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An investigation into cyclohexanone ammoximation over Ti-MWW in a continuous slurry reactor

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1. Introduction

Cyclohexanone oxime is an important captive intermediate with a constantly increasing presence on the world market because it is readily transformed through the Beckmann rearrangement to ε -caprolactam (CPL), a core ingredient for the nylon-6 manufacturing industry. Starting from benzene or toluene as a raw material, the conventional manufacturing processes of CPL include noncatalytic oximation of cyclohexanone with hydroxylamine and liquid-phase Beckmann rearrangement of the oxime in oleum. These processes are encountering serious disadvantages because they require multiple reaction steps, use harmful oximation agents such as hydroxylamine and sulfuric acid catalyst, and in particular, coproduce a large quantity of less valuable byproducts such as ammonium sulfate or phosphate [1,2]. These drawbacks not only bring about environmental pollution, but also decrease the profitability of the CPL process. Hence, an environmentally benign, material-saving and zero-emission CPL process, which avoids using hazardous reagents and generating valueless ammonium salts, is urgently required.

The discovery of titanium silicalite-1 (TS-1) opened up new possibilities of developing zeolite-based green catalytic processes

ABSTRACT

In the present study, the liquid-phase ammoximation of cyclohexanone with ammonia and hydrogen peroxide was studied using a MWW-type titanosilicate (Ti-MWW) catalyst in a continuous slurry reactor to develop a clean process for producing cyclohexanone oxime. The reaction parameters, which governed the cyclohexanone conversion, oxime selectivity and catalyst deactivation, were investigated by simulating the operating conditions of an industrial process. Under optimized reaction conditions, Ti-MWW produced a cyclohexanone conversion and oxime selectivity over 96% and 99%, respectively. Moreover, Ti-MWW was extremely robust and showed a longer lifetime than the conventional titanium silicalite-1 catalyst. The causes of deactivation were elucidated to be the coke deposition and partial dissolution of the zeolite framework of Ti-MWW during ammoximation. The deactivated Ti-MWW catalyst was regenerated effectively by a combination of acid treatment and cyclic amine-assisted structural rearrangement.

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because TS-1 is capable of catalyzing a variety of oxidation reactions with aqueous hydrogen peroxide as an oxidant and water as the sole byproduct. Enichem first reported that TS-1 is an efficient catalyst for the ammoximation of cyclohexanone [2]. The direct route combines in situ formation of hydroxylamine intermediate and subsequent oximation of cyclohexanone, avoiding co-production of ammonium salts and reducing the capital investment of establishing a CPL process. In 2003, Sumitomo Chemical Co. and Sinopec commercialized successfully this innovative technology of cyclohexanone oxime processes with the capability to upscale worldwide [3]. Moreover, Sumitomo has further combined the TS-1-catalyzed liquid-phase ammoximation and the silicalite-1-catalyzed gas-phase Beckmann rearrangement, leading to an extremely clean route for CPL production. These new processes exclude the dangerous reagents and the co-production of massive valueless ammonium salts.

The successes achieved with TS-1 have spurred intensive research on new titanosilicate catalysts to obtain novel materials which possess a better catalytic performance and are capable of overcoming the drawbacks encountered with TS-1. Being a typical of medium pore zeolite of 10-membered ring (MR), TS-1 suffers constraints and mass transfer limitations. The manufacturing cost of TS-1 is generally high because of using expensive tetrapropylammonium hydroxide as a structure-directing agent. In addition, a relatively high concentration of TS-1 catalyst is needed to achieve a reasonable catalytic activity level. Moreover, a high performance

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TS-1 catalyst made up of small particles leads to difficult membrane separation for a slurry-bed reactor.

With great efforts made in past decades, a number of new titanosilicates with different zeolite structures have been developed, i.e., Ti-MWW [4-6], TS-2 [7], Ti-MOR [8] and Ti-Beta [9]. In particular, by possessing a pore system that consists of two independent interlayer and intralayer 10-MR channels as well as 12-MR supercages and side cups, Ti-MWW shows a unique solvent effect and high catalytic activities for the epoxidation of various alkenes with H_2O_2 [10–13]. We have previously investigated the catalytic properties of Ti-MWW in the ammoximation of ketones using a batch-type reactor [14-16]. Ti-MWW was capable of catalyzing the ammoximation of cyclohexanone and methyl ethyl ketone in the presence of water producing a ketone conversion and oxime selectivity both as high as 99%. This implies that Ti-MWW is a promising catalyst for the clean synthesis of oximes. Nevertheless, the production of bulk chemicals like cyclohexanone oxime on a large scale favors a continuous slurry-bed reactor, which is equipped with a membrane separator to save the labor found in batchwise processes.

In this study, by simulating the operating conditions in a commercial processing procedure, we applied Ti-MWW to the ammoximation of cyclohexanone in a continuous slurry reactor, and investigated the effects of reaction parameters, deactivation behavior and catalyst regeneration by comparing them with those from conventional TS-1 under the same operating conditions. Ti-MWW was expected to exhibit a higher catalytic activity than TS-1 because of its structural advantages. The present results lay a solid foundation for the industrial use of Ti-MWW, and are also help-ful for clarifying the chemical engineering issues involved in the liquid-phase ammoximation of cyclohexanone.

2. Experimental

2.1. Catalyst preparation and characterization methods

Ti-MWW was prepared following the procedures reported previously [5]. Ti-containing MWW lamellar precursor was first hydrothermally crystallized in boric acid system with piperidine (PI) as a structure-directing agent (SDA). The synthetic gel had a molar composition of $1SiO_2:0.67B_2O_3:0.05TiO_2:1.4PI:19H_2O$. The precursor was refluxed with 2 M HNO₃ at a solid to liquid weight ratio of 1:50 to remove the extraframework Ti species. For control experiments, conventional TS-1 catalyst (Si/Ti = 30) was hydrothermally synthesized following the procedures widely adopted [17]. Both catalysts were activated by calcination in air at 773 K for 10 h.

The samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer (Cu-K α radiation). Fourier-transformed infrared (FT-IR) were recorded on a Nicolet Fourier transform infrared spectrometer (NEXUS 670) using KBr technique. The inductively coupled plasma (ICP) elemental analysis was completed on a Thermo IRIS Intrepid II XSP atomic emission spectrometer to determine the amounts of Si, Ti, and B species in Ti-MWW and TS-1. UV-visible spectra were recorded on a Shimadzu 2400PC spectrophotometer with BaSO₄ as a reference. BET surface area was measured by N2 adsorption on an Autosorb Quancachrome 02108-KR-1 instrument. The amounts of coke after ammoximation were measured by combustion in a TGA/SDTA851 thermo-gravimetric analyzer. The samples were heated from 298 K to 1073 K at 10 K min⁻¹ in the flow of air. The weight loss above 473 K was attributed to coke. The solid-state ²⁹Si MAS NMR spectra were performed at ambient temperature on a VARIAN VNMRS-400WB spectrometer at 79.5 MHz by using a spinning rate of 3.0 kHz. The chemical shift was referred to an external standard of 2,2-dimethyl-2-silapentane-5-sulfonic acid.

2.2. Catalytic reactions

The liquid-phase ammoximation of cyclohexanone was carried out continuously in a 160 mL glass slurry reactor equipped with a glass sand filter and a magnetic stirrer. For a typical reaction, a desirable amount of catalyst powder (0.8–3.2 g) and 120 mL of tertbutanol aqueous solution (85 wt%) were added in the reactor and heated under stirring at a determined temperature (328-353 K). The mixture of cyclohexanone and 85 wt% *t*-BuOH aqueous solution (weight ratio of 1:2.94) and 27 wt% H₂O₂ were then fed into the reactor separately with a micro-pump. The feeding rate of the mixture of cyclohexanone and t-BuOH was always kept constant at 96 mL h⁻¹. Meanwhile, ammonia gas (99.9%) was charged into the reaction system with a mass flowmeter at a constant rate. The molar ratios of H₂O₂/ketone and NH₃/ketone were varied in the range of 0.95–1.2 and 1.0–2.2, respectively. With the reaction proceeding, the reaction mixture overflowed from the outlet filter and the catalyst powder remained in the reactor. The ammonia unconverted and not soluble in the reaction mixture was exhausted through a condenser vent. The organic products were analyzed on a gas chromatograph (Shimadzu 14B) with a flame ionization detector and a HP-5 capillary column to calculate the conversion of cyclohexanone and the selectivity of oxime. The content of unconverted H₂O₂ was determined by iodometric titration.

The used catalyst was gathered by filtration and dried at 353 K. Three regeneration ways have been attempted on the deactivated Ti-MWW: (i) directly calcination in air at 823 K for 10 h; (ii) first calcined as method (i), then structural rearrangement in an autoclave with an aqueous solution of PI (6.5 wt%) at 443 K for 24 h, and further calcined at 823 K for 10 h; (iii) first washed with 0.3 M HNO₃ at 353 K for 4 h, and then regenerated as method (ii).

3. Results and discussion

3.1. Characterization of titanosilicate catalysts

The Si/Ti atomic ratio was 38 for Ti-MWW and 30 for TS-1. The XRD patterns confirmed that both titanosilicates had the expected crystalline structures (data not shown). In the UV–visible and IR spectra, the samples showed characteristic adsorption bands at 220 nm and 960 cm⁻¹, respectively, which are assigned to the tetrahedral Ti species isolated in the zeolite framework [1]. The specific surface areas (Langmuir) determined from N₂ adsorption at 77 K were 552 m² g⁻¹ for Ti-MWW and 530 m² g⁻¹ for TS-1. These physicochemical properties indicate that these titanosilicates were qualified as liquid-phase oxidation catalysts with aqueous H₂O₂ as an oxidant.

3.2. Effects of reaction parameters on the continuous ammoximation of cyclohexanone using Ti-MWW as a catalyst

3.2.1. Effect of reaction temperature

The reaction temperature greatly affected the ammoximation of cyclohexanone over Ti-MWW in a continuous slurry reactor. When the reaction was carried out at ratios of $H_2O_2/cyclohexanone$ at 1.1 and NH₃/cyclohexanone at 1.7, the conversion of cyclohexanone increased with rising temperature and almost leveled off at 335–348 K, while the selectivity to produce oxime was maintained over 99% (Fig. 1). The conversion and the selectivity decreased sharply to 20% and 80%, respectively, when the temperature was further raised to 353 K, which was mainly attributed to the faster vaporization and decomposition rates of the reactants. Particularly, H_2O_2 easily underwent nonproductive decomposition at higher temperature in basic media. The above results indicated that Ti-MWW possessed a relatively wide window of operating temperature for producing a cyclohexanone conversion of over 96% at



Fig. 1. Effect of reaction temperature on the ammoximation of cyclohexanone on Ti-MWW. Ammoximation conditions: Ti-MWW, 3.2 g; $H_2O_2/cyclohexanone = 1.1:1$; WHSV for cyclohexanone, 6.3 h^{-1} ; NH₃/cyclohexanone = 1.7:1; solvent, *t*-BuOH (85%).

99% oxime selectivity. Nevertheless, the ammoximation proceeded most effectively at an optimum reaction temperature of 343 K.

3.2.2. Effect of NH_3 /cyclohexanone and H_2O_2 /cyclohexanone ratios

The effect of NH₃/cyclohexanone molar ratio on ammoximation was investigated at 343 K and $H_2O_2/cyclohexanone$ of 1.1 (Fig. 2). The cyclohexanone ammoximation requires stoichiometrically equivalent moles of NH₃ and cyclohexanone, but the cyclohexanone conversion was only 83% at a NH₃/cyclohexanone ratio of 1.0. Nevertheless, the cyclohexanone conversion and oxime selectivity reached ca. 96% and 100%, respectively when the NH₃/cyclohexanone ratio was over 1.7. The lower cyclohexanone conversion obtained at an equivalent ratio of NH₃ is probably because gaseous NH₃ partially evaporates and dissolves inefficiently in the liquid-phase because the reaction is occurring in an open reactor system at normal pressure. Thus, the reaction needs an excess amount of NH₃ to supple-



Fig. 2. Effect of NH₃/cyclohexanone ratio on the ammoximation of cyclohexanone on Ti-MWW. Other conditions, see Fig. 1.



Fig. 3. Effect of $H_2O_2/cyclohexanone$ ratio on the ammoximation of cyclohexanone on Ti-MWW. Other conditions, see Fig. 1.

ment this loss. Moreover, this is in agreement with a previous report that suggests ammoximation prefers a basic environment created by an excess of NH₃ [18]. Nevertheless, no further changes were observed for either the cyclohexanone conversion or the oxime selectivity at NH₃/cyclohexanone ratios above 1.7, because the excess NH₃ was no longer being dissolved in the reaction mixture which would be evaporated easily into the atmosphere.

Fig. 3 shows the effect of the $H_2O_2/cyclohexanone$ ratio on the cyclohexanone ammoximation. In contrast to the fact that the remainingNH₃ is recycled in an actual industrial process, the excessive H₂O₂ may explode during separation. Thus, it is preferable to use the stoichiometric amount of H₂O₂ whenever possible. By increasing $H_2O_2/cyclohexanone$ ratio, the cyclohexanone conversion and oxime selectivity increased simultaneously. Because of the nonproductive decomposition of H₂O₂, ammoximation needed slightly more H₂O₂ than cyclohexanone to proceed to its highest possible level. The conversion of cyclohexanone reached the maximum (>96%) at a H_2O_2 /cyclohexanone ratio of 1.1, while the oxime selectivity was maintained at over 99%. However, cyclohexanone conversion decreased to 86% when the H₂O₂/cyclohexanone ratio was higher than 1.2, and oxime selectivity also declined slightly. The excess H_2O_2 in the reaction system would accelerate the deep oxidation of oxime to organic by-products such as nitrocyclohexane [19], and also induce successive oxidation of hydroxylamine intermediates. Moreover, H₂O₂ may decompose more easily at higher concentrations. These side reactions could decrease oxime selectivity.

3.2.3. Effect of catalyst amount

The effect of catalyst amount on ammoximation was investigated by keeping the feeding rates of cyclohexanone constant, NH_3 , H_2O_2 and solvent, and varying the amount of Ti-MWW catalyst between 1.0 g and 3.2 g. The initial cyclohexanone conversion and oxime selectivity in these cases all reached about 96% and greater than 99% respectively, even when the catalyst amount was only 1.0 g (Fig. 4). Thus, a relatively low concentration of Ti-MWW catalyst is sufficient to achieve high cyclohexanone conversion and oxime selectivity. However, the ammoximation lifetime of the Ti-MWW catalyst depended greatly on the loading. The amount of cyclohexanone converted was almost proportional to the amount of Ti-MWW used in the ammoximation process. When the amount



Fig. 4. The ammoximation on Ti-MWW with catalyst loading of 3.2 g (a), 2.0 g (b), 1.5 g (c), and 1.0 g (d). Ammoximation conditions: temp, 343 K; others, see Fig. 1.

of catalyst was nearly doubled from 1.5 g to 3.2 g, the ammoximation lifetime was prolonged from 91 h to 214 h.

3.3. Comparison of the ammoximation lifetime between Ti-MWW and TS-1

In addition to high catalytic activity and oxime selectivity, the real applicability of titanosilicates depends also on their lifetime and reusability. Fig. 5 shows that Ti-MWW exhibited a much longer ammoximation lifetime than the conventional TS-1 catalyst. The ammoximation runs were carried out under optimized conditions where the conversion and oxime selectivity reached >96% and ca. 100%, respectively, but at the same weight hourly space velocity (WHSV). Ti-MWW remained active for 214 h in the cyclohexanone ammoximation, whereas TS-1 deactivated at 120 h. Clearly, Ti-MWW was superior to TS-1 in terms of catalyst lifetime. We previously reported that Ti-MWW was a promising catalyst for ammoximation according to the results observed in a batchwise reactor within an extremely short reaction time of 2 h [14]. The outstanding duration that Ti-MWW showed here in a continuous



Fig. 5. The ketone conversion (\blacksquare , \Box) and the oxime selectivity (\bullet , \bigcirc) of the ammoximation of cyclohexanone on Ti-MWW and TS-1. Ammoximation conditions: Ti-MWW, 343 K; TS-1, 349 K; others, see Fig. 1.



Fig. 6. $\rm H_2O_2$ conversion, efficiency and unconverted $\rm H_2O_2$ in the cyclohexanone ammoximation on Ti-MWW.

reactor suggests that it is an important catalyst for cyclohexanone ammoximation from the viewpoint of industrialization.

3.4. Deactivation behavior of Ti-MWW catalyst

The cyclohexanone conversion and oxime selectivity of the Ti-MWW catalyst were constant during the 214 h of time on stream (TOS), but declined sharply within 2h (Fig. 5). TS-1 also showed a very similar deactivation behavior, although it was considerably shorter in catalytic life. The comparison was carried out at optimized reaction temperature for each catalyst while keeping other conditions the same. As far as the conversion of H₂O₂ was concerned, Ti-MWW was fairly stable during the whole process. When the catalyst began deactivating, the conversion of ketone decreased, and the amount of H₂O₂ consumed in producing cyclohexanone oxime also decreased, leading to a higher concentration of unconverted H₂O₂ in the reaction mixture (Fig. 6). At the same time, the utilization efficiency of H₂O₂ decreased significantly because of nonproductive decomposition. Excessive H₂O₂ concentration in the reaction system may promote the deep oxidation of cyclohexanone oxime, which could account for the lowered oxime selectivity (Fig. 3). To clarify the main reasons for the deactivation of Ti-MWW during ammoximation, we have evaluated the reactions at catalyst loading of 1.5 g, which exhibited a lifetime of about 93 h (Fig. 4c). This allowed us to follow the ammoximation performance of Ti-MWW within a relatively shortened time.

The XRD patterns and UV-visible spectra of fresh and used catalysts at TOSs of 30 h, 60 h, 90 h, and 93 h (deactivated catalyst) are shown in Figs. 7 and 8, respectively. The XRD patterns verified that the used catalysts still possessed the typical MWW structure, but its crystallinity decreased to a certain extent with prolonged reaction time (Fig. 7a-e). The used catalysts and deactivated catalyst showed very similar UV-visible spectra to the fresh catalyst, exhibiting the characteristic band because of the tetrahedral Ti species at 220 nm (Fig. 8) and indicating that most of the Ti species still occupied the tetrahedral sites in the zeolite framework after ammoximation. However, a shoulder around 275 nm appeared in the spectra of the used catalysts. This band became more intensive with reaction time, in particular it was clearly observed for the deactivated catalyst (Fig. 8d). The band is generally attributed to the octahedral Ti species developed by the coordination of adsorbate molecules to the tetrahedral Ti species. This UV-visible band has been considered a clear indication of the propensity of Ti species to increase



Fig. 7. The XRD patterns of fresh Ti-MWW (a), after used for 30 h (b), 60 h (c), 90 h (d), and 93 h (e) (deactivated catalyst). Ammoximation conditions: Ti-MWW, 1.5 g; others, see Fig. 1.

coordination number in TS-1 in the presence of ligands such as NH_3 , H_2O or H_2O_2 [20]. When the deactivated catalysts were calcined to remove any adsorbed inorganic and organic species, a spectrum nearly same as that of the fresh catalyst was obtained, but a weak shoulder was still present around 275 nm (Fig. 8e).

Fig. 9 shows the FT-IR spectra of the Ti-MWW samples. The main absorption bands were observed at 1400, 1300–1000, and 960 cm⁻¹, which were in agreement with the IR spectra of Ti-MWW reported previously [12]. The band at 960 cm⁻¹ is closely related to the stretching mode of the [SiO₄] tetrahedrally bonded with the Ti ions and can be considered the fingerprint of the Ti framework. As the ammoximation proceeded with TOS, bands in the range of 2900–3000 cm⁻¹, assigned to the stretching of saturated C-H bonds, were developed in the used catalysts. Furthermore, the intensity of these bands became stronger with prolonged TOS. This revealed that some organic substances with high boiling temperatures were deposited gradually inside the channels of Ti-MWW (Fig. 9c and d), especially for the deactivated catalyst (Fig. 9e). These bands disappeared completely when the deactivated catalyst was calcined at 773 K in air to burn off the organic species (Fig. 9f).



Fig. 8. The UV-visible spectra of fresh Ti-MWW (a), after used for 60 h (b), 90 h (c), 93 h (d) (deactivated catalyst), and deactivated catalyst after calcination (e). Ammoximation conditions: Ti-MWW, 1.5 g; others, see Fig. 1.



Fig. 9. The IR spectra of fresh Ti-MWW (a), after used for 30 h (b), 60 h (c), 90 h (d), 93 h (e) (deactivated catalyst), and deactivated catalyst after calcination (f). Ammoximation conditions: Ti-MWW, 1.5 g; others, see Fig. 1.

The N₂ adsorption investigation verified that both the surface area and the pore volume of Ti-MWW decreased greatly during ammoximation, especially within the first 30 h (Table 1, No. 2). A further decrease was observed for the deactivated catalyst at a TOS of 93 h (Table 1, No. 5). The surface area and pore volume of the deactivated catalyst were recovered significantly by regeneration treatments (Table 1, Nos. 6 and 7).

TD-DTA profiles were recorded to obtain the information concerning the coke deposition in Ti-MWW (Fig. S1). The weight loss below 473 K could be assigned to physically adsorbed water, while that at higher temperatures is presumed to be because of dehydroxylation and coke desorption. The weight loss increased with the reaction time, indicating the formation and deposition of organic by-products with high molecular weights on the surface or inside the pores of Ti-MWW. In particular, coke deposition increased from 7.8% at 90 h (not yet deactivated) to 17.7% at 93 h (deactivated catalyst) (Table 1, Nos. 4 and 5). This implied that the channels of Ti-MWW became severely blocked and the Ti active sites were covered by the by-product molecules within a reaction period of only 3 h. Although the absolute amount of coke was extremely low, we used GC-MS to detect the by-products after dissolving the deactivated Ti-MWW catalyst in HF solution. Table 2 lists the molecular formula and molecular weight of the representative organic byproduct species found.

To investigate the effects of coke formation during the deactivation of Ti-MWW, we compared the reactions among different catalyst loadings. When the amount of Ti-MWW employed was decreased from 1.5 g to 1.0 g, the cyclohexanone conversion and oxime selectivity still reached 96% and 99% respectively, but the ammoximation lifetime was shortened from 93 h to 21 h (Fig. 4c and d). The lifetime was 6 h at a catalyst loading of 0.8 g. The TG-DTA investigation indicated that the Ti-MWW catalyst that deactivated at a TOS of 6 h showed a weight loss (also considered as the amount of organic species) of 10.1%, which was comparable with that shown by the catalyst deactivating at a TOS of 21 h (Fig. S1g and h). The results suggested that the coke formation and deposition took place easily when the amount of catalyst was low, because of higher weight ratio of by-products to catalyst. This then induces a rapid deactivation of the catalyst.

As the catalyst was always immersed in basic media with the presence of excess NH₃, a partial dissolution of the silicalite framework was unavoidable. However, the desilication degree is

No.	Samples	Surface area $(m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)	Weight loss ^a (%)	Si/B ^b	Si/Ti ^b	Q ₂ (%)	Q3 (%)
1	Fresh	552	0.27	2.0	30	26	1.5	8.0
2	TOS 30 h	297	0.17	5.1	76	24		
3	TOS 60 h	291	0.17	6.7	95		22	
4	TOS 90 h	263	0.16	7.8	114		20	
5	TOS 93 h ^c	157	0.13	17.7	114	20	1.7	12.6
6	Regenerated 1 ^d	486	0.26	1.0				
7	Regenerated 2 ^e	530	0.26				1.3	7.4

Table 1 Characterization results of Ti-MWW catalysts.

^a Given by TG-DTG analysis at 473–1073 K.

^b Given by ICP analysis.

^c Deactivated Ti-MWW sample.

^d Regenerated by calcination at 773 K in air.

e Regenerated by acid treatment first (0.3N HNO₃, solid to liquid ratio of 1:10), and then rearrangement with PI at 343 K for 24 h and further calcination at 773 K.

reasonably lower at a TOS of 6 h in the case of a 0.8 g catalyst loading than at 93 h with a 1.5 g loading of Ti-MWW, suggesting that the coke formation on the internal surface, rather than the structural degradation, was the main reason for catalyst deactivation. The coke formation is a common phenomenon in zeolite-catalyzed reactions, and an important factor governing catalyst lifetime. Although the deactivation was mainly ascribed to pore blocking by coke, it was not able to restore the original catalytic activity when the deactivated Ti-MWW catalyst was regenerated by air calcination at 773 K (not shown).

The ammoximation lifetime of the Ti-MWW catalyst was greatly prolonged by increasing the catalyst amount. The lifetime of Ti-MWW was nearly proportional to the catalyst loading in the range 1.5–3.2 g (Fig. 4a–c). However, the lifetime was greatly shortened to 8 h at 1.0 g of catalyst loading (Fig. 4d). When the amount of catalyst was low, a mass of by-product molecules could deposit on the surface, or even enter the channels. This would close off the active sites of Ti-MWW, leading to catalyst deactivation within a

short time. However, the pore blocking could be postponed or temporarily suppressed when the catalyst was high enough for splitting the adsorption or deposition of by-products with a high molecular weight in the reaction system.

In addition to coke formation, decreased crystallinity also occurred in the ammoximation as a result of framework desilication (Fig. 7). The desilication made the apparent Si/Ti ratio of Ti-MWW decrease from 26 to 20 after ammoximation was conducted for 93 h to deactivation (Table 1), suggesting that the content of Ti increased relatively to that of Si. The change of the silica matrix, that is, the scaffolds where the Ti active sites exist, is presumed to vary the coordination states of the Ti species or to leach some Ti molecules out of the framework. In fact, the deactivation of TS-1 in the ammoximation of cyclohexanone is likely to be attributed to another reason, that is, dissolution of framework [21].

Besides the catalytic activity and selectivity, the most important property that titanosilicate should have is that it is robust against Ti leaching, a notable problem commonly encountered in liquid-

Table 2

Major by-products detected in cyclohexanone ammoximation by GC-MS.

	•		
 No.	Molecular weight	Compound	Formula
1	100	Cyclohexanol	ОН
2	127	Cyclohexanecarboxamide	NH ₂
3	180	2-Cyclohexylcyclohexanone	
4	179	N-Cyclohexylidenecyclohexanamine	
5	113	ε-Caprolactam	O NH



Fig. 10. ²⁹Si MAS NMR spectra of fresh (a), deactivated at TOS of 93 h (b) and regenerated (c) Ti-MWW catalysts. The regeneration involved acid washing first and then PI-assisted structural rearrangement.

phase reactions. The state of Ti in TS-1 has been intensively studied and considered to be Ti(OSi)₄, which has an important role in oxidation reactions [22–25]. The Ti species are generally believed to be stable enough in the liquid-phase oxidation of simple alkenes; however, TS-1 slowly dissolves in an alkaline solution of ketone ammoximation. The Ti species are then continuously extracted from the zeolitic framework, and changes to a less active species. Similarly, Ti-MWW is stable against Ti leaching in the liquid-phase oxidation of alkenes [10,11], but it would also be subject to the leaching and coordination state change of the Ti species, especially when the dissolution of the framework occurs after a long run in the cyclohexanone ammoximation process.

Because Ti-MWW was synthesized in the presence of boric acid, it contained a relatively high amount of tetrahedral boron species, corresponding to an Si/B ratio of 30 (Table 1, No. 1). The fresh Ti-MWW catalyst developed a strong Si–O–B stretching band around 1400 cm⁻¹ [5]. The 1400 cm⁻¹ band almost disappeared for the deactivated catalyst (Fig. S2). The B species leached gradually in the ammoximation of cyclohexanone because its ionic radius is relatively tiny compared with that of Si, and produced a Si/B ratio of 114 for the deactivated catalyst (Table 1, No. 5). The loss of B may decrease the framework electronegativity and vary the electron density in the vicinity of the Ti sites, enhancing hydrophobicity. Thus, the leaching of B could not be a decisive factor for the deactivation of Ti-MWW.

Fig. 10 shows the ²⁹Si MAS NMR spectra of the Ti-MWW samples. The resonances at -94 ppm and -101 ppm are attributed to the Si(OSi)₂(OH)₂ (Q²) and Si(OSi)₃OH (Q³) groups [26]. In comparison with fresh Ti-MWW, the Q² and Q³ groups increased clearly in the spectra of the deactivated catalyst (Fig. 10a and b). These results also verified that the desilication and deboronation of the Si framework occurred during the ammoxi-



Fig. 11. Effect of silica species addition on the ammoximation over Ti-MWW. Ammoximation reaction without (a) and with (b) 5 ppm colloidal silica addition. Reaction conditions: Ti-MWW, 1.5 g; others, see Fig. 1.

mation of cyclohexanone, forming defect sites such as hydroxyl nests.

3.5. Enhancing the ammoximation lifetime and regeneration of deactivated Ti-MWW

As shown above, the framework desilication took place readily in the ammoximation process. It is possible to restrain this desilication by controlling its dynamic equilibrium. We have tried to suppress Si leaching by feeding 5 ppm colloidal silica solution (30%) continuously into the reaction mixture. Interestingly, the oxime selectivity was maintained at over 99% irrespective of silica addition. As shown in Fig. 11, the addition of a small amount of silica gel postponed the deactivation of Ti-MWW effectively, and prolonged the ammoximation lifetime from 93 h to 105 h. In contrast, these results suggested that the dissolution of the framework restricted the catalytic activity of Ti-MWW in a basic environment.

On the basis of the above results, the main reasons for catalyst deactivation are assumed to be the coke formation as well as the destruction of the -Ti-O-Si- sites accompanying framework desilication. We first tried to regenerate the deactivated catalyst by removing any high boiling point organic substances deposited inside the pores. After calcination in air at 773 K for 10 h, the color of the deactivated catalyst changed from light yellow to snow-white. TG-DTA analysis showed that a complete removal of heavy organic species was achieved. However, the catalyst that was regenerated was almost inactive for the ammoximation of cyclohexanone, indicating a simple calcination in air was insufficient for recovering the initial reactivity of Ti-MWW. The deactivated Ti-MWW catalyst after calcination was then subjected to a secondary treatment with an aqueous solution of PI at molar ratios of PI/Si = 0.3 and $H_2O/Si = 15$ at 443 K for 1 day. This treatment would cause a reversible structural rearrangement for the MWW structure, partially mend the defect vacancies and enhance the hydrophobicity of the framework [13,27]. This would be a useful technique in regenerating the deactivated catalyst of Ti-MWW. The treated sample was applied to the cyclohexanone ammoximation under the same conditions after burning off the organic species of PI at 773 K in air. The regenerated Ti-MWW restored the initial activity completely, producing a conversion of cyclohexanone greater than 96% (Fig. 12c). However, its lifetime was ca. 18 h, which was much shorter than that of the fresh Ti-MWW.



Fig. 12. Aammoximation on regenerated Ti-MWW catalysts. Regenerated by calcination only and then structurally rearranged (a), regenerated by acid treatment in advance and then structurally rearranged (b), and fresh Ti-MWW (c). Reaction conditions: Ti-MWW, 1.5 g; others, see Fig. 1.

Nevertheless, when the deactivated Ti-MWW catalyst was first treated with 0.3 M HNO₃ for 2 h at 353 K, then structurally rearranged with PI and calcined, the ammoximation lifetime was recovered effectively. The regenerated catalyst showed a lifetime of about 67 h (Fig. 12b), corresponding to 70% of that of the fresh catalyst. The acid treatment in advance would remove selectively the extra-framework Ti species as well as organic substances, which are both formed during ammoximation. The consequent structural rearrangement assisted with PI then removed some of the defect sites, while avoiding the deposition of inactive Ti species on the zeolites. Also, the regenerated catalyst showed a reduced number of Q² and Q³ groups in the ²⁹Si MAS NMR spectrum when compared with that of the deactivated catalyst (Fig. 10c and Table 1, No. 7).

4. Conclusion

Ti-MWW was capable of effectively catalyzing the ammoximation of cyclohexanone in a continuous slurry reactor, producing a cyclohexanone conversion of over 96% and an oxime selectivity of over 99%. The unique catalytic properties of Ti-MWW as heterogeneous catalyst led to a considerably longer ammoximation lifetime than TS-1 for the production of cyclohexanone oxime. The ammoximation behavior of Ti-MWW implied that the main reasons for catalyst deactivation were the coke deposition inside the micropores and the partial destruction of the –Ti–O–Si– sites. A combination of acid treatment and PI-assisted structural arrangement was effective for restoring the conversion, selectivity, and even the lifetime of regenerated Ti-MWW. Ti-MWW is thus considered to be a promising catalyst for developing a much cleaner process of cyclohexanone ammoximation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.10.037.

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