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A novel titanosilicate with MWW structure: Highly effective liquid-phase ammoximation of cyclohexanone

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Abstract

The liquid-phase ammoximation of cyclohexanone with ammonia and hydrogen peroxide was conducted over Ti-MWW. Ti-MWW is capable of giving both cyclohexanone conversion and oxime selectivity >99% under optimum reaction conditions. It is a highly active, selective, and reusable catalyst for the synthesis of cyclohexanone oxime in the presence of water. In comparison to other titanosilicates, Ti-MWW shows much higher catalytic activity, even superior to that of TS-1. The catalytic performance of Ti-MWW depends greatly on the operating conditions of the reaction, especially the method of adding substrates. The reason why the method of adding substrates plays such an important role in the ammoximation of ketones or aldehydes over Ti-MWW was investigated after a detailed evaluation of the reaction mechanism.

Keywords: Ti-MWW; TS-1; Titanosilicate; Liquid-phase ammoximation; Cyclohexanone oxime

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1. Introduction

The discovery of the first titanosilicate with the MFI structure (TS-1) has opened up new possibilities for developing environmentally benign processes based on zeolite catalysts, because TS-1 is capable of catalyzing a variety of organic compounds with hydrogen peroxide as an oxidant and with water as the sole byproduct [1]. After the industrialization of phenol hydroxylation using TS-1/H_2O_2 catalytic systems, the commercial application of TS-1 to the process of liquid-phase ammoximation of cyclohexanone to corresponding oxime in 2003 is considered a new milestone in the field of zeolite catalysis.

The bulk chemical of cyclohexanone oxime is a key intermediate for the manufacture of ε-caprolactam (CPL), a starting material for nylon-6 synthesis that had an annual world market of 3.6 million tons in 1998 [2]. Conventionally, CPL is manufactured first by the noncatalytic oximation of cylcohexanone with hydroxylamine derivatives to give oxime, and then by liquid-phase Beckmann rearrangement of the oxime in oleum. These processes have encountered serious difficulties, including the use of poisonous hydroxylamine and corrosive fuming sulfuric acid and the production of large amounts of the byproducts ammonium sulphate and nitrogen oxides, leading to environmental problems. In particular, as much as 2.8 tons of ammonium sulfate results from the product separation process in the production of every 1 ton of CPL [1]. By combining the ammoximation in the TS-1/H_2O_2/NH_3 system and the heterogeneous vapor-phase Beckmann rearrangement over highly siliceous ZSM-5 (silicalite-1), Sumitomo Chemical commercialized a revolutionary 60,000-ton capacity CLP process in 2003.

Although this innovative process is environmentally friendly from the standpoint of zero emissions, it has some drawbacks, including a high cost of TS-1 production due to the use of the expensive structure-directing agent (SDA) tetrapropylammonium hydroxide and an organic silicon source, the need for a relatively high weight ratio of TS-1 catalyst to substrates, and the use of a volatile solvent of *tert*-BuOH [3]. To develop more efficient ammoximation processes, other titanosilicates, such as TS-2 [4], Ti-MOR [5], and Ti-Beta [6], have been developed for

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the liquid-phase ammoximation of cyclohexanone by several groups. TS-2 and Ti-Beta generally show worse catalytic performance than TS-1 because of their crystalline structure and hydrophilic/hydrophobic characteristics unsuitable to the ammoximation, whereas Ti-MOR shows some effectiveness but at a relatively high ratio of catalyst to cyclohexanone. Moreover, Ti-MOR can be synthesized only through a troublesome posttreatment method involving dealumination and gas-phase titanation, and thus the prospect of using Ti-MOR in a larger-scale production is uncertain.

We have recently developed a new titanosilicate with the MWW structure, Ti-MWW [7–9]. Structurally analogous to the well-known aluminosilicate of MCM-22, Ti-MWW has a pore system consisting of 12-membered ring (MR) side cups and two independent interlayer and intralayer 10-MR channels, one of which contains the $0.7 \times 0.7 \times 1.8$ nm supercages [10,11]. This unique pore structure leads to superior catalytic activity and product selectivity in the epoxidation of various alkenes with H_2O_2 in comparison with conventional TS-1 [12,13]. Because Ti-MWW is synthesized from an inorganic silica source and an inexpensive SDA of piperidine or hexametheleneimine, it also has an advantage over TS-I in terms of the cost of catalyst manufacturing.

In this study, we have applied Ti-MWW to the ammoximation of cyclohexanone and found that it is extremely effective in the presence of water. This may bring about a much cleaner process for oxime synthesis. Furthermore, the high performance of Ti-MWW depends greatly on the operating conditions of the reaction. This interests us in regard to clarifying the reaction mechanism, which will be useful to addressing the chemical engineering issues involved in liquid-phase ammoximation.

2. Experimental

2.1. Catalyst preparation and characterization

Following previously reported methods, Ti-MWW catalysts were hydrothermally synthesized (Ti-MWW-HTS) or post-synthesized (Ti-MWW-PS) [14–16]. For control experiments, other titanosilicates of TS-1 [17], Ti-MOR [5], and Al-free Ti-Beta [18,19] were also prepared as described previously. For both Ti-MWW and TS-1, a series of samples with different Si/Ti molar ratios were prepared by varying the Ti content in the synthesis.

All of the catalysts were characterized by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer, X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer (Cu-K_α), N_2 adsorption on an Autosorb Quancachrome 02108-KR-1, scanning electron microscopy (SEM) on a JEOL JSM-T220, and UV–vis (Shimadzu UV-2400PC) and IR (Shimadzu FTIR-8100) spectroscopy.

2.2. Catalytic reactions

The ammoximation runs were performed batchwise in a 25-mL three-neck flask equipped with a magnetic stirrer and a condenser. In a typical run, 50 mg of catalyst, 10 mmol of cyclohexanone, 5 mL of solvent, and 12 mmol of NH_3 aqueous solution (25%) were charged into the flask, and the mixture was heated to the desired temperature (303–373 K). The reaction was then initiated by adding diluted aqueous H_2O_2 (5%, 12 mmol) at a constant rate continuously with a micropump for 1 h. After the addition of H_2O_2, the mixture was stirred for another 0.5 h. The reaction mixture was converted into a homogeneous phase by adding 15 g of ethanol. After the catalyst solid was removed, the analyses were performed on a gas chromatograph (Shimadzu 14B with a flame ionization detector) equipped with a 30-m DB-1 capillary column, using toluene as an internal standard. The amounts of ammonia and H_2O_2 remaining in the mixture were quantified by acid–base titration method and iodometry, respectively.

The ammoximation of other ketones and aldehydes (acetone, cyclopentanone, cycloheptanone, acetophenone, *n*-butylaldehyde, *p*-tolualdehyde, and benzoaldehyde) were carried out in a similar way. The oxidation of hydroxylamine and non-catalytic oximation of ketones and aldehydes were performed using a commercially available chloride.

3. Results and discussion

3.1. Characterization of titanosilicate catalysts

XRD confirmed that all of the titanosilicates prepared had the objective crystalline structures intended to obtain. In UV–vis and IR spectra, the samples showed the characteristic adsorption bands at 220 nm and 960 cm^{-1}, respectively [14], which are assigned to the tetrahedral Ti species isolated in the zeolite framework [1]. The specific surface areas (Langmuir) determined from N_2 adsorption at 77 K were 580–630 $m^2\,g^{-1}$ for Ti-MWW, 510–550 $m^2\,g^{-1}$ for TS-1, 553 $m^2\,g^{-1}$ for Ti-MOR, and 653 $m^2\,g^{-1}$ for Ti-Beta. Thus, on the basis of the crystallinity, surface area, and the nature of Ti species, these titanosilicates were qualified as liquid-phase oxidation catalysts with H_2O_2 as an oxidant.

3.2. Comparison of ammoximation of cyclohexanone among various titanosilicates

Table 1 compares the results of cyclohexanone ammoximation over different titanosilicate catalysts. The products were mainly cyclohexanone oxime, along with some higher boiling compounds such as peroxydicyclohexyl amine and others. The products other than oxime generally became obvious only at a low cyclohexanone conversion, but their absolute amount was very low. Under optimized conditions (details of which are given later in the paper), Ti-MWW-PS showed cyclohexanone conversion and oxime selectivity as high as 99% in the presence of water when H_2O_2 was added into system slowly and gradually (Table 1, no. 1). Although somewhat lower in the conversion of cyclohexanone than Ti-MWW-PS, good performance was also achieved with Ti-MWW-HTS when more catalyst was used (Table 1, no. 2). The Ti species achieved by postincorporation are assumed to occupy the framework sites that are

Table 1
The results of cyclohexanone ammoximation over different titanosilicate catalysts[a]

No.	Catalyst	Si/Ti	Solvent	Conversion (mol%)	Oxime selectivity[b] (mol%)	TON[e]
1	Ti-MWW-PS	55	H_2O	99.4	99.9	656
2	Ti-MWW-HTS[c]	50	H_2O	97.0	99.9	291
3	TS-1[d]	51	H_2O–*t*-BuOH	97.0	99.9	155
4	TS-1	51	H_2O	16.2	72.8	99
5	Ti-MOR[d]	90	H_2O	60.0	95.0	122
6	Ti-Beta[d]	76	H_2O	15.0	4.0	37

[a] Reaction conditions: catalyst, 50 mg; cyclohexanone, 10 mmol; solvent, 5 mL; NH_3 (25%), 12 mmol; H_2O_2 (5%), 12 mmol; temperature, 338 K; time, 1.5 h. H_2O_2 was added dropwise at a constant rate within 1 h.

[b] Byproducts were mainly peroxydicyclohexyl amine, etc.

[c] The amount of catalyst used was 100 mg.

[d] The amount of catalyst used was 200 mg. Reaction time was 5 h. Similar reaction conditions to those reported in the literature [20] have been adopted.

[e] TON, turnover number in mol $\text{mol}_{\text{Ti}}^{-1}$.

Table 2
Effect of adding method of substrates on the cyclohexanone ammoximation over Ti-MWW[a]

No.	Conversion (mol%)	Oxime selectivity (mol%)	H_2O_2 conversion (mol%)	NH_3 conversion (mol%)
1[b]	99.4	99.9	98.4	96.0
2[c]	2.8	Trace	99.7	81.2
3[d]	4.8	95.0	99.8	84.3

[a] Reaction conditions: catalyst, Ti-MWW-PS (Si/Ti = 55); others, see Table 1.

[b] A desirable amount of H_2O_2 was added dropwise for 1 h to the reaction mixture of cyclohexanone, NH_3, H_2O and Ti-MWW.

[c] All the substrates were added once from the beginning.

[d] A desirable amount of NH_3 solution was added dropwise for 1 h to the reaction mixture of cyclohexanone, H_2O_2, H_2O and Ti-MWW.

more accessible to substrate molecules than those obtained by direct hydrothermal synthesis, leading to a higher intrinsic activity (TON) of Ti-MWW-PS. Adopting the same reaction conditions as reported previously [20], TS-1 showed comparably high conversion for cycohexanone and selectivity to oxime in a co-solvent of *t*-BuOH and water (Table 1, no. 3). Note that compared with Ti-MWW, achieving these results necessitated increasing the amount of TS-1 relative to cyclohexanone and prolonging the reaction time. But TS-1 was significantly retarded in a single solvent of water (Table 1, no. 4). In terms of TON, TS-1 was obviously less active than Ti-MWW. The superiority of Ti-MWW over TS-1 has also been observed in the epoxidation of various kinds of alkenes, which has been attributed to the unique pore system of MWW zeolite favoring the adsorption and access of substrate molecules to the Ti active sites [8,9,12–14]. Ti-MOR and Ti-Beta turned out to be less active and selective in the ammoximation of cyclohexanone (Table 1, nos. 5 and 6). Despite different optimized reaction conditions, particularly the solvent effect, the titanosilicates investigated for the ammoximation showed the following order of catalytic performance: Ti-MWW-PS > Ti-MWW-HTS > TS-1 > Ti-MOR > Ti-Beta.

3.3. *Effects of reaction parameters on the ammoximation over Ti-MWW*

3.3.1. *Effect of adding method of substrates*

Table 2 presents the results of cyclohexanone ammoximation on Ti-MWW using different methods of adding the substrates. The Ti-MWW (Si/Ti = 55) sample was adopted as a catalyst. High cyclohexanone conversion and oxime selectivity (both > 99%) were obtained only when a desirable amount of H_2O_2 was added dropwise into the reaction mixture of cyclohexanone, ammonia, water, and Ti-MWW catalyst (Table 2, no. 1). When all of the substrates were added at once in the reactor, Ti-MWW showed nearly no catalytic activity for oxime conversion (only 2.8%), along with very low oxime selectivity (Table 2, no. 2). The color of the reaction mixture turned to deep red, due mainly to the formation of peroxydicyclohexyl amine and other byproducts. On the other hand, when a desirable amount of NH_3 solution was added dropwise into the reaction mixture of cyclohexanone, H_2O_2, H_2O, and Ti-MWW, cyclohexanone conversion was also low (4.8%), although oxime selectivity was relatively high (95%) (Table 2, no. 3). Despite greatly varying conversion of cyclohexanone depending on the method of adding substrates, conversion of NH_3 and H_2O_2 was always high (nearly 100% for H_2O_2 and >80% for NH_3), suggesting that the oxidation of NH_3 by H_2O_2 occurred readily in all cases. The effects of the method of adding substrates on cyclohexanone ammoximation have been reported for other titanosilicate catalysts [5,20]. Compared with adding all of the substrates at once, somewhat improved cyclohexanone conversion was reported for TS-1 when slowly adding H_2O_2 or NH_3 into the reaction system [20], whereas this approach had no effect on Ti-MOR [5]. We have also investigated the effects of the method of adding substrates on the ammoximation over TS-1. Adding H_2O_2 dropwise resulted in only a slight increase in the conversion of cyclohexanone, from 95.1 to 97%. The aforementioned large difference between Ti-MWW and other titanosilicates is presumed to be related to their catalytic properties and the ammoximation mechanism, which is discussed in detail later in the paper.

3.3.2. *Effect of reaction temperature*

The reaction temperature had a great effect on the ammoximation of cyclohexanone over Ti-MWW. To observe an obvious change, the reaction was carried out using a reduced amount of catalyst. As shown in Fig. 1, the conversion of cyclohexanone increased with increasing temperature and reached a maximum at 348 K, whereas the selectivity to oxime was maintained at >99% at 338–358 K. Further increasing the temperature to 373 K resulted in a rapid decrease in the conversion and the selectivity to 15 and 52%, respectively. The decrease in the conversion of ketone at high temperatures is partially attributed to easier vaporization and decomposition of reactants, particularly NH_3 and H_2O_2. More important, the oxime was readily oxidized to cyclohexanone at higher temperatures. As shown in Fig. 2, when the oxidation of oxime was performed with H_2O_2 in water, the conversion increased greatly with increasing re-

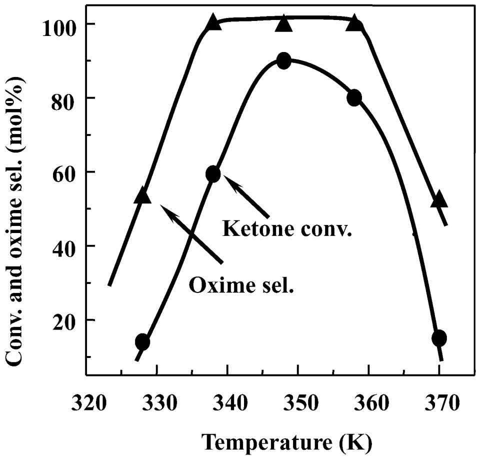

Fig. 1. Effect of reaction temperature on the cyclohexanone ammoximation on Ti-MWW. Ammoximation conditions: Ti-MWW-PS (Si/Ti = 55), 30 mg; others, see Table 1.

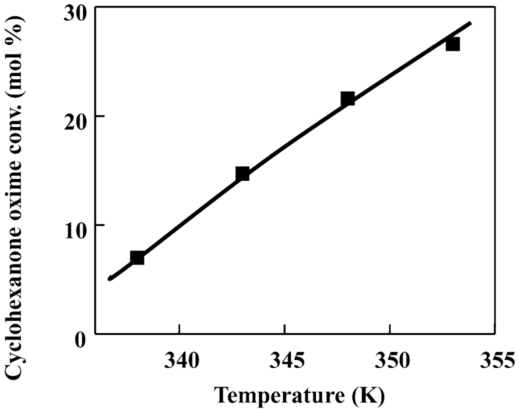

Fig. 2. Effect of reaction temperature on the oxidation of cyclohexanone oxime on Ti-MWW. Reaction conditions: Ti-MWW-PS (Si/Ti = 55), 50 mg; cyclohexanone oxime, 10 mmol; H_2O, 5 mL; and H_2O_2 (30%), 12 mmol; time, 1.5 h.

action temperature, reaching 27% at 353 K. Thus the reverse reaction (i.e., oxidation of oxime) also may correspond to a decrease in cyclohexanone conversion in the ammoximation at high temperatures. Consequently, the foregoing experiments show that the ammoximation proceeds most effectively at an optimum reaction temperature of 348 K.

3.3.3. *Effect of solvent*

The titanosilicate-catalyzed reactions are well known to depend greatly on the nature of the solvent. In the case of the ammoximation over TS-1, Roffia et al. have reported that the reaction proceeds effectively in the co-solvent of H_2O and *t*-butanol [21], whereas Thangaraj et al. have shown that the most suitable solvent is water [20]. In contrast, Wu et al. have reported that water is the best solvent for the ammoximation over Ti-MOR [5]. The present study compared the ammoximation of cyclohexanone over Ti-MWW using water, methanol, *t*-butanol, and acetonitrile as solvents (Fig. 3). Oxime selectivity was >99% for all solvents except acetonitrile, for which it was 82%. Oxime yield increased in the following order: H_2O > MeOH > *t*-butanol > acetonitrile, indicating that water is the most effective solvent for ammoximation over Ti-MWW. The effect of solvent is one of the most complicated issues in the catalytic system of titanosilicate/H_2O_2. It is related to the polarity of the solvent, the hydrophilic/hydrophobic character of the titanosilicate surface, the solubility of the substrates, and other factors. One big difference in ammoximation in water derives from the fact that the reaction proceeds in two liquid phases, which does not favor the adsorption of cyclohexanone molecules into the pores of Ti-MWW and the successive diffusion to the Ti active sites in comparison with the single liquid phase in organic solvents of *t*-butanol, MeOH, or acetonitrile. But, water solvent has the highest ammoximation efficiency, implying that the ketone molecules do not need to enter the pores of the catalyst during ammoximation. This finding can be interpreted based on the ammoximation mechanism described later in the paper.

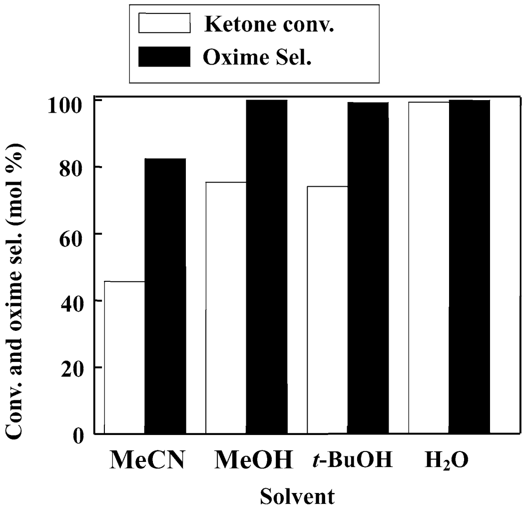

Fig. 3. Effect of solvent on the cyclohexanone ammoximation on Ti-MWW. Ammoximation conditions: Ti-MWW-PS (Si/Ti = 55), 50 mg; solvent, 5 mL; others, see Fig. 1.

3.3.4. *Effect of catalyst/cyclohexanone ratio*

The effect of the catalyst/cyclohexanone ratio on ammoximation was studied by keeping the amounts of substrate and solvent constant and simply varying the amount of Ti-MWW in the range of 30–70 mg. Cyclohexanone conversion increased dramatically with an increasing amount of catalyst, reaching 99.6% at 40 mg of Ti-MWW (corresponding to 4.1 wt% of cyclohexanone), whereas oxime selectivity always remained >99% (Fig. 4). Thus, a relatively small amount of Ti-MWW was sufficient to achieve high cyclohexanone conversion and high oxime selectivity

3.3.5. *Effect of NH_3/cyclohexanone and H_2O_2/cyclohexanone ratios*

The effect of the NH_3/cyclohexanone molar ratio on ammoximation is shown in Fig. 5A. Although the cyclohexanone ammoximation stoichiometrically needs equal moles of NH_3 and cyclohexanone, cyclohexanone conversion was only 72% at a NH_3/cyclohexanone ratio of 1.0. Nevertheless, both cyclohexanone conversion and oxime selectivity reached nearly

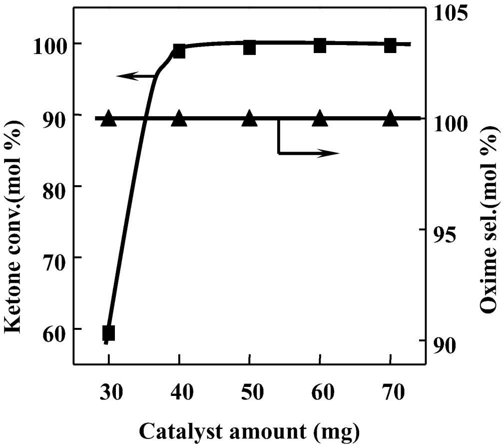

Fig. 4. Effect of catalyst amount on the cyclohexanone ammoximation over Ti-MWW. Ammoximation conditions: catalyst, Ti-MWW-PS (Si/Ti = 55); others, see Fig. 1.

100% when the NH_3/cyclohexanone ratio was >1.1. The high cyclohexanone conversion obtained in an excessive amount of NH_3 was probably due to a partial loss of NH_3 from vaporization and the fact that a suitable basic environment is required for ammoximation. Regardless, no further changes in either cylcohexanone conversion or oxime selectivity were observed at NH_3/cyclohexanone ratios > 1.3.

The effect of H_2O_2/cyclohexanone ratio on cyclohexanone ammoximation is shown in Fig. 5B. With increasing H_2O_2/cyclohexanone ratio, cyclohexanone conversion and oxime selectivity increased simultaneously. Because of unproductive decomposition of H_2O_2, ammoximation requires more H_2O_2 than cyclohexanone to proceed to a high level. At a H_2O_2/cyclohexanone ratio of 1.2, cyclohexanone conversion and oxime selectivity reached the maxima (both nearly 100%). At higher H_2O_2/cyclohexanone ratios, cyclohexanone conversion decreased greatly but oxime selectivity was unchanged. The likely reason for these findings is that the existence of too much free H_2O_2 in the reaction system accelerated the oxidation of the oxime back to cyclohexanone as well as the successive oxidation of the ammoximation intermediate of hydroxylamine.

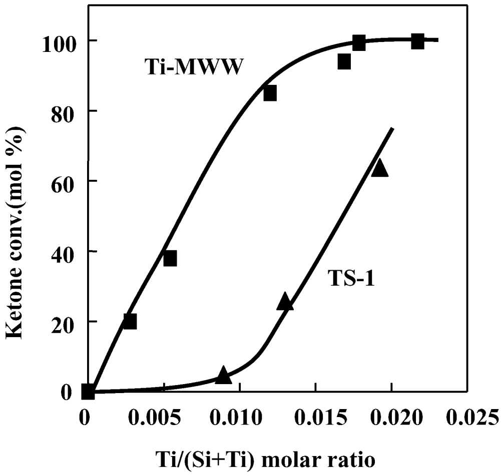

Fig. 6. Dependence of the cyclohexanone conversion on the Ti content. Reaction conditions: catalyst, 50 mg; cyclohexanone, 10 mmol; solvent, 5 mL; NH_3 (25%), 12 mmol; H_2O_2 (5%), 12 mmol; temperature, 338 K; time, 1.5 h. Solvent was H_2O and H_2O–t-BuOH for Ti-MWW-PS and TS-1, respectively. H_2O_2 was added dropwise at a constant rate within 1 h.

3.3.6. Effect of Ti content

A series of Ti-MWW catalysts with Si/Ti ratios of 38–320 were prepared and used in the ammoximation of cyclohexanone and the results were compared with those using TS-1 catalyst with Si/Ti ratios of 51–110. To fairly compare the catalytic activity of these two titanosilicates, the reactions were carried out at a same weight ratio of catalyst to substrate but in different optimum solvents, that is, in H_2O for Ti-MWW and in the co-solvent of H_2O/t-BuOH for TS-1. The oxime selectivity was >99% in all cases. Reasonably, the conversion of cyclohexanone increased with an increasing amount of Ti active sites for Ti-MWW as well as TS-1 (Fig. 6). Obviously, Ti-MWW was superior to TS-1 in terms of catalytic activity, giving a cyclohexanone conversion of nearly 100% when the Si/Ti ratio was ≈60. Nevertheless, the intrinsic activity tended to decrease with increasing Ti content. For example, the TON of Ti-MWW-PS dropped from 850 to 580 mol mol_{Ti}^{-1}, as the extra-framework Ti species may occur at a higher Ti content.

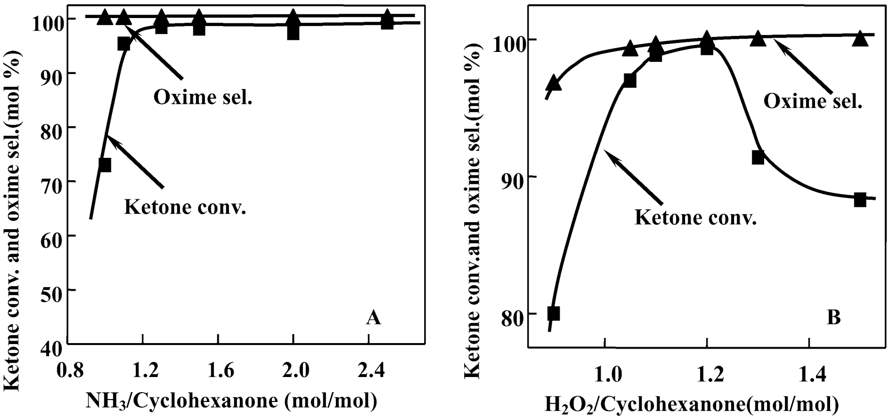

Fig. 5. Effect of NH_3/cyclohexanone ratio (A) and H_2O_2/cyclohexanone ratio (B) on the cyclohexanone ammoximation over Ti-MWW. Ammoximation conditions: catalyst, Ti-MWW-PS (Si/Ti = 55); others, see Fig. 1.

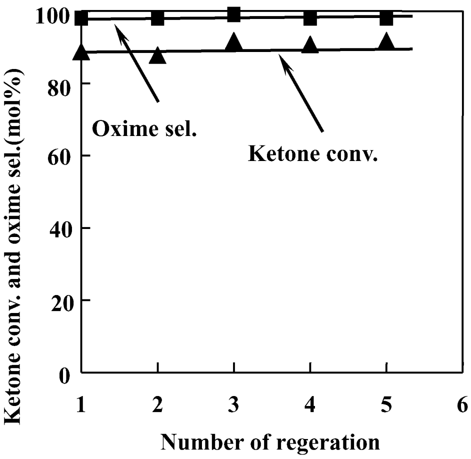

Fig. 7. The conversion of cyclohexanone and oxime selectivity of the ammoxiamtion performed on regenerated Ti-MWW-PS (Si/Ti = 55). The used catalyst was regenerated by acetone washing and then drying at 393 K for 5 h.

3.4. The stability and reusability of Ti-MWW

The stability and reusability of Ti-MWW in ammoximation were checked (Fig. 7). The experiments were initiated with an enlarged reaction scale using 1.4 g of Ti-MWW but at a deliberately lower conversion level (87%), to observe any variation. The used Ti-MWW was regenerated by washing with acetone and drying at 393 K in air, then subjected to repeated ammoximation at a constant ratio of catalyst/substrate/solvent. After five recycles of reaction–regeneration, the catalyst maintained its activity (88% conversion). Elemental analysis indicated that Ti leaching was within 5% after the repeated cycling. Furthermore, the used catalyst showed essentially the same UV–vis spectrum as that of fresh catalyst. This indicates that Ti-MWW is extremely stable against Ti leaching and serves as a reusable catalyst for the ammoximation of cyclohexanone. These results are consistent with those observed in the epoxidation of various alkenes over Ti-MWW [12,13].

3.5. Investigation into the reaction mechanism of ammoximation

The foregoing results verify that Ti-MWW is an effective catalyst, superior to other titanosilicates reported so far for the selective liquid-phase ammoximation of cyclohexanone to oxime. Nevertheless, Ti-MWW differs greatly from TS-1 in terms of optimum ammoximation conditions. The catalytic activity of Ti-MWW greatly depends on the method of adding substrates, particularly H_2O_2. To make this issue clear, we have investigated the ammoximation mechanism.

Ammoximation was once considered to proceed through a TS-1-catalyzed oxidation of an intermediate of cyclohexylimine formed by the noncatalytic reaction of cyclohexanone with ammonia [20] (Fig. 8A). IR spectroscopy has provided somewhat reasonable evidence of the formation of imine intermediate by adsorbing cycohexanone and dry ammonia gas onto TS-1 [22]. However, the formation of imine intermediate in an actual ammoximation (i.e., in an aqueous solution) has been claimed, because the imine has been proven unstable in the presence of water [5]. The fact that no obvious steric hindrance and diffusion problems are observed in the ammoximation of ketones and aldehydes with different molecular dimensions leads to a reaction mechanism of the hydroxylamine route [21,23]. As shown in Fig. 8B, the ammoximation is assumed to consist of the catalytic formation of hydroxylamine as a result of oxidation of ammonia with hydrogen peroxide on the Ti sites and the noncatalytic oximation of ketone with hydroxylamine to oxime. A detailed study of ammoximation over Ti-MOR has clearly verified this plausible reaction pathway [5].

In the present study, concerning the ammoximation mechanism related to hydroxylamine, we carried out the oxidation of NH_3 and H_2O_2 in the absence of cylcohexanone on Ti-MWW under the same conditions applied to real ammoximation. After the oxidation was carried out for the desired time, the Ti-MWW catalyst was removed by filtration. Following a standard procedure for indirect confirmation and quantification of hydroxylamine [24], an excessive amount of cyclohexanone was then

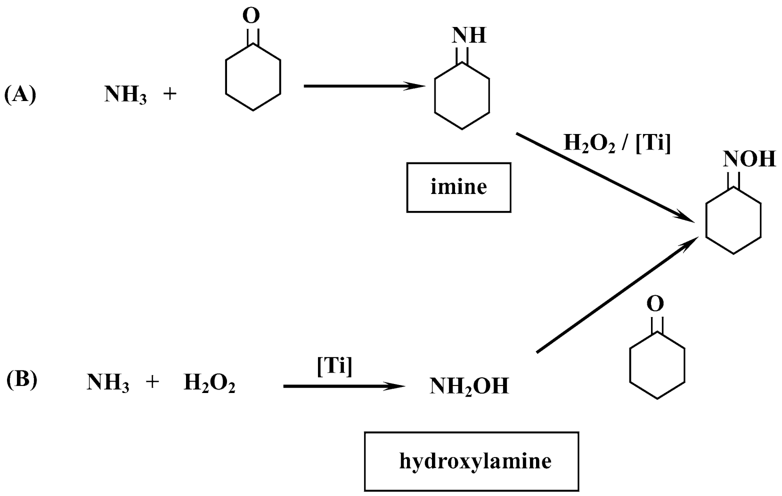

Fig. 8. Possible ammoximation pathways.

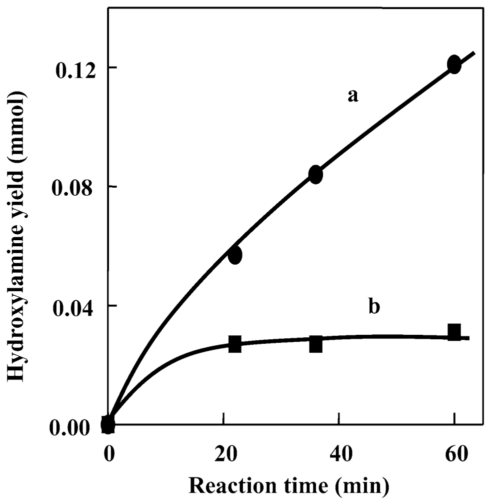

Fig. 9. Dependence of hydroxylamine amount on the oxidation time of NH_3 with H_2O_2 over Ti-MWW. (a) H_2O_2 was added dropwise at a constant rate; (b) H_2O_2 was added all at once. NH_3 oxidation conditions: Ti-MWW-PS (Si/Ti = 55), 50 mg; H_2O, 5 mL; NH_3 (25 wt%), 12 mmol; H_2O_2, 12 mmol; temperature, 338 K. The amount of hydroxylamine was quantified from that of oxime formed by the reaction of cyclohexanone with the filtrate of NH_3 oxidation after the removal of Ti-MWW catalyst.

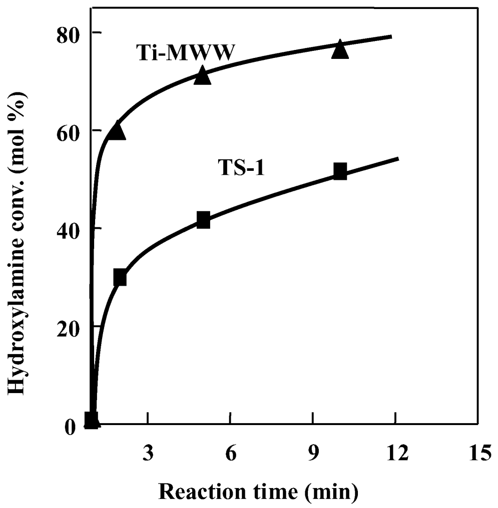

Fig. 11. The oxidation of NH_2OH by H_2O_2 over Ti-MWW-PS and TS-1. Reaction conditions: catalyst, 0.05 g; NH_2OH (in chloride form), 10 mmol; H_2O_2, 12 mmol; water, 5 mL; temperature, 318 K.

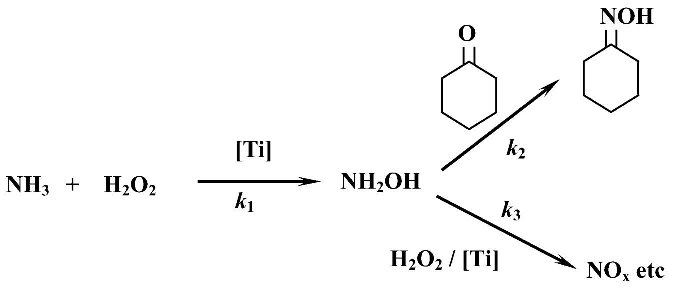

Fig. 10. The reaction steps involved in the ammoximation.

added into the filtrate and stirred for another 0.5 h, long enough to complete the oximation reaction. Gas chromatography analysis of the reaction mixture indicated that cyclohexanone oxime (i.e., hydroxylamine) was actually formed, with its amount depending on the method used to add H_2O_2 (Fig. 9). The amount of hydroxylamine intermediate obtained when adding H_2O_2 dropwise was more than that obtained when adding H_2O_2 all at once at the beginning and increased with increasing oxidation time. This suggests that, similar to Ti-MOR and TS-1 [5,21], ammoximation over Ti-MWW also probably proceeds through the oxidation of ammonia by hydrogen peroxide to an intermediate of hydroxylamine, followed by the oximation of ketone with hydroxylamine to oxime.

We next considered why, in comparison to TS-1 and Ti-MOR, oxime formation and even hydroxylamine formation over Ti-MWW depend so greatly on the method of adding H_2O_2 (Table 2; Fig. 9). We assume that it is probably due to the varying specific catalytic oxidation ability of the Ti species of these titanosilicates. As shown in Fig. 10, along with the steps of hydroxylamine formation and noncatalytic oximation, the nonproductive oxidation of hydroxylamine by H_2O_2 on Ti sites to NO_x and other compounds also occurs during the ammoximation process [21,23]. Thus oxime formation is competed by hydroxylamine oxidation. The reaction rate of noncatalytic oximation of ketone with hydroxylamine (k_2) is independent of the type of titanosilicate used, but the formation rate (k_1) and oxidation rate of hydroxylamine (k_3) should depend on the catalytic ability of the Ti species. Over the more active Ti-MWW catalyst, which has a TON about 2–4 times that of TS-1 (Table 1), hydroxylamine is produced rapidly, but the oxidation and decomposition of hydroxylamine become obvious and subsequently decrease the oxime yield, particularly when free H_2O_2 exists in the reaction system, that is, when H_2O_2 is added all at once. This corresponds to the different effects of the H_2O_2 adding method in Ti-MWW and TS-1.

To confirm this hypothesis, we carried out the oxidation of hydroxylamine with H_2O_2 under similar conditions over Ti-MWW and TS-1. The most common form of NH_2OH, hydroxylamine chloride commercially available was used as the substrate. After oxidation was carried out for the desired time, the catalyst was removed from the reaction mixture and cyclohexanone was added to allow the formation of oxime with remaining hydroxylamine. The conversion of hydroxylamine was then calculated after quantifying the amount of oxime. As shown in Fig. 11, hydroxylamine was readily oxidized by H_2O_2 within a short time at a relatively low temperature (318 K). Ti-MWW showed much higher oxidation activity for hydroxylamine than TS-1. Easier oxidation of hydroxylamine over Ti-MWW would make the oximation of this intermediate with ketone depend more on the concentration of free H_2O_2 in the reaction mixture (i.e., its adding rate).

To further verify the importance of the balance of hydroxylamine oxidation and oximation in oxime formation, along with the comparison between Ti-MWW and TS-1, ammoximation of ketones and aldehydes with various molecular sizes and reactivities were compared on Ti-MWW catalyst. As shown in Table 3, when H_2O_2 was added into the reaction system all at once at the beginning, the ketones or aldehydes were converted to corresponding oximes selectively (oxime selectiv-

Table 3
Ammoximation of various ketones and aldehydes over Ti-MWW catalyst[a]

Ketone or aldehyde	Conversion (mol%)	
	(A)[b]	(B)[b]
Acetophenone	0.0	20.0
Cyclohexanone	1.3	99.4
Acetone	2.3	98.4
p-Tolualdehyde	42.4	99.2
Benzaldehyde	55.6	99.7

[a] Ammoximation conditions: Ti-MWW-PS (Si/Ti = 55), 0.05 g; others, see Table 1.

[b] (A) H_2O_2 was added to the reaction mixture once; (B) H_2O_2 was added dropwise at a constant rate within 1 h.

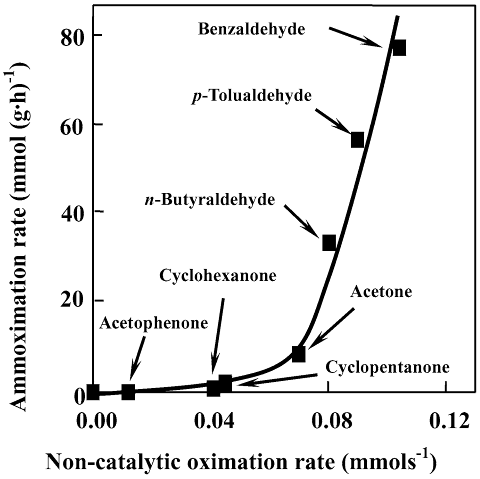

Fig. 12. The correlation between the catalytic ammoximation rate of Ti-MWW and the noncatalytic oximation rate. Ammoximation conditions: catalyst, Ti-MWW-PS (Si/Ti = 55); others, see Table 1. Oximation conditions: ketone or aldehyde, 5 mmol; NH_2OH (in chloride form), 6 mmol; H_2O, 5 mL; temperature, 338 K.

ity >99% in all cases) but to a limited extent (<56%). The conversion occurred in the following order: benzaldehyde > *p*-tolualdehyde > acetone > cyclohexanone > acetophenone. Nevertheless, when H_2O_2 was added into the reaction system dropwise, high conversion (>98%) comparable to that found for cyclohexanone was obtained with the exception of acetophenone, which had an extremely low reactivity itself [4,5]. These results indicate that there was no consistency between the molecular dimension of ketone or aldehyde and conversion, which implies that the ketone or aldehyde molecules not needed for entry into the channels of titanosilicate. This then can be taken as evidence supporting the mechanism of hydroxylamine intermediate. Secondarily, the different conversions among substrates when H_2O_2 was added all at once suggest the importance of the reactivity of ketone or aldehyde in ammoximation. High activity of ketone or aldehyde with hydroxylamine would lead to a high reaction rate of the whole ammoximation.

Consequently, we measured the noncatalytic oximation rates of various ketones and aldehydes with hydroxylamine, and related these to the rate of catalytic ammoximation over Ti-MWW when H_2O_2 was added all at once (Fig. 12). There was a good correlation between the two variables. The faster the oximation rate (i.e., k_2 in Fig. 10), the less the decomposition of hydroxylation and the higher the conversion of ketones and the yield of oxime. Noncatalytic oximation turned to be the rate-determining step of the ammoximation over Ti-MWW. Thus, to make the competitive reactions favorable for the oximation of hydroxylamine, it is necessary to reduce free H_2O_2 in reaction mixture to avoid the extensive oxidation of hydroxylamine.

4. Conclusion

Ti-MWW is capable of catalyzing the liquid-phase ammoximation of cyclohexanone to oxime at a conversion and selectivity >99% in the presence of water under optimum conditions, and proves to be a promising catalyst for oxime synthesis. Ammoximation proceeds through an intermediate of hydroxylamine, and the noncatalytic oximation of ketone and hydroxylamine is the rate-determining step. The catalytic behavior of Ti-MWW in ammoximation depends greatly on the method used to add H_2O_2. Ti-MWW shows high conversion of ketone to oxime only when H_2O_2 is added slowly into the reaction system. To achieve high conversion of ketone to oxime, the presence of free H_2O_2 and the extensive oxidation of hydroxylamine on the Ti species of Ti-MWW with extremely high oxidation ability must be avoided.

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