphs of ZSM-5 and ZSM-11 and have the MFI and MEL structures, respectively. The titanium silicates were found to catalyze the conversion of cyclohexanone into cyclohexanone oxime in the presence NH_3 and H_2O_2 with high selectivities without the coproduction of any ammonium sulfate (16–20).

We report here ammoximation of various ketones catalyzed by various TS-1 and amorphous SiO_2–TiO_2. The influences of steric conformation of ketone and its diffusion, and the reaction site of TS-1 are also discussed.

EXPERIMENTAL

TS-1 was prepared by a method reported in a literature (21). Tetraethyl orthosilicate (TEOS) (Tokyo Chemical Industry), tetrabutyl orthotitanate (TBOT) (Kanto Chemical), and tetrapropylammonium hydroxide (TPAOH) (20 wt% aq., Tokyo Chemical Industry) were used. Aqueous TPAOH (one-fifth of the total amount) was first added to TEOS. Then TBOT in 2-propanol and finally the rest of TPAOH were added to give a clear solution with the composition

$$\mathrm{TEOS : TBOT : TPAOH : H_2O} = 1 : 0.02 : 0.34 : 15.$$

After alcohols were removed at 353 K, this solution was heated in a Teflon-lined autoclave at 423 K for 50 h. The product recovered by filtration was calcined in air at 823 K for 6 h. The Si/Ti ratio of this sample (TS-1-S1) was 79.

Other samples (TS-1-S2-S6) of TS-1 with a different crystal size and Si/Ti ratio were prepared in a similar manner and by changing the compositions of reactant mixture, hydrolysis conditions, and temperature program in hydrothermal synthesis. A recently reported method (22) using a mixture of tetrapropylammonium and tetraethylammonium hydroxides (TEAOH, 10 wt% aq., Tokyo Chemical Industry) was also adopted to obtain TS-1 (TS-1-S7) of increased crystal size. Following the method described in a patent (23), TS-1(TS-1-S8) of large crystal size was synthesized; colloidal silica (Snowtex 40, Nissan Chemical Industries) was employed as a silica source and hydrothermal synthesis was carried out at 428 K for 6 days.

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Amorphous SiO_2–TiO_2 was prepared by hydrolysis of TEOS and tetraethyl orthotitanate (Tokyo Chemical Industry) at 423 K. The product recovered by filtration was calcined in air at 823 K for 6 h. The Si/Ti ratio of this sample was 85.

Chemical composition of the samples was obtained by ICP (Japan Jarrell-Ash ICAP 575 Mark II) after solubilization of the samples in HF, HCl, and HNO_3. X-ray powder diffraction patterns were collected on a Rigaku Denki RU-200A diffractometer using Cu$K\alpha$ radiation. SEM micrographs were obtained with a JEOL JSM 5400 microscope equipped with an ED probe. The Fourier transform infrared spectra (IR) were obtained on a Perkin Elmer 1600 spectrometer using the KBr pellet technique. UV–Vis spectra were obtained on a Hitachi 340 spectrophotometer. Liquid-phase adsorption experiments were carried out at 303 K using 1,3,5-triisopropylbenzene, whose dimensions were too large to enter the pores of the MFI zeolite, as a solvent (24). Adsorption measurements of *o*-xylenes were conducted on a highly sensitive microbalance. After zeolite samples (0.25 g) were evacuated at 473 K, the measurements were performed at 393 K and an *o*-xylene pressure of 0.39 kPa to estimate the time taken to reach 30% of the amount of *o*-xylene adsorbed at infinite time.

The oxidation reactions were carried out in a three-neck flask (50 ml). One neck was fitted with a condenser and another neck was fitted with a rubber septum. All ketones were purchased from Tokyo Chemical Industry. To a mixture of 10 mmol of ketone and 2 ml of water was added 1.4 ml of NH_3 (28 wt% aq.) and then 50 mg of catalyst. The resulting mixture was heated with a water bath kept at 353 K under vigorous stirring. Hydrogen peroxide (5 wt%) was injected dropwise through the septum with a feed pump for 2 h. The ketone : NH_3 : H_2O_2 molar ratio was 1 : 2 : 1. After addition of hydrogen peroxide, the reaction was continued for 3 h. After the reaction, the products were extracted with ether and analyzed on a Shimadzu GC 14A gas chromatograph equipped with a 50-m OV-1 capillary column. Cyclopentanone, 2-pentanone, or cyclohexanone was used as an internal standard for gas chromatographic analysis.

RESULTS AND DISCUSSION

Ammoximation of Cyclic Ketones on TS-1 and Amorphous SiO_2–TiO_2

Ammoximation of various cyclic ketones on a TS-1 sample (TS-1-S1, Si/Ti = 79) and amorphous SiO_2–TiO_2 (Si/Ti = 85) was carried out under the standard conditions. The results are presented in Table 1. The experimental error was about ± 0.15%. On TS-1 δ-valerolactam (0.2% yield) and ε-caprolactam (0.1% yield) were also obtained from cyclopentanone and cyclohexanone, respectively. Since these lactams are considered to be formed via oximes, their yield was included in the oxime yield in Table 1. The reactivity of the cyclic ketones on the TS-1 catalyst followed the decreasing order

TABLE 1

Ammoximation of Ketones on TS-1 and Amorphous SiO_2–TiO_2[a]

Reactant	Oxime yield (%)	
	TS-1[b]	Amorphous SiO_2–TiO_2[c]
Cyclopentanone	30	3.2
Cyclohexanone	24	3.3
Cycloheptanone	39	4.0
Cyclooctanone	21	2.3

[a] Catalyst, 50 mg; ketone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h.

[b] TS-1-S1, Si/Ti = 79.

[c] Si/Ti = 85.

$$\text{cycloheptanone} > \text{cyclopentanone} > \text{cyclohexanone} > \text{cyclooctanone}.$$

The reactivity of the cyclic ketones on amorphous SiO_2–TiO_2 followed the order

$$\text{cycloheptanone} > \text{cyclopentanone} \fallingdotseq \text{cyclohexanone} > \text{cyclooctanone}.$$

Although small amounts of peroxydicycloalkylamine and aldol condensation products were also formed on TS-1, the selectivity to oximes including lactams was >97%. In the reaction of cyclohexanone on TS-1 the conversion of H_2O_2 was 94% and hence the yield of cyclohexanone oxime based on the converted H_2O_2 was only 26%, indicating that H_2O_2 extensively decomposed without oxidizing the substrate. However, it is unlikely that this nonproductive decomposition occurs on extraframework titanium on TS-1; even in the absence of catalyst H_2O_2 conversion (decomposition) was 92%. Because of low concentration (4.4 g/liter) of TS-1 nonproductive thermal decomposition of H_2O_2 was an inevitable concomitant. It is noteworthy that our catalyst concentration is much lower than that of Roffia *et al.* (18) who observed that lowering catalyst concentration results in a considerable decrease in the cyclohexanone conversion and the oxime yield based on H_2O_2.

Except for cycloheptanone, the reactivity of cyclic ketones on the TS-1-S1 catalyst decreased with the increases in their size; it was in good agreement with that on amorphous SiO_2–TiO_2, where cycloheptanone still showed the highest activity. This is consistent with the observation by Armor *et al.* (13), who found that the cycloheptanone was more reactive than other cyclic ketones in the ammoximation of ketones with NH_3 and O_2. Thus the reactivity of cyclic ketones on the TS-1 sample apparently reflects the inherent reactivity, as yet not clarified, in the absence of steric restriction in the MFI structure.

Amorphous SiO_2–TiO_2 was found to be much less active than crystalline zeolite TS-1 in the ammoximation of cyclic ketones. These results suggest that Ti^{4+} present in zeolite TS-1 is different from Ti^{4+} present in amorphous SiO_2–TiO_2, resulting from the difference in dispersion and coordination state of Ti (*vide infra*). By-products such as lactam, peroxydicycloalkylamine, and aldol condensation products were negligible on amorphous SiO_2–TiO_2.

Influence of Organic Amine on Ammoximation of Cycloheptanone

The pore sizes of titanium silicate TS-1 with an MFI structure are 0.53 × 0.56 nm for the straight channel and 0.51 × 0.55 nm for the sinusoidal channel (25), and these dimensions are about the same as those of cross-section of C_5–C_8 cyclic ketones. It is important to distinguish between the reactions on outer and inner surfaces. It is proposed that hydroperoxy or peroxy Ti species over TS-1 is the active site for ammoximation reaction (16, 26). To clarify contribution from inner and outer surfaces of the TS-1 catalyst, organic amines of different size were used to poison catalyst surface selectively.

The ammoximation of cycloheptanone was carried out in the presence of triphenylamine or triethylamine. The results are compared in Table 2. It was found that when triethylamine was added, the reactivity of cycloheptanone was severely retarded and no aldol condensation products were formed. Reddy *et al.* (27) reported similar inhibition of aldol condensation when NH_3 was added in excess. The cycloheptanone oxime yield was only slightly decreased by the addition of triphenylamine. As the size of triphenylamine is too large to enter the pore of MFI zeolite, only the outer surface of TS-1 would be poisoned by triphenylamine. The reactivity of cycloheptanone was only slightly decreased because the triphenylamine-poisoned outer surface is considerably small compared to the inner surface. Triethylamine can enter the pore of the molecular sieve and poisoned both the outer and the inner surface, resulting in remarkably decreased activity. It is concluded that the ammoximation of cycloheptanone took place mostly inside the TS-1 molecular sieve. The poisoning was not due to suppression of NH_3 activation, since oxyfunctionalization of hexane on TS-1 was similarly inhibited by triethylamine (28).

On the other hand, the cycloheptanone oxime yield was largely decreased by addition of either triphenylamine or triethylamine over amorphous SiO_2–TiO_2. Since the average pore diameter of amorphous SiO_2–TiO_2 was 22 nm, it is conceivable that both amines easily entered the pore, inhibiting the ammoximation.

TABLE 2

Influence of Organic Amine on Ammoximation of Cycloheptanone on TS-1 and Amorphous SiO_2–TiO_2[a]

	Oxime yield (%)		
Catalyst	None	Triphenylamine	Triethylamine
TS-1[b]	39	32	5.4
SiO_2–TiO_2[c]	4.0	1.0	1.4

[a] Catalyst, 50 mg; ketone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); organic amine : ketone = 1 : 1, temperature, 353 K; reaction duration, 5 h.

[b] TS-1-S1, Si/Ti = 79.

[c] Si/Ti = 85.

Reactivity of Methylcyclohexanones on TS-1

The reactivity and adsorbed amount of cyclohexanone and methylcyclohexanones on the TS-1-S1 catalyst are listed in Table 3. The reactivity of the methylcyclohexanones followed the decreasing order

$$\begin{aligned} \text{cyclohexanone} &> \text{2-methylcyclohexanone} \\ &\fallingdotseq \text{3-methylcyclohexanone} \\ &> \text{2,6-dimethylcyclohexanone.} \end{aligned}$$

Methylcyclohexanones showed lower reactivity than cyclohexanone, indicating the steric restriction imposed by the methyl branch. However, except for 2,6-dimethylcyclohexanone the amount of adsorption of these methylcyclohexanones was almost the same as that of cyclohexanone. The low adsorbed amount of 2,6-dimethylcyclohexanone accounts for the low reactivity. The reactivity of 2-methylcyclohexanone and 3-methylcyclohexanone was about half of that of cyclohexanone. To explain different reaction behavior of ammoximation of methylcyclohexanones on the TS-1 catalyst, adsorption rate of methylcyclohexanones on the catalyst was measured. The results are shown in Fig. 1. The adsorption of cyclohexanone was fast and nearly saturated adsorption (58 mg/g) was attained only after 15 min. This capacity happened to be almost equal to the cyclohexane adsorption capacity

TABLE 3

Reactivity and Adsorbed Amount of Cyclic Ketones on TS-1

Reactant	Oxime yield[a] (%)	Adsorbed amount[b] (mg/g-cat)
Cyclohexanone	24	66
2-Methylcyclohexanone	12.4	65
3-Methylcyclohexanone	12.6	67
2,6-Dimethylcyclohexanone	5.0	6.0

[a] Catalyst (TS-1-S1), 50 g; ketone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h.

[b] Solvent, 1,3,5-triisopropylbenzene; 303 K; 3 h.

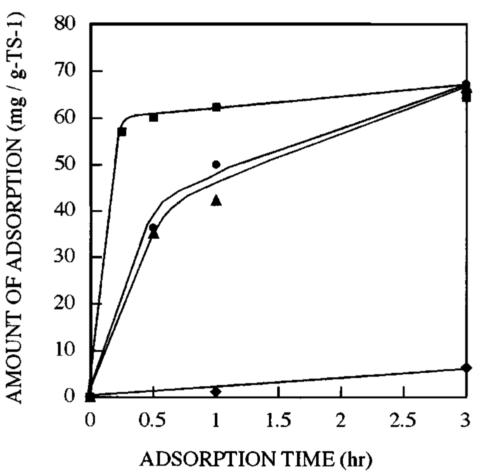

FIG. 1. Time course of adsorption of ketone on TS-1. Catalyst (TS-1-S1), 100 mg; solvent, 1,3,5-triisopropylbenzene; 303 K. (■) cyclohexanone; (▲) 2-methylcyclohexanone; (●) 3-methylcyclohexanone; (◆) 2,6-dimethylcyclohexanone.

(59 mg/g) obtained by Mirajkar *et al.* (29), although our experimental conditions (cyclohexanone in liquid phase at 303 K) considerably differed from theirs (cyclohexane in vapor phase at 298 K).

The adsorbed amount of 2-methylcyclohexanone and 3-methylcyclohexanone gradually increased to reach the level similar to cyclohexanone after 3 h. The adsorbed amount of 2,6-dimethylcyclohexanone increased very slowly. The order of adsorption rate (diffusivity) was

cyclohexanone > 2-methylcyclohexanone
≒ 3-methylcyclohexanone
> 2,6-dimethylcyclohexanone.

The reactivity of the methylcyclohexanones on the TS-1 catalyst obeyed the same order as their adsorption rate. These results show that the diffusivity of the reactant controlled the rate in the ammoximation of methylcyclohexanones over the TS-1 catalyst.

Influence of Steric Factor in Ammoximation of Dimethylcyclohexanones on TS-1

It was thought that the low reactivity of dimethylcyclohexanones may also result from the difficulty in the access of carbonyl group to active sites of TS-1 caused by the steric hindrance of their methyl substituents. To investigate the effect of the methyl substituent on the reactivity, a comparison was made among the ammoximation rates of 2,6- and 2,5-dimethylcyclohexanones. Dimethylcyclohexanone contains *cis*- and *trans*-isomers. The *cis*/*trans* ratios of 2,6-dimethylcyclohexanone and 2,5-dimethylcyclohexanone are 5.25 and 0.28, respectively. The results of ammoximation of mixture of *cis*- and *trans*-isomers on the TS-1 catalyst (TS-1-S1) are presented in Fig. 2. The reactivity of *cis*- and *trans*- forms followed the order

trans-2,6-dimethylcyclohexanone
> *cis*-2,5-dimethylcyclohexanone
> *cis*-2,6-dimethylcyclohexanone
> *trans*-2,5-dimethylcyclohexanone.

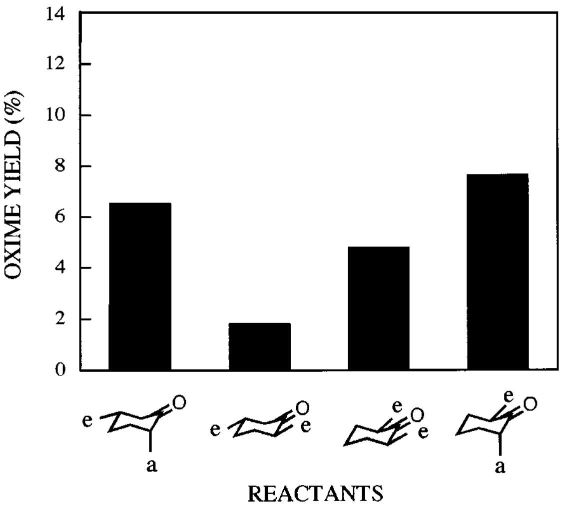

FIG. 2. Influence of methyl substituents on ammoximation of dimethylcyclohexanone on TS-1. Catalyst (TS-1-S1), 50 mg; ketone, 10 mmol (2,5-dimethylcyclohexanone:*cis*/*trans* = 0.28; 2,6-dimethylcyclohexanone: *cis*/*trans* = 5.3); ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h.

The stable conformation of each isomer is shown in Fig. 3. A molecule of *trans*-2,6-dimethylcyclohexanone exists as a pair of conformational enantiomers. In either conformation, only one methyl group can occupy an equatorial position. On the other hand, the *cis*-isomer exists as two conformational diastereomers. In the more stable conformation of *cis*-2,6-dimethylcyclohexanone, both methyl groups occupy equatorial positions. Similarly, the more stable conformation of *trans*-2,5-dimethylcyclohexanone is

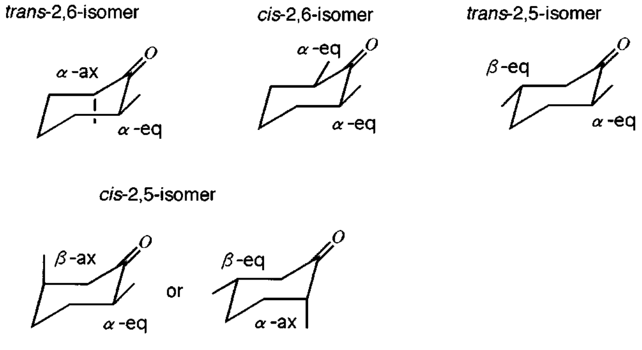

FIG. 3. The stable conformation of dimethylcyclohexanone isomers.

the diequatorial one. In the *cis*-2,5-dimethylcyclohexanone isomer there is one equatorial and one axial methyl group.

Dimethylcyclohexanones have not only difficulty in diffusion inside the TS-1 pore, but also their methyl substituents causes steric hindrance to the access of carbonyl group to active sites of TS-1. Comparison of the reactivity shown in Fig. 3 suggests that the steric hindrance of the methyl group to the access of carbonyl group decreases in the order

$$\beta\text{-}equatorial > \alpha\text{-}equatorial > \beta\text{-}axial > \alpha\text{-}axial.$$

This is contrary to what would be expected; it is generally considered that the α-methyl group, which is close to the carbonyl group, causes more steric hindrance than the β-methyl group. The large retarding effect of the β-methyl group in the equatorial position may be due to the remote geometrical restriction inside the zeolite pore accommodating the reactant.

Factors Determining the Activity in Ammoximation of Cyclic Ketones

Diffusion may be an important step in catalytic reactions, but it is difficult to determine the diffusivity directly under the reaction conditions. According to the report of Olson and Haag, the time necessary for 30% adsorption ($t_{0.3}$) of *o*-xylene can be used as a criterion to measure the diffusivity of reactant and product inside zeolite; $t_{0.3}$ is proportional to r^2/D, where r is the crystal radius and D is the diffusivity of the molecule (30). Van der Pol *et al.* have reported that smaller crystals of TS-1 have higher activity in the hydroxylation of phenol (31).

Seven more samples of TS-1 with varying crystal size and Si/Ti ratio were prepared. The samples TS-1-S2-S6 were prepared in a similar manner to TS-1-S1. X-ray diffractograms showed good crystallinity for all the TS-1 samples. The results of ICP, SEM, IR, and UV–Vis of all samples the shown in Table 4. SEM observation revealed that these samples were spherulitic particles under 0.3 μm. Sample TS-1-S7 was synthesized using a mixture of TPAOH and TEAOH and consisted mostly of hexagonal crystals of 1.5–3 μm. With colloidal silica as a silica source TS-1-S8 was obtained, TS-1-S8 comprised mainly crystals of over 5 μm and in the shape of hexagonal coffins. Thagaraj *et al.* observed that the intensity ratio of the 960 cm^{-1} band to the 550 cm^{-1} band (I_{960}/I_{550}) in the IR spectra increased with the Ti content of the TS-1 framework (21). The ratio can be employed to present the relative concentration the Ti content in the framework. The UV–Vis spectra of TS-1-S1-S8 samples exhibited the ligand to metal charge transfer band assigned to isolated Ti in tetrahedral framework position in the range from 210 to 230 nm. The TS-1-S3-S5 sample had also a broad shoulder due to extraframework Ti in the region of 240 to 250 nm. The low relative intensity I_{960}/I_{550}, for the samples TS-1-S3-S5 is in agreement with the presence of extraframework Ti suggested by their UV–Vis spectra. The presence of a broad shoulder at about 270 nm in the case of TS-1-S6 could be due to hexacoordinated Ti species containing Ti–O–Ti bonds. The absence of adsorption of about 340 nm in all samples indicate the absence of titanium oxide (anatase) impurities (32). It is noteworthy amorphous SiO_2–TiO_2 showed the band assigned to anatase.

With these TS-1 catalysts, ammoximation of cyclohexanone was performed. Figure 4 illustrates the dependence of the turnover number (mol-products/mol-Ti) of ammoximation of cyclohexanone on the characteristic diffusion time, $t_{0.3}$. It is found that high turnover numbers were attained for the low $t_{0.3}$ samples (lower than 100 s), where the diffusion should occur effectively. For the large $t_{0.3}$ samples, the turnover numbers were severely suppressed. Since there is a clear correlation between the turnover number and $t_{0.3}$ for the TS-1 samples with $t_{0.3} > 180$ s, it is suggested

TABLE 4

Characterization of TS-1 Samples and Amorphous SiO_2–TiO_2

Catalyst	Si/Ti	Crystal size (μm)	$I_{960\ \mathrm{cm}^{-1}}/I_{550\ \mathrm{cm}^{-1}}$	UV-Vis (nm)
TS-1-S1	79	0.1–0.3	0.25	210–230
TS-1-S2	92	0.1–0.3	0.16	210–230
TS-1-S3	61	0.1–0.3	0.15	210–230
TS-1-S4	52	0.1–0.3	0.14	210–250
TS-1-S5	58	0.1–0.3	0.10	210–240
TS-1-S6	120	0.3–0.5	0.03	210–270
TS-1-S7	56	1.5–3.0	0.10	210–230
TS-1-S8	53	>5	0.13	230
SiO_2–TiO_2	85	—	—	300–350

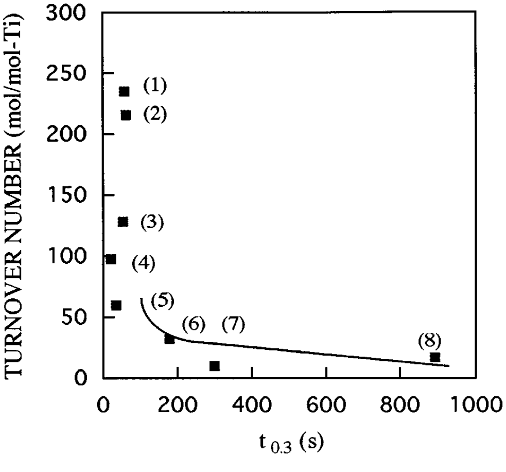

FIG. 4. Relationship between $t_{0.3}$ and activity in ammoximation cyclohexanone. Catalyst (TS-1-S1-S8), 50 mg; cyclohexanone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h. Numbers in parentheses indicate the sample number n of TS-1-S n.

that the ammoximation of cyclohexanone on the catalysts with large crystal size was strongly affected by diffusion of cyclohexanone or its oxime products. Scatter in the data for $t_{0.3} < 100$ s suggests that for the TS-1 samples with small crystal size, the reaction was not governed by diffusional factors.

The oxime yield is plotted against the I_{960}/I_{550} ratio in Fig. 5. Except for the samples TS-1-S7 and TS-1-S8 whose $t_{0.3}$ was >100 s, the oxime yield was found to be virtually proportional to the relative intensity I_{960}/I_{550}. Therefore, for the zeolite crystals with a size under 0.3 μm the oxime productivity was simply determined by the number of active sites present in the TS-1 framework. There was no clear relation between the presence/absence of extraframework Ti species deduced from the UV–Vis and the catalytic performance. For the samples having no extraframework Ti, TS-1-S1 and TS-1-S2 exhibited relatively high turnover number and oxime yield but TS-1-S6 and TS-1-S7 not.

The ammoximation of cyclohexanone and cyclooctanone was carried out using the catalyst with longest $t_{0.3}$ (TS-1-S8) and the standard catalyst (TS-1-S1). Results are compared in Table 5. The specific activity of TS-1-S1, expressed in terms of oxime yield per relative intensity I_{960}/I_{550}, for the ammoximation of cyclohexanone and cyclooctanone was lower than that of TS-1-S8. Ammoximation of cyclooctanone was slower than that of cyclohexanone, probably due to the low diffusivity of cyclooctanone and its oxime compared to that of cyclohexanone and its oxime. Comparison of the reactivity ratio of cyclooctanone/cyclohexanone for the two TS-1 samples shows more suppression of reactivity for cyclooctanone for the sample with larger crystal size (long $t_{0.3}$), suggesting that the ammoximation of cyclooctanone also takes place mainly inside the TS-1 zeolite; if the reaction occurs on the external surface, one would not expect significant difference in the reactivity ratio between the two samples.

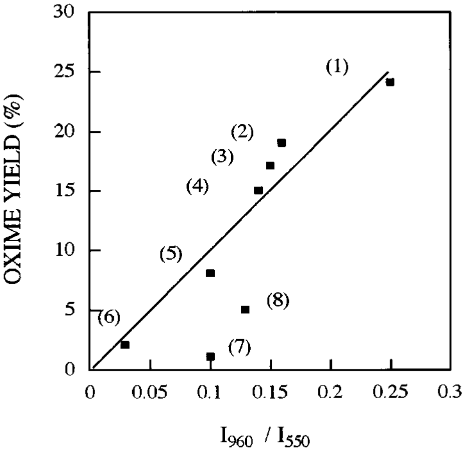

FIG. 5. Relationship between oxime yield an I_{960}/I_{550}. Catalyst (TS-1-S1-S8), 50 mg; cyclohexanone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h. Numbers in parentheses indicate the sample number *n* of TS-1-S *n*.

TABLE 5

Oxime Yield from Cyclic Ketones on TS-1 with Different Crystal Size[a]

			Oxime yield/($I_{960\,cm^{-1}}/I_{550\,cm^{-1}}$)		
Catalyst	Si/Ti	$t_{0.3}$	Cyclohexanone	Cyclooctanone	C_8/C_6
A	79	58	96	84	0.88
B	53	891	38	22	0.58

[a] Catalyst (A = TS-1-S1, B = TS-1-S8), 50 mg; ketone, 10 mmol; ketone : NH_3 : H_2O_2 = 1 : 2 : 1 (molar ratio); H_2O_2 (5 wt% aq. solution); NH_3 (28 wt% aq. solution); temperature, 353 K; reaction duration, 5 h.

CONCLUSIONS

The reactivity of ketones over TS-1 shows the order

cycloheptanone
> cyclopentanone > cyclohexanone
> cyclooctanone > 2-methylcyclohexanone
≒ 3-methylcyclohexanone
> 2,6-dimethylcyclohexanone.

The active sites of TS-1 for ammoximation of cycloheptanone are mostly inside the molecular sieve. From the relative reactivity of dimethylcyclohexanone isomers, it is concluded that the steric hindrance of the substituent methyl group to the access of carbonyl group inside the zeolite decreases in the order *β-equatorial*> *α-equatorial* > *β-axial* > *α-axial*. Diffusion of cyclohexanone or its oxime has been found to play an important role in the ammoximation when the TS-1 crystals larger than 1.5 μm are employed as a catalyst. For the TS-1 crystals smaller than 0.3 μm, the ammoximation activity is determined by the number of active Ti sites present in the zeolite framework.

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