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Ammoximation of Ketones over Titanium Mordenite

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The liquid-phase ammoximation of various ketones to the corresponding oximes with ammonia and hydrogen peroxide was conducted over titanium mordenite (Ti-M) prepared from dealuminated mordenites and $TiCl_4$ vapor by a secondary synthesis method. The catalytically active sites, the effects of reaction variables and residual Al within Ti-M on the ammoximation performance and the shape-selectivity for various ketones were studied to clarify the reaction mechanism for the liquid-phase ammoximation. The ammoximation was catalyzed effectively by tetrahedrally coordinated Ti atoms in the framework sites in the presence of water at an optimum reaction temperature of 333 K. There was no direct correlation between the ammoximation activity and the molecular size of ketone. Ti-M was even active for bulky ketones which were hardly adsorbed into the pores. The ammoximation has been proposed to proceed through a consecutive reaction, including the oxidation of NH_3 by H_2O_2 over Ti sites to form a hydroxylamine intermediate, and the subsequent reaction of hydroxylamine with ketone mainly in the solution to give oxime. The second-step reaction has been suggested to be the rate determining step in the ammoximation. © 1997 Academic Press

INTRODUCTION

MFI-type Ti-containing silicalite (TS-1) was first hydrothermally synthesized by a group at ENI (1), and has been demonstrated to be a remarkable catalyst in the selective oxidation of a large family of organic molecules using hydrogen peroxide as an oxidant. Such reactions include epoxidation of olefins (2), oxidation of alkanes (3), alcohols (4), and amines (5), hydroxylation of aromatics (6), and ammoximation of ketones (7, 8). The outstanding catalytic activity and selectivity of TS-1 have made it a commercial catalyst in Italy for the manufacture of cathecol and hydroquinone from phenol. The reactions are generally operated under mild conditions (<373 K, 1 atm). TS-1-catalyzed processes are also advantageous from an environmental point of view as the by-product is mainly water. The successes in TS-1 have stimulated researchers to synthesize other Ti-containing zeolites and zeolite-like porous materials, e.g., TS-2 (9), Ti-ZSM-48 (10), Ti-β (11, 12), Ti-ZSM-12 (13), TAPSO-5 (14), and recently, Ti-MCM-41 (15, 16).

The liquid-phase ammoximation of cyclohexanone over titanium zeolite in the presence of NH_3 and H_2O_2 to synthesize oxime is another important process attracting the industrial interests as cyclohexanone oxime is the key intermediate in the manufacture of caprolactam through Beckmann rearrangement. Compared with the current commerical process, this technology shows various advantages, such that only one step is involved, without use of environmentally undesirable chemicals like oleum, halides, and oxide of nitrogen, and only a small amount of byproducts are formed. Despite of the excellent catalytic performances reported by several groups using TS-1 and TS-2 zeolites, the reaction mechanism for the liquid-phase ammoximation, however, is still debated. In order to explain the formation of oxime and a by-product of peroxydicyclohexylimine, Ratnasamy *et al.* have proposed a possible mechanism that the ammoximation proceeds through an intermediate of unstable imine (7, 17). This mechanism is similar to that reported for the gas-phase ammoximation of cyclohexanone in the presence of NH_3 and O_2 (18), and has been supported by IR spectroscopy which proves the formation of adsorbed imine species formed from cyclohexanone and NH_3 on the surface of TS-1 (19). The groups from Italy, on the other hand, postulated a different pathway for the ammoximation, that is, through an intermediate of hydroxylamine, NH_2OH since TS-1 still showed high activity for those ketones hardly diffusing into the pores (8) and NH_2OH was really produced from the oxidation of NH_3 with H_2O_2 in the absence of ketone (20). Therefore, a clear clarification of the liquid-phase ammoximation mechanism is not only scientifically valuable, but also industrially important for this reaction of commerical potential.

Titanium zeolite with mordenite structure (MOR) has been seldom reported in the open literature. Kraushaar *et al.* reported for the first time a new method for the preparation of TS-1 using dealuminated ZSM-5 and $TiCl_4$ vapor (21). A similar treatment of highly siliceous zeolite with various metal chloride vapors at elevated temperatures has been proved to be a useful way for preparing metallosilicates with MFI and MOR structures and this kind of framework insertion, as one of secondary synthesis methods, was named as “atom-planting” (22–25). Recently, we have applied the $TiCl_4$ treatment to mordenite and demonstrated

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that the incorporation of Ti atoms into the framework sites of dealuminated mordenite was also possible (26). Titanium mordenite (Ti-M) thus prepared has been demonstrated to exhibit higher activity than TS-1 in the hydroxylation of bulkier aromatics with H_2O_2 (27). In this study, we have performed the ammoximation of ketones over Ti-M. The study has been focused on the catalytically active sites, the effects of reaction parameters on the performance of the catalyst and the reaction mechanism.

EXPERIMENTAL

Titanium mordenite (Ti-M) catalysts were prepared with the secondary synthesis method using dealuminated mordenites and $TiCl_4$ vapor. Various dealuminated mordenites with Si/Al molar ratios of 11–350 were obtained by the dealumination of H-mordenites, M(11) (Tosoh Co. Ltd., framework Si/Al atomic ratio of 11) and M(8.2) (hydrothermally synthesized in our laboratory). The dealumination method was the calcination in air followed by a reflux with nitric acid as described in detail elsewhere (24). Dealuminated mordenite, M(71) was also provided by Tosoh and used without further dealumination.

The treating procedure with $TiCl_4$ vapor was similar to the alumination treatment (24, 25). After calcination at 773 K for 4 h, 2 g of dealuminated mordenite was treated with $TiCl_4$ vapor (1.7 kPa) in a flowing helium at 773 K for a prescribed process time (5 min–2 h). The sample was then purged with pure helium at 773 K for 1 h to remove any unreacted $TiCl_4$ from the zeolite. After cooling to the room temperature, the $TiCl_4$-treated sample was washed with deionized water and dried at 383 K for 24 h to obtain Ti-containing mordenite, Ti-M(*n*), where *n* was the Si/Al ratio of the parent zeolite. A reference sample, TS-1 (Si/Ti = 70) was hydrothermally synthesized according to the patent (1).

The samples were characterized with IR (Shimadzu FTIR-8100) and diffuse reflectance UV-visible (Shimadzu MPS-2000) spectroscopy.

The ammoximation runs were performed in a 50 ml flask with a magnetic stirrer at desirable temperatures (298–373 K). In a typical run, 0.2 g of catalyst, 19.34 mmol of ketone, 12 ml of H_2O, and 2 ml of H_2O_2 (30 wt%) were mixed in the flask. When the mixture reached the reaction temperature, 2 ml of NH_3 aqueous solution (25 wt%) was added to start the ammoximation. After the reaction was carried out under vigorous agitation for 2 h, 20 ml of ethanol was added to make the reaction mixture into one phase. The mixture was then analyzed with gas chromatography after the catalyst was removed out.

The adsorption experiments of ketones in liquid phase were performed under agitation at 333 K for 2 h, by adding 2 ml of ketone solution (1 wt% in 1,3,5-triisopropylbenzene) to 0.1 g of catalyst. The solution was injected into the gas chromatography for analysis to determine the adsorption capacity (28).

RESULTS AND DISCUSSION

Our previous IR and UV experiments have revealed that the titanium species introduced into the zeolite crystals by the treatment of dealuminated mordenites with $TiCl_4$ vapor mainly occupied the framework sites in a tetrahedral coordination, and it has been found that Ti-containing mordenite, Ti-M thus prepared was an active catalyst for the hydroxylation of aromatics with hydrogen peroxide (26, 27). In the present study, Ti-M was applied to the liquid-phase ammoximation of ketones to yield oximes in the presence of NH_3 and H_2O_2 with the purpose to clarify the catalytically active sites, the effects of reaction variables on the ammoximation and the reaction mechanism.

Catalytically Active Sites

Ti-M(300) containing a low Al content and exhibiting a high intrinsic activity as will be shown later was compared with other catalysts in the ammoximation of cyclohexanone at 333 K (Table 1). The main product was cyclohexanone oxime, together with a small amount of higher boiling compounds which were not well identified. Unlike the ammoximation over TS-1 and TS-2 where the major by-products are reported to be caprolactam and peroxydicyclohexylimine (7, 17), the present reaction over Ti-M showed no major one among the by-products. These by-products were yielded even from the reaction run without any catalyst, indicating they are noncatalyzed products. It is obvious that both dealuminated mordenite, M(300) and $Ti(SO_4)_2$ supported M(300) were not the effective catalysts for the oxime formation. The oxime was produced with good yield only over Ti-M(300) and TS-1 (70), both of which contained tetrahedral Ti species in the framework sites. Ti-M(300) even exhibited both higher conversion of ketone and higher selectivity to

TABLE 1

Ammoximation of Cyclohexanone over Various Catalysts[a]

Catalyst	Ti content[b] (mmol g^{-1})	Ketone conv. (%)	Oxime sel. (%)
Without catalyst	0	22.3	2.9
M(300)	0	14.6	3.8
Ti/M(300)[c]	0.50	14.2	21.4
Ti-M(300)	0.18	97.3	99.7
TS-1(70)	0.23	38.5	92.8

[a] Ammoximation conditions: cat., 0.2 g; ketone, 19.34 mmol, H_2O, 10 ml; NH_3 solution (25 wt%); H_2O_2 (30 wt%), 2 ml; ketone : NH_3 : H_2O_2 = 1 : 1.5 : 1.2, temp., 333 K; time, 2 h.

[b] Determined by ICP.

[c] M(300) supported with $Ti(SO_4)_2$ followed by a calcination in air at 773 K for 5 h.

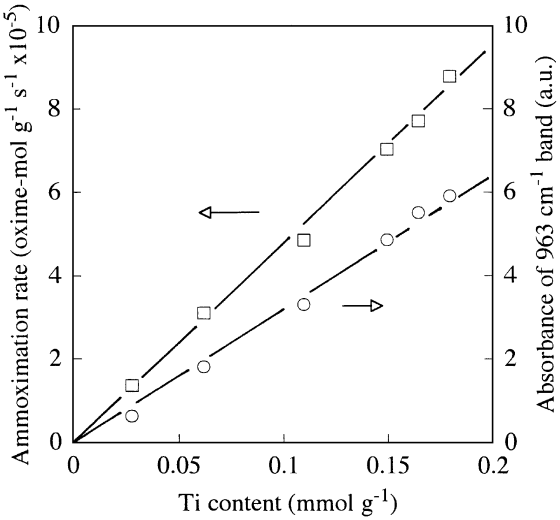


FIG. 1. The intensity of the 963 cm^{-1} band and the activity of cyclohexanone ammoximation as a function of the Ti content. Atom-planting conditions: parent, M(300); temp., 773 K; $TiCl_4$ vapor, 1.7 kPa; treatment time, 5 min–2 h. Ammoximation conditions: cat., 50 mg; others, see Table 1.

oxime than TS-1 under the present conditions, suggesting Ti-M is a more effective catalyst for the ammoximation.

To confirm that the active sites in Ti-M are really the framework Ti species like in the case of TS-1 (7, 8), several samples with various Ti content were prepared by the treatment of M(300) with $TiCl_4$ vapor for a desirable period of time (5 min–2 h). All these samples exhibited the 963 cm^{-1} IR band (26), which is assigned to the isolated framework Ti in a tetrahedral coordination (29, 30). The intensity of the band was proportional to the bulk Ti content (Fig. 1). Moreover, no obvious band was observed between 300 and 350 nm in their UV spectra (27), indicating that the amount of nonframework Ti species such as anatase is very small. Thus, the Ti species incorporated into the mordenite crystals mainly occupied the framework sites. These samples were used as catalysts in the ammoximation of cyclohexanone, and the initial formation rate for the oxime is plotted against the Ti content in Fig. 1. The linear relationship between the two variables gives further evidence that the active sites in Ti-M catalyst are those framework Ti species.

In general, the catalytic activity increased upon increasing the Ti content of the samples prepared from the same parent of dealuminated mordenite with the atom-planting method just as shown in Fig. 1. However, a great difference in catalytic activity has been observed between Ti-M catalysts prepared from the different dealuminated parents. This is suggested to be related with the Al content in the catalysts, since Ti-M obtained from dealuminated mordenite and $TiCl_4$ vapor, different from TS-1 which can be hydrothermally synthesized in an Al-free form, always contained a small amount of Al within its crystals. To clarify the influence of the residual Al species on the ammoximation, a series of Ti-M catalysts were prepared from the dealuminated mordenites with various Si/Al ratios, and were used as the catalysts for the ammoximation of cyclohexanone as illustrated in Fig. 2. The catalytic activity was expressed as the turnover number (TON) for the oxime formation per Ti site at a reaction time of 2 h. Both the activity and the selectivity increased with increasing the Si/Al ratio from 11 to 200, that is, with decreasing the Al content in Ti-M. Since the absolute amount of by-products mainly through the noncatalyzed reaction was almost independent of the Al content and it must be hard for Al ions to act as acid sites in the basic solution (NH_3 was at least 150 times more than the residual Al in Ti-M), the lower selectivity observed for Ti-M catalysts with higher Al contents was not due to side reaction occurring on acid sites but due to lower yield of the main product, oxime. When the Si/Al ratio was over 200, the TON reached a maximum of about 650 oxime-mol (Ti-mol)$^{-1}$, and the selectivity was nearly 100%. This suggests that only those Ti sites in Al-free region show higher intrinsic activity for the ammoximation. It should be noted that all these Ti-M samples exhibited the 963 cm^{-1} band in their IR spectra and only the 220 nm band in their UV spectra, which confirms that they contained mainly the tetrahedrally coordinated Ti species located in the framework sites. Therefore, the lower activity over Ti-M catalysts with the Si/Al ratio below 200 is not due to the presence of the nonframework Ti species. The easier decomposition of H_2O_2 on Al ions may be responsible for the reduction in the activity with increasing in Al content. Secondarily, as the reaction was performed in H_2O, the higher hydrophilicity of Ti-M containing a higher Al content would make the Ti sites surrounded easily by H_2O molecules. Subsequently, the Ti sites cannot act as active sites effectively. Moreover, Al atoms in the vicinity of Ti sites have been postulated to change the electronic density around the Ti sites through altering the

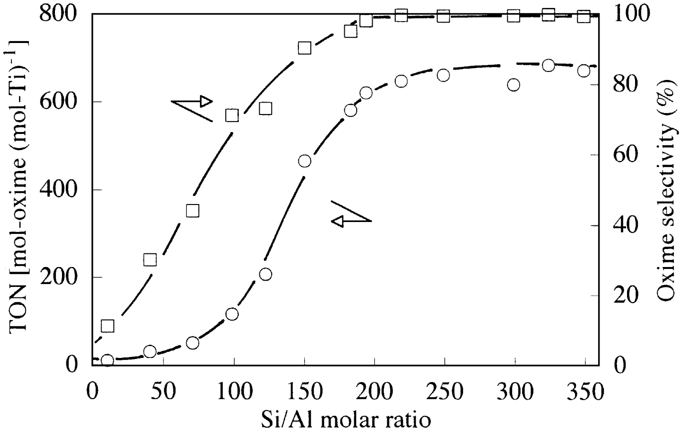


FIG. 2. Ammoximation activity and oxime selectivity as a function of Si/Al molar ratio. Atom-planting conditions: parent, dealuminated mordenites (Si/Al = 11–350); temp., 773 K; $TiCl_4$ vapor, 1.7 kPa; treatment time, 1.5 h. Ammoximation conditions: see Table 1.

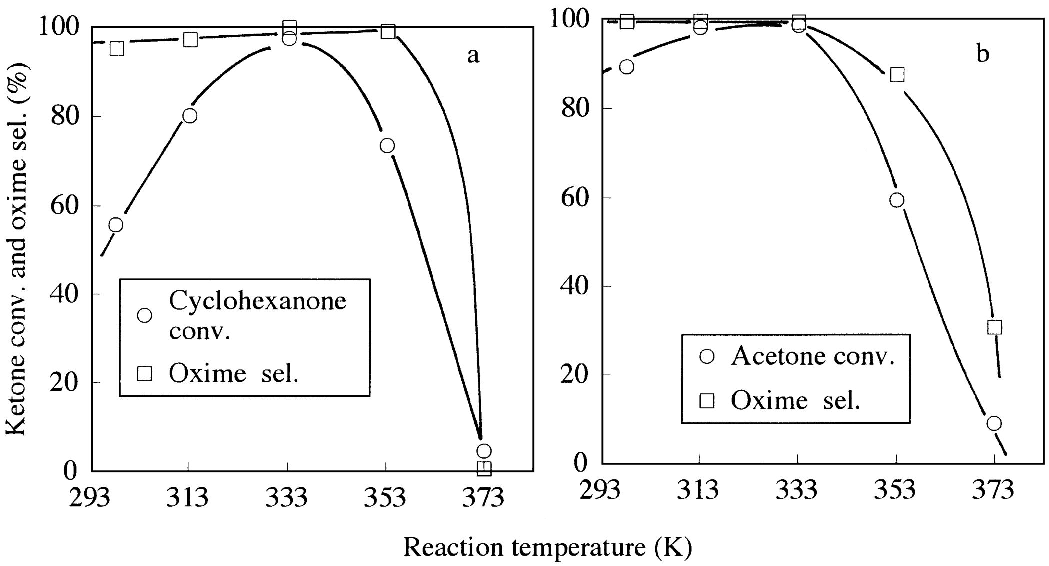


FIG. 3. Effect of reaction temperature on the ammoximation of cyclohexanone (a) and acetone (b). Ammoximation conditions: Ti-M(300) (Ti content: 0.18 mmol g^{-1}), 0.2 g; others, see Table 1.

electronegativity of the zeolite framework, which results in a loss of their catalytic activity for the alkene oxidation (12). It is concluded that in order to obtain Ti-M catalysts with higher hydrophobicity and with more Ti sites in Al-free region, mordenite is required to be dealuminated to have the Si/Al ratio over 200.

Effect of Reaction Parameters

1. Effect of reaction temperature. Among various reaction parameters, the reaction temperature was found to play the most important role on the catalytic performance of Ti-M. The influence of reaction temperature was studied using the ammoximation reaction of cyclohexanone and that of acetone over Ti-M(300). As shown in Fig. 3a, the conversion of cyclohexanone increased greatly with increasing the reaction temperature up to 333 K, and the selectivity to oxime also increased slightly. Both the conversion and the selectivity reached maxima at 333 K. The further increase in temperature up to 373 K resulted in the rapid decrease in both the conversion and the selectivity to nearly zero. Very similar phenomena have also been observed for the ammoximation of acetone (Fig. 3b). The decrease in the conversion of ketone at temperatures higher than 333 K is reasonably attributed to easier vaporization and decomposition of reactants, particularly NH_3 and H_2O_2. More importantly, we found that cyclohexanone oxime could be oxidized with H_2O_2 at the higher temperatures to yield cyclohexanone over Ti-M catalyst. Figure 4 shows the effect of reaction temperature on the oxidation of cyclohexanone oxime. Like the ammoximation, the oxime oxidation was also carried out in the presence of water and with a H_2O_2 to oxime molar ratio of 1.2. The products were mainly cyclohexanone and trace amount of large-molecular-weight conjugated products such as 2-(1-cyclohexen-1-yl)-cyclohexanone and 2-cyclohexylidenecyclohexanone formed through the aldol condensation of cyclohexanone. The oxidation of oxime did not occur significantly at the temperatures below 333 K, but occurred readily with increasing the temperature from 333 to 373 K. Thus, when the ammoximation is carried out at higher temperatures (over 333 K), the oxidation of oxime formed from the ammoximation back to ketone may also be responsible for the decrease in ketone conversion. As the

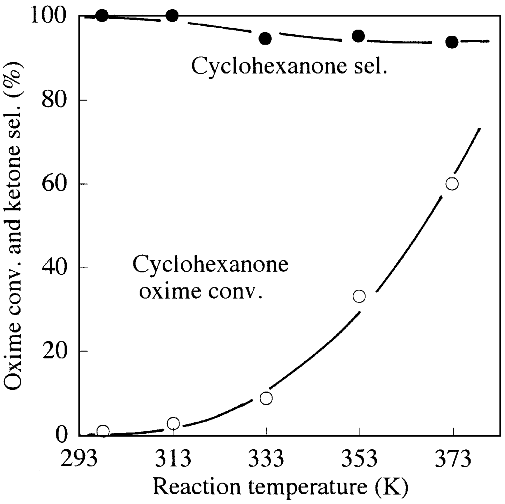


FIG. 4. Effect of reaction temperature on the oxidation of cyclohexanone oxime. Reaction conditions: Ti-M(300) (Ti content: 0.18 mmol g^{-1}), 50 mg; oxime, 4.84 mmol; H_2O, 10 ml; H_2O_2 (30 wt%), 0.5 ml; time, 2 h; oxime : $H_2O_2 = 1:1.2$.

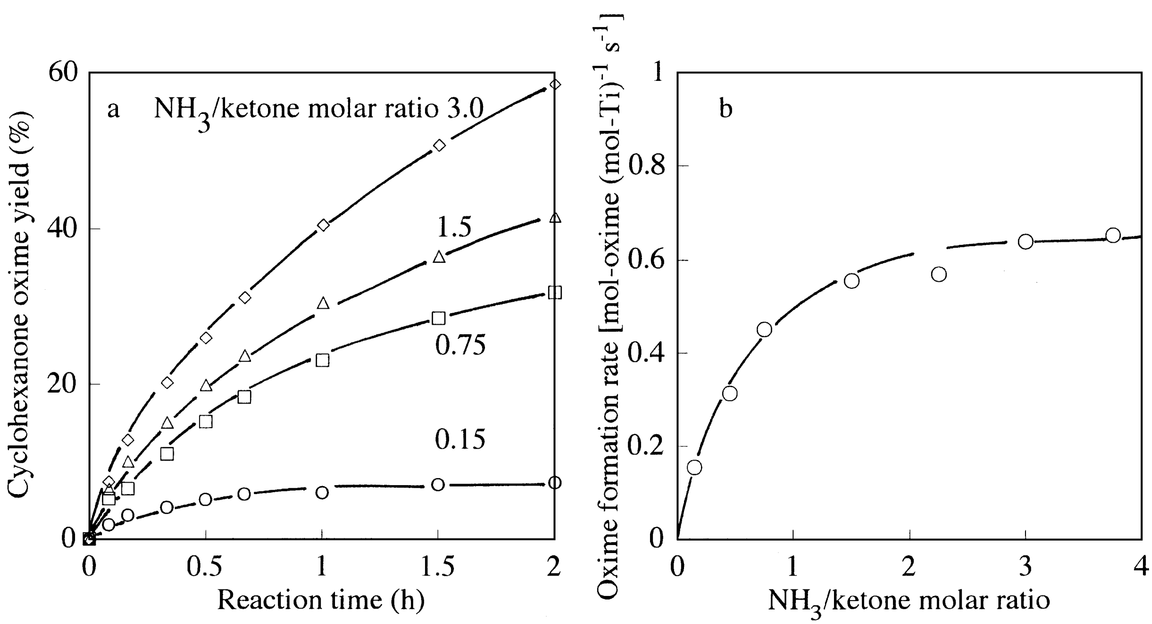


FIG. 5. Effect of NH_3/ketone molar ratio on the ammoximation of cyclohexanone: oxime yield as a function of reaction time (a) and initial formation rate for oxime as a function of the NH_3/ketone molar ratio. Ammoximation conditions: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 50 mg; the amount of NH_3 was varied to change the NH_3/ketone molar ratio; others, see Table 1.

amount of the by-products formed from the noncatalyzed reaction does not decrease with increasing the temperature, the decrease in the catalytic activity for the formation of oxime at higher temperatures would lower the oxime selectivity as expected. As a result, the above experiments show that the catalytic ammoximation of ketone takes place most effectively at the optimum reaction temperature of 333 K.

2. Effect of NH_3/ketone and H_2O_2/ketone molar ratio. The ammoximation of ketone to oxime stoichiometrically requires equal moles of ketone, NH_3 and H_2O_2. However, the loss of NH_3 and H_2O_2 due to the vaporization and the decomposition will have an influence on the reaction. In fact, it has been reported for the ammoximation over TS-1 (7) that the NH_3/H_2O_2 molar ratio greatly affects the ketone conversion and the oxime selectivity. Therefore, it is necessary to investigate the effects of the ratios of NH_3/ketone and H_2O_2/ketone on the ammoximation over Ti-M catalyst. Figure 5 shows the NH_3/ketone ratio on the ammoximation of cyclohexanone at 333 K and at H_2O_2/ketone of 1.2. As the reaction was too fast to be followed when 0.2 g of catalyst was used, the amount of catalyst was reduced to 50 mg. As expected, the oxime yield at the same reaction time increased with increasing the NH_3/ketone ratio (Fig. 5a). The initial rate for oxime formation increased rapidly with the NH_3/ketone ratio up to 1.5 and only showed a slight increase with further increasing the ratio to 3.0 (Fig. 5b). On the other hand, the selectivity to oxime was lower (90–95%) for the NH_3/ketone ratios below 1.5, while higher selectivities (nearly 100%) were obtained with the ratios over 1.5. The results are very similar to those reported for the ammoximation over TS-1 (7). As mentioned earlier, the noncatalyzed reaction yielding the higher boiling by-products always occurs in parallel with the catalyzed one yielding the oxime. Therefore, using a NH_3/ketone ratio higher than 1.5 is favorable to accelerate the main reaction to yield the oxime rapidly at higher selectivity.

Concerning the reactant of H_2O_2, it has been reported for TS-1 that its addition mode can influence the oxime formation (7). In the case of the ammoximation of cyclohexanone over Ti-M, we have not observed obvious differences in both the ketone conversion and the oxime selectivity when the H_2O_2 solution was added directly at one time or dropwise within a period of 0.5 to 2 h, suggesting the ammoximation can be operated more easily over Ti-M. Only the amount of H_2O_2 (relative to that of ketone) was found to exhibit a significant effect on the reaction as shown in Fig. 6. When the ammoximation was performed at 333 K with the NH_3/ketone ratio of 1.5, different H_2O_2/ketone ratios resulted in almost the same oxime yield within the first 10 min. For the reaction time longer than 10 min, the oxime yield increased with increasing the H_2O_2/ketone ratio from 0.2 to 1.2, and then decreased with the further increase in the ratio up to 3.0 (Fig. 6a). The oxime selectivity, on the other hand, was nearly 100% for the H_2O_2/ketone ratio lower than 1.2, while it was 80–90% for the ratio over 1.2. This suggests that adding an excess amount of H_2O_2 (corresponding to the H_2O_2/ketone ratio over 1.2) would make the concentration of unreacted H_2O_2 high in the reaction mixture, and this excess H_2O_2 would oxidize the oxime formed back to a ketone,

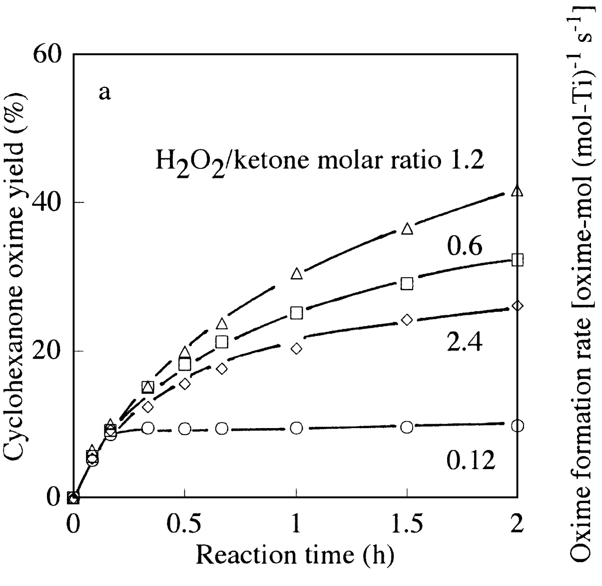


FIG. 6. Effect of H_2O_2/ketone molar ratio on the ammoximation of cyclohexanone: oxime yield as a function of reaction time (a) and initial formation rate for oxime as a function of the H_2O_2/ketone molar ratio. Ammoximation conditions: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 50 mg; the amount of H_2O_2 was varied to change the H_2O_2/ketone molar ratio; others, see Table 1.

just as indicated earlier. Interestingly, the H_2O_2/ketone ratio did not influence the initial formation rate for the oxime in a wide range, 0.06–3.0 (Fig. 6b), indicating that the reaction rate is almost zero order with respect to the concentration of H_2O_2. The catalytically active sites of titanium zeolites in the presence of H_2O_2 have been postulated to be Ti-hydroperoxo complex (Ti-OOH), formed from the interaction of the framework Ti with H_2O_2. The color change of the catalyst from white to bright yellow upon the contact with H_2O_2 indicates that the formation of this complex occurs readily and rapidly, which has already been verified by the physicochemical characterization with IR and UV spectroscopy (31). The reaction rate thus depends on the concentration of Ti-hydroperoxo complex, but not on that of H_2O_2 unless the amount of H_2O_2 added is in far excess of the Ti content in the catalyst. In fact, the amount of H_2O_2 added into the reaction mixture was about 150 times that of Ti, even for the lowest H_2O_2/ketone ratio of 0.06. Therefore, the concentration of Ti-hydroperoxo complex is the same, independent of the various H_2O_2/ketone ratios, and the initial formation rate for the oxime should be reasonably constant just as observed.

3. Effect of catalyst/ketone ratio. The effect of the catalyst to ketone ratio on the ammoximation was studied by setting the amounts of all three reactants at constants, but only by varying the amount of catalyst. Both the cyclohexanone conversion and the oxime selectivity increased dramatically with increasing the catalyst/ketone ratio (Fig. 7). When a ratio of ca 10 g mol^{-1} (corresponding to 0.2 g of catalyst) was used, both the conversion and the selectivity reached nearly 100%. Again, as the noncatalyzed reaction yielding by-products always competes with the main catalytic reaction yielding the oxime, the above results suggest that using the catalyst/ketone ratio over 10 g mol^{-1} is helpful to produce the oxime effectively and selectively.

4. Effect of solvent. The titanium zeolite-catalyzed reactions have been reported to depend greatly on the nature of the solvent used. Roffia *et al.* have suggested that the ammoximation over TS-1 proceeds very well in the cosolvent of H_2O and *t*-butanol (32), while Thangaraj *et al.*

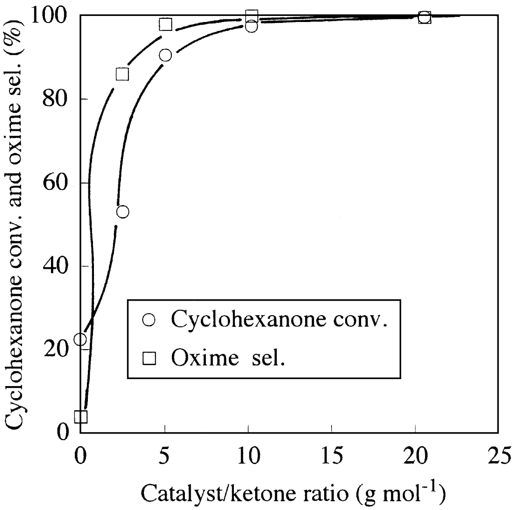


FIG. 7. Effect of catalyst content on the ammoximation. Ammoximation conditions: Ti-M(300) (Ti content: 0.18 mmol g^{-1}); the amount of catalyst was varied to change the catalyst/ketone ratio; others, see Table 1.

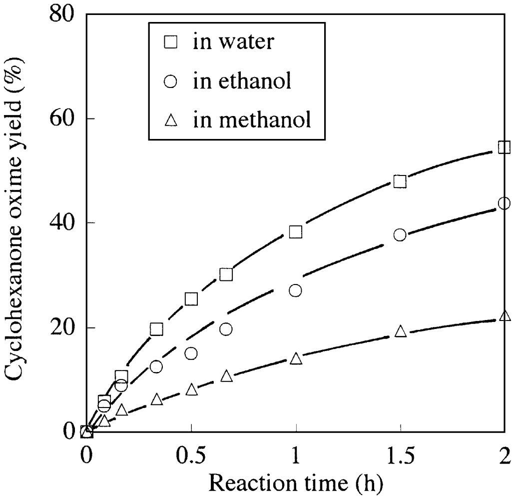


FIG. 8. Effect of the solvent on the ammoximation. Ammoximation conditions: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 50 mg; solvent, 10 ml; others, see Table 1.

have shown that the best solvent for the ammoximation of cyclohexanone over TS-1 is water (7). In the present study, the ammoximation of cyclohexanone has been carried out with H_2O, methanol, and ethanol as a solvent, respectively (Fig. 8). The oxime yield increased in the order of $H_2O > EtOH > MeOH$. The oxime selectivity was in the same order, that is, about 100% for H_2O, 85% for EtOH, and 65% for MeOH. Thus, the best solvent for the ammoximation over Ti-M catalyst is H_2O. The solvent effects for the liquid phase reactions may be due to its homogenization of the reaction mixture, or due to its polarity (33). Disregarding the difference in the polarities of the present three polar solvents, the most significant difference between the inorganic solvent of H_2O and the organic solvents of EtOH and MeOH seems to be that the reaction proceeds in two liquid phases in the former, while in one liquid phase in the latter ones. Cyclohexanone molecules are expected to be adsorbed into the pores of Ti-M and to reach the active sites more easily in EtOH or in MeOH. However, the results from Fig. 8 show that a lower oxime yield was obtained for these two solvents. This can be well interpreted by the ammoximation mechanism which will be discussed later in detail. It is to be seen that ketone molecules do not need to enter the pores of the catalyst during the ammoximation. Therefore, organic solvents make the ketone diffuse easily into the pores to retard the diffusion of NH_3 and H_2O_2. Furthermore, the nonaqueous, one liquid phase condition with EtOH or MeOH as solvent is reasonably favorable to the noncatalyzed reaction yielding by-products; thus these alcohols lower the oxime selectivity.

Reaction Mechanism

The diffusion problems have been suggested as important for the titanium zeolites in the oxidation of alkane and alkenes with H_2O_2. For example, the catalytic activity of TS-1 decreased gradually by increasing the carbon number of the linear alkanes and alkenes, and decreased dramatically to almost zero for the branched and cyclic substrates (12, 34, 35). We have also observed shape-selectivity over a Ti-M catalyst in the hydroxylation of alkyl aromatics (27). In the present ammoximation over Ti-M, the cyclohexanone as a cyclic ketone reacted at a comparable rate to the linear acetone with relatively smaller molecular size, and it exhibited a very high TON within the reaction of 2 h (Fig. 2). These observations make us wonder whether Ti-M also shows shape-selectivity for the ammoximation. The ammoximation reactions of various ketones (including some aldehydes) were thus conducted to investigate the influence of the molecular size on the catalytic performance as shown in Table 2. The oxime selectivity was nearly 100% for all the ketones, while the conversion varied among the ketones. The conversion seemed to decrease with an increase in the number of carbon rings for the cyclic ketones. However, no obvious difference in the conversion was observed between the smallest acetone and the cyclic ketones, such as cyclopentanone, cyclohexanone, and cycloheptanone. Moreover, Ti-M was even active for the largest cyclododecanone. To clarify whether the activity is determined by the molecular size of the ketones, their adsorption capacities were measured to characterize their abilities to diffuse to the active sites located in the pores of the Ti-M. The adsorption experiments were performed in the liquid phase using 1,3,5-triisopropylbenzene (TIPB) as a solvent at 333 K and under vigorous agitation, that is,

TABLE 2

Ammoximation of Various Ketones and Aldehydes over Ti-M Catalyst

Ketone or aldehyde	Ammoximation[a] Conv. (%)	Ammoximation[a] Oxime sel. (%)	Adsorption[b] capacity (mmol g^{-1})
Acetone	98.8	99.7	1.45
Cyclopentanone	95.8	99.4	0.81
Cyclohexanone	93.6	99.3	0.79
Cycloheptanone	93.2	99.7	0.65
Cyclooctanone	57.5	99.5	n.d.[c]
Cyclododecanone	16.7	99.8	0.05
4-*t*-Butyl cyclohexanone	93.0	99.3	0.26
Benzophenone	0.1	100	0.26
Benzaldehyde	96.1	97.1	0.72
p-Tolualdehyde	95.2	99.3	0.53
m-Tolualdehyde	94.8	99.5	0.45
Acetophenone	30.9	99.7	0.49

[a] Ammoximation conditions: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 0.2 g; others, see Table 1.

[b] Adsorption conditions: cat., 0.1 g; adsorbate (1 wt% in 1,3,5-TIPB), 2 ml; temp., 333 K; time, 2 h.

[c] Not determined, due to the fact that the present GC could not separate cyclooctanone from 1,3,5-TIPB.

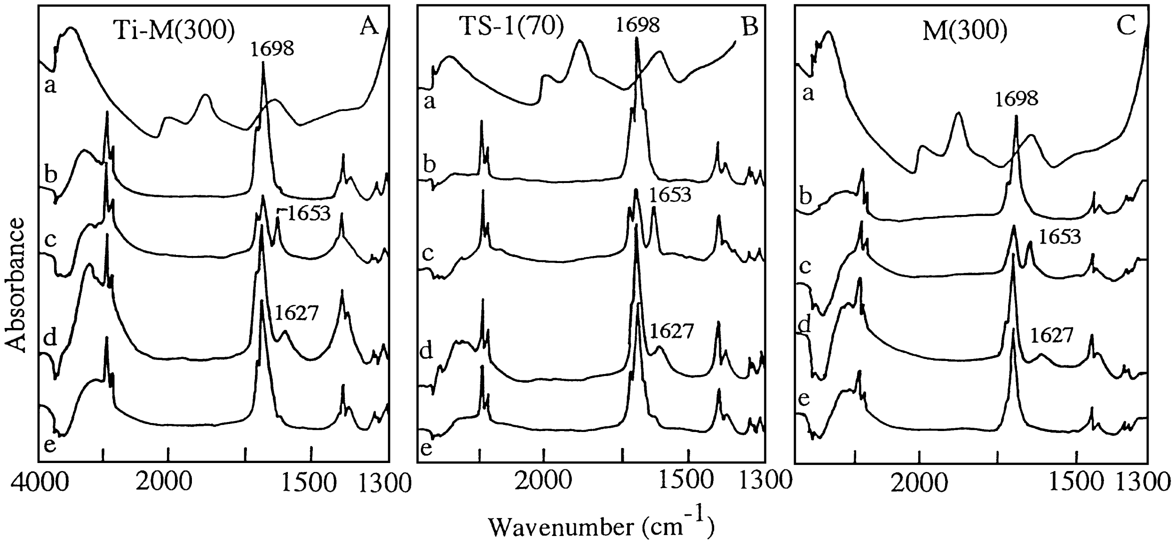
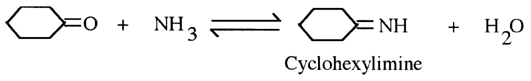


FIG. 9. IR spectra of Ti-M (A), TS-1 (B), and M(300) (C). (a) After a brief evacuation at 333 K for 10 min; (b) adsorbed with cyclohexanone (10 torr) and followed by an evacuation at 333 K for 1 min (difference spectrum); (c) contact with NH_3 gas (10 torr) at 333 K and after a brief evacuation; (d) exposed to H_2O_2 vapor (10 torr) at 333 K for 10 min without evacuation; (e) as d evacuated at 333 K for 2 min.

under conditions similar to those applied for the ammoximation. From the adsorption capacity shown in Table 2, cyclododecanone hardly diffused into the pores of the catalyst. However, it still showed higher conversion than benzophenone which diffused relatively more easily through the channels. On the other hand, 4-*t*-butyl cyclohexanone with an adsorption capacity of only one third of that of cyclohexanone still showed a comparable conversion. Very similar results have also been observed for the ammoximation of aromatic ketones and aldehydes (Table 2). In the hydroxylation of alkyl aromatics with H_2O_2 over Ti-M, we have observed that an increase in one carbon number from toluene to xylene isomers decreased the activity greatly as a consequence of the diffusion restriction (27). In the present study, increasing one carbon number from benzaldehyde to *p*- and *m*-tolualdehyde, the adsorption capacity on Ti-M decreased as expected, but the conversion in the ammoximation was not affected significantly. On the other hand, increasing similarly one carbon number to acetophenone resulted in a great decrease in the conversion, although acetophenone showed a comparable adsorption capacity to tolualdehyde isomers (Table 2). All these results strongly suggest that the shape-selectivity is not so important in the liquid-phase ammoximation and that the reactants of ketones (or aldehydes) need not enter into the pores of Ti-M. As the difference in the activity among the various ketones is not due to the diffusivity, it may be due to the intrinsic reactivity of the ketone itself.

As mentioned in the Introduction, two reaction pathways have been hypothesized for the ammoximation of cyclohexanone over TS-1, i.e., the imine path (7, 17) and the hydroxylamine path (8). The cyclohexylimine intermediate formed through the reaction between cyclohexanone and NH_3 has been observed over TS-1 with IR spectroscopy (19). The latter mechanism includes the oxidation of NH_3 by H_2O_2 over Ti sites to form hydroxylamine, NH_2OH, as a first step and the reaction of NH_2OH with cyclohexanone to give oxime as a second step. This mechanism was supported by the fact that NH_2OH was produced from NH_3 and H_2O_2 over TS-1 in the absence of ketone (20). UV studies gave further evidence as NH_3 could interact with H_2O_2 over TS-1 (8).

Considering the imine path, we investigated the interaction between cyclohexanone and NH_3 over Ti-M with IR spectroscopy. As shown in Fig. 9A, an adsorption of cyclohexanone on pre-evacuated Ti-M(300) at 333 K followed by a brief degassing gave the characteristic bands of ketone in the spectrum (b) at 1698 cm^{-1} due to C=O stretching, around 3000 cm^{-1} due to CH stretching and between 1500 and 1300 cm^{-1} corresponding to different deformation modes of CH_2 groups (18). When the sample with adsorbed cyclohexanone species was exposed to NH_3 gas, a new band was developed at 1653 cm^{-1} upon a decrease in the intensity of the C=O band (c). This new band has been assigned to a C=N stretching (18, 19), indicating the formation of surface imine species over Ti-M according to



[1]

The 1653 cm^{-1} band disappeared completely upon a subsequent introduction of H_2O_2 vapor, while the 1698 cm^{-1} band was nearly restored to its initial intensity and a new band appeared at 1627 cm^{-1} due to adsorbed H_2O species (d). However, the characteristic band expected for oxime at 1481 cm^{-1} (OH associated) (36) was not observed.

After pumping out the adsorbed H_2O species, the spectrum turned to be very similar to that of initially adsorbed cyclohexanone (e). The same IR experiments were also carried out on TS-1 and dealuminated mordenite, M(300), which resulted in very similar spectra (Figs. 9B and C). The above results show that cyclohexanone really interacts with NH_3 over the catalyst to form the imine species independent of the presence of the framework Ti species as described in [1]. The imine species thus formed, however, is unstable and tends to decompose back to a ketone, according to the reverse reaction of [1] in the presence of a large amount of H_2O vapor (H_2O is always present in a great amount in an aqueous H_2O_2 solution of 30 wt%). Thus, the imine species with a too-short lifetime are hard to interact with the Ti-OOH species to give the oxime. Subsequently, the mechanism of an imine path proposed for the gas-phase ammoximation process with NH_3 gas and O_2 over amorphous silica (18, 37) and postulated with IR spectroscopy for TS-1 in the absence of H_2O (19) does not best explain what is occurring during the liquid-phase ammoximation in the presence of H_2O. The imine path has also been used to explain the formation of the by-product of peroxydicyclohexylimine (7). However, it was not a typical by-product in the present study, and it may be produced directly from the noncatalyzed reaction between cyclohexanone, NH_3 and H_2O_2 (38). Moreover, if the ammoximation really proceeds through the imine path, the imine should diffuse into the pores to interact with Ti sites, which is contradictory to the fact that Ti-M did not exhibit shape-selectivity for ketones with various molecular sizes as described above. Thus, the imine path should be ruled out.

With respect to the hydroxylamine path, we first carried out the oxidation of NH_3 with H_2O_2 in the absence of a ketone over Ti-M under the same conditions used for the ammoximation. After the catalyst was filtered off, we then added cyclohexanone into the filtrate solution to verify whether the oxime could be formed. Figure 10 shows the result of the reaction of cyclohexanone with the filtrate for 0.5 h which was confirmed to be long enough to finish the reaction. The *x*-axis represents the reaction time of the NH_3 oxidation. Like the one-step ammoximation, the present two-step process also yields the oxime at a high selectivity. It is deduced that the NH_2OH intermediate which reacts easily with a ketone to give an oxime, through so-called oximation, has been formed in the first step as follows:

$$NH_3 \quad + \quad H_2O_2 \quad \xrightarrow{\text{Ti-M}} \quad \underset{\text{Hydroxylamine}}{NH_2OH} \quad + \quad H_2O \qquad [2]$$

The ketone conversion increased rapidly with the reaction time of NH_3 oxidation, reached a maximum of ca 50% at 0.5 h and showed no further increase up to 3 h. Unlike the one-step ammoximation (Fig. 3), the ketone conversion in the two-step process did not approach 100%, probably because the first step, i.e., the reaction of NH_3 and H_2O_2 to form NH_2OH, has already reached an equilibrium after 0.5 h. As the thermodynamic data of NH_2OH, especially its Gibbs free energy, are not available in the open literature, the exact equilibrium concentration of NH_2OH cannot be calculated. It should be noted that the oxime was formed without Ti-M in the second step, i.e., the second step can be the noncatalyzed reaction. In fact, the oxime formation is not due to the presence of a Ti species released from Ti-M during the NH_3 oxidation, because no peaks due to a Ti species was detected in the UV spectrum of the filtrate.

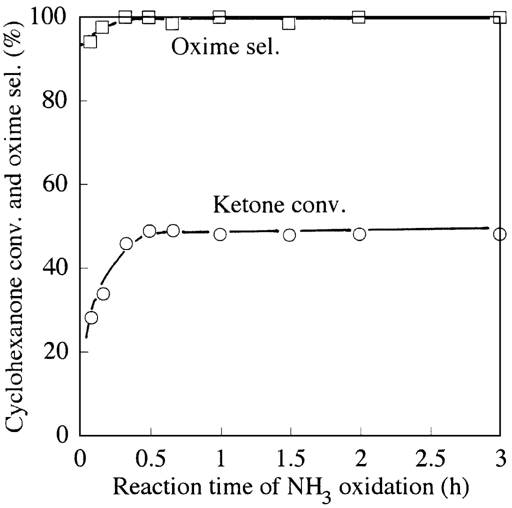


FIG. 10. Oxime formation by the reaction of cyclohexanone with the filtrate from the oxidation of NH_3 with H_2O_2. Preparation conditions for the filtrate: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 0.2 g; H_2O, 10 ml; NH_3 (25 wt%), 2 ml; H_2O_2 (30 wt%), 2 ml; temp., 333 K. Reaction conditions for cyclohexanone with the filtrate: cyclohexanone, 19.34 mmol; temp., 333 K; time, 0.5 h.

Figure 10 has demonstrated that a NH_2OH intermediate was really formed from the NH_3 oxidation by H_2O_2 over Ti-M. When a ketone, NH_3, H_2O_2, and Ti-M are coexistent, the NH_2OH formed in the first step would remain in a different amount in the ammoximation mixture if the reaction rate of the second step (the reaction between the ketone and NH_2OH) is different. The total yield of NH_2OH formed, the amount of NH_2OH remaining in the reaction mixture, and the yield of oxime formed during the ammoximation have been compared under the same conditions between cyclohexanone, cyclooctanone, cyclododecanone, and benzophenone, whose ammoximation conversions differed greatly, as shown in Table 2. After the ammoximation was performed for a certain period of time, the catalyst was filtered off, and a certain amount of acetone (19.34 mmol) was added into the filtrate immediately to react with any unreacted NH_2OH for 30 min. The amount of NH_2OH remaining in the mixture was thus determined from the amount of acetone oxime formed. The total amount of NH_2OH formed should be the sum of the amount of acetone

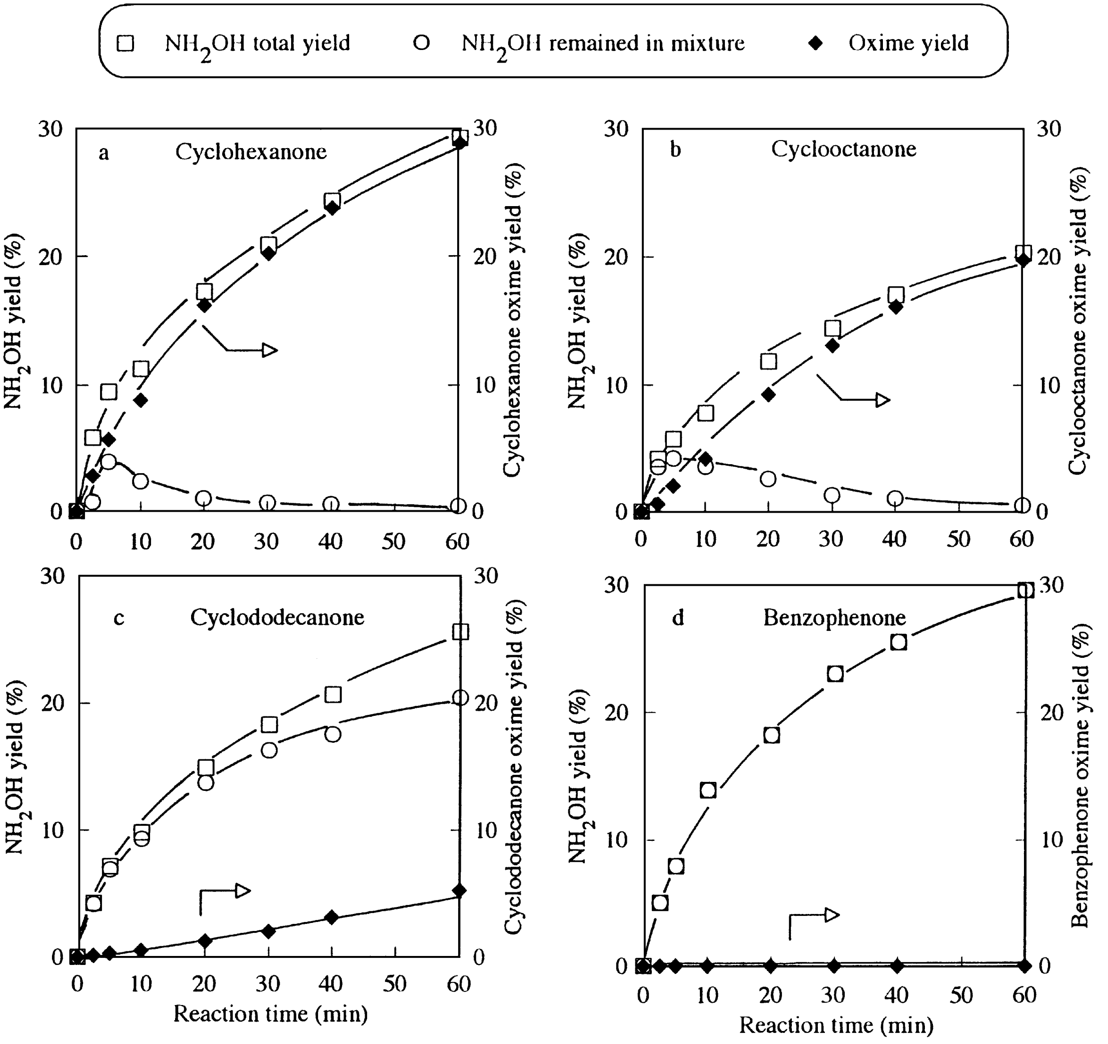


FIG. 11. Formation of NH_2OH and oxime as a function of reaction time in the ammoximation of cyclohexanone (a), cyclooctanone (b), cyclododecanone (c) and benzophenone (d). Ammoximation conditions: Ti-M(300) (Ti content: 0.15 mmol g^{-1}), 50 mg; others, see Table 1. The amount of NH_2OH remained was determined from that of acetone oxime by adding 19.34 mmol of acetone into the reaction mixture after the catalyst was filtered off.

oxime and that of cyclohexanone oxime (in the case of cyclohexanone ammoximation). This method was reported to be accurate and effective for routine hydroxylamine determination over a range of concentration in a reasonable time period (39).

In the case of cyclohexanone ammoximation (Fig. 11a), NH_2OH remaining in the mixture was maximized at 5 min and was hardly detected after 30 min. Although the amount of NH_2OH remaining was always smaller than that of the cyclohexanone oxime formed, the total yield of NH_2OH was two times more than that of the cyclohexanone oxime at the initial stage. For the cyclooctanone ammoximation (Fig. 11b), the NH_2OH remaining was even more than the cyclooctanone oxime at the initial stage; it then decreased gradually upon the oxime formation and disappeared after 60 min. The changes in the amount of remaining NH_2OH and the yield of cyclooctanone oxime are characteristic curves of a consecutive reaction. The NH_2OH formed was almost unreacted with the ketone and remained in the mixture at the first stage for the cyclododecanone ammoximation (c). The obvious difference between the total NH_2OH and the remaining NH_2OH was observed only when cyclododecanone oxime was formed after 20 min. Finally, in the case of benzophenone (d), the NH_2OH remained almost completely in the mixture unreacted with the benzophenone, which resulted in no oxime formation even after 1 h of reaction. The above results clearly indicate that the liquid-phase ammoximation of a ketone over Ti-M is a consecutive reaction with NH_2OH as the intermediate and that the initial rate of NH_2OH formation is faster than that of oxime formation. Thus, the difference in the conversion observed for various ketones (Table 2) must be the result of

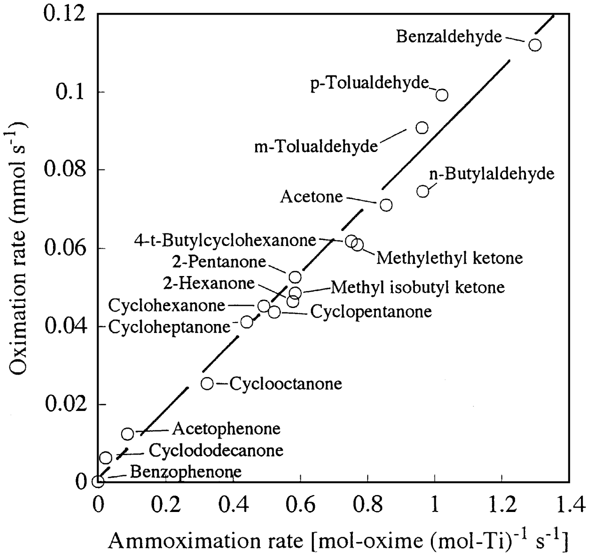
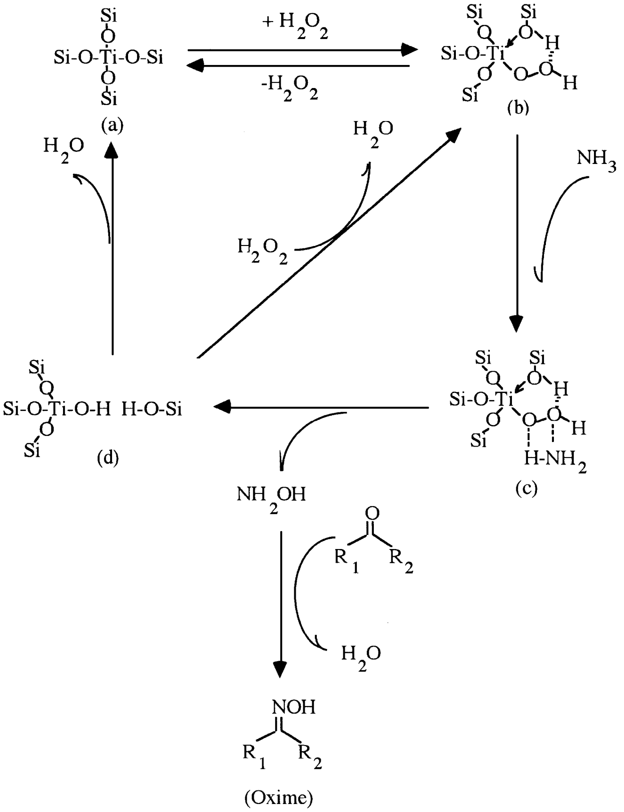


FIG. 12. The correlation between the ammoximation rate and the oximation rate. Ammoximation conditions: see Table 1. Oximation conditions: ketone, 4.84 mmol; NH_2OH (in chloride form), 0.4 g; H_2O, 10 ml; temp., 333 K; NH_2OH : ketone = 1.2 : 1.

the different intrinsic reactivity of the ketones themselves with NH_2OH.

The initial rate of oxime formation in the ammoximation has been determined for various ketones and aldehydes from the oxime-formation curves as shwon in Fig. 11. The initial formation rate of the corresponding oxime in the oximation has also been measured by carrying out the reactions of ketones or aldehydes with hydroxylamine chloride (the most common form of NH_2OH commercially available) under similar conditions without Ti-M. Figure 12 depicts the relationship between these two formation rates. For all the ketones and aldehydes used, there is a good correlation between the ammoximation and the oximation rates, which strongly supports the idea that the liquid-phase ammoximation over Ti-M proceeds through NH_2OH as an intermediate and indicates that the rate-determining step is the reaction between a ketone (or aldehyde) and the NH_2OH intermediate. This result is very consistent with the mechanism of the NH_2OH intermediate proposed for TS-1 previously (8, 20). On the basis of above results and discussion, the ammoximation mechanism is summarized graphically in [3]. H_2O_2 first interacts with the tetrahedrally coordinated Ti sites in a regular form (a) or in a hydrated form (d) to form Ti-OOH species (b), which is probably present in a five-membered cyclic structure through the interaction with a protic molecule (29, 30) which is H_2O here. The NH_3 molecule then penetrates into the pores to attack this active site to form a precursor for the formation of NH_2OH (c). The hydroxyl group from the Ti-hydroperoxo complex is transferred to adsorbed NH_3 to form NH_2OH. NH_2OH released from the Ti site reacts immediately in the pores with ketone which is small enough to penetrate the channel, or diffuses out of the pores to react with the ketone in the solution to yield the oxime. The latter is expected to mainly occur since NH_2OH whose molecular size is much smaller than the pores of mordenite can diffuse more easily out of the pores into the solution than a cyclic ketone diffusing into the pores. The resulting Ti site (d) goes further into the catalytic cycles by interacting again with H_2O_2.



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