

## Highly Effective Synthesis of Cyclohexanone Oxime over a Novel Titanosilicate Ti-MWW

Fen Song, Yueming Liu, Haihong Wu, Mingyuan He, Peng Wu,\* and Takashi Tatsumi†

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, P. R. China

†Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503

(Received July 19, 2005; CL-050929)

Liquid-phase ammoximation of cyclohexanone proceeds extremely efficiently, selectively, and stably over a novel titanosilicate Ti-MWW in a clean solvent of water, which would lead to a potential process more environmentally benign for synthesizing cyclohexanone oxime.

Cyclohexanone oxime is a key intermediate for the manufacture of  $\epsilon$ -caprolactam (CPL) with an annual world market of 3.6 million tons in 1998.<sup>1</sup> Over 90% of the world installed production capacity of CPL is based on the non-catalytic oximation of cyclohexanone with hydroxylamine derivatives, followed by the liquid-phase Beckmann rearrangement in oleum. These conventional commercial processes have been encountering serious disadvantages, such as using poisonous hydroxylamine and corrosive fuming sulfuric acid and producing a large quantity of by-products. Particularly, the by-product of ammonium sulphate counts high as 2.8 times as much as product CPL.<sup>2</sup> A breakthrough has been made in the industrial production of CPL in 2003 by Sumitomo, which started the operation of a new CPL process by combining together the liquid-phase ammoximation of cyclohexanone with aqueous ammonia and hydrogen peroxide over titanosilicate catalyst and the heterogeneous vapour-phase Beckmann rearrangement over a highly siliceous ZSM-5 (silicalite-1). The process is extremely environmentally friendly from the viewpoint of zero emission. The catalytic ammoximation technique in the first step of this novel process is initially developed by Enichem using the MFI type titanosilicate, TS-1.<sup>1</sup> However, this process still has some drawbacks, such as a high cost for TS-1 manufacture due to using expensive structure-directing agent of tetrapropylammonium hydroxide and organic silicon source, necessity of a high TS-1 amount relative to substrate and a volatile solvent of *tert*-BuOH.<sup>3</sup> To develop more efficient titanosilicates, TS-2,<sup>4</sup> Ti-MOR,<sup>5</sup> and Ti- $\beta$ <sup>6</sup> have been developed. However, none of them shows potential capability of substituting for TS-1 in the liquid-phase ammoximation.

Ti-MWW with the MWW structure (generally known as MCM-22 for its alluminosilicate analogue), a novel titanosilicate recently developed by us, shows superior activity and product selectivity to conventional titanosilicates in the epoxidation of alkenes with H<sub>2</sub>O<sub>2</sub>.<sup>7</sup> The unique catalytic properties of Ti-MWW has been closely related to its pore system consisting of 12-membered ring (MR) side cups and two independent inter-layer and intralayer 10-MR channels.<sup>8</sup>

We report here that Ti-MWW is a more effective catalyst for the liquid-phase ammoximation of cyclohexanone in the presence of water, which may bring out a much greener process for the oxime synthesis than TS-1.

Ti-MWW catalysts were synthesized by hydrothermal synthesis<sup>9</sup> and postsynthesis methods,<sup>10</sup> which were denoted

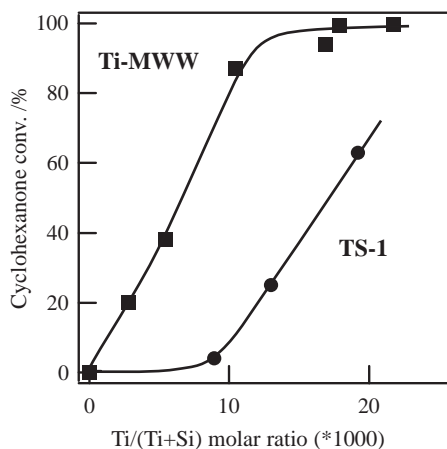
by Ti-MWW-HTS and Ti-MWW-PS, respectively. A rough estimation based on the prices of raw materials indicates that the manufacture costs of these two Ti-MWW catalysts are approximately half and two third that of TS-1, respectively. Other titanosilicates for control experiments, TS-1,<sup>11</sup> Ti-MOR,<sup>5</sup> and Ti- $\beta$ <sup>12</sup> were prepared according to the procedures reported elsewhere. All the catalysts have been characterized thoroughly by various techniques (XRD, IR, SEM, UV, ICP, and N<sub>2</sub>-adsorption). The ammoximation runs were performed batchwise in a 25-mL 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<sub>3</sub> aqueous solution (25%) were charged into the flask and the mixture was heated to a desirable temperature (303–353 K). The reaction was then started by adding a diluted aqueous H<sub>2</sub>O<sub>2</sub> (5%, 12 mmol) continuously with a micro-pump for 1 h. After finishing the addition of H<sub>2</sub>O<sub>2</sub>, the mixture was further stirred for 0.5 h. After the removal of solid catalyst, the products were analyzed by a gas chromatograph (Shimadzu 14B, FID detector) equipped with a 30-m DB-1 capillary column, using toluene as an internal standard. The amounts of ammonia and H<sub>2</sub>O<sub>2</sub> remaining in the mixture were quantified by the acid–base titration method and iodometry, respectively.

Table 1 shows the results of ammoximation on various catalysts. The product was predominately cyclohexanone oxime when the reaction proceeded to high levels, while peroxydicyclohexyl amine, and the products due to the aldol condensation of cyclohexanone were also co-produced particularly at a lower conversion of cyclohexanone. The solvent effect investigated on Ti-MWW-PS showed a catalytic activity order of H<sub>2</sub>O > MeOH > *t*-BuOH > MeCN (Table 1, Nos. 1–4). Both the con-

**Table 1.** The results of cyclohexanone ammoximation<sup>a</sup>

No.	Cat.	Si/Ti	Solvent	Conv. <sup>b</sup> /%	Oxime sel. <sup>c</sup> /%
1	Ti-MWW-PS	55	H <sub>2</sub> O	99.4	99.9
2	Ti-MWW-PS	55	MeCN	45.7	82.4
3	Ti-MWW-PS	55	MeOH	75.4	99.9
4	Ti-MWW-PS	55	<i>t</i> -BuOH	74.1	99.9
5	Ti-MWW-HTS <sup>d</sup>	50	H <sub>2</sub> O	97.0	99.9
6	TS-1 <sup>e</sup>	51	H <sub>2</sub> O- <i>t</i> -BuOH	97.0	99.9
7	TS-1 <sup>e</sup>	51	H <sub>2</sub> O	16.2	72.8
8	Ti-MOR	90	H <sub>2</sub> O	60.0	95.0
9	Ti- $\beta$	76	H <sub>2</sub> O	15.0	4.0
10	Ti-MWW-PS <sup>f</sup>	60	H <sub>2</sub> O	99.0	99.9

<sup>a</sup>Reaction conditions: cat., 50 mg; cyclohexanone, 10 mmol; solvent, 5 mL; NH<sub>3</sub> (25%), 12 mmol; H<sub>2</sub>O<sub>2</sub> (5%), 12 mmol; temp., 338 K; time, 1.5 h. H<sub>2</sub>O<sub>2</sub> was added dropwise at a constant rate within 1 h. <sup>b</sup>The conversion of cyclohexanone. <sup>c</sup>By-products were mainly peroxydicyclohexyl amine etc. <sup>d</sup>Cat., 100 mg. <sup>e</sup>Cat., 200 mg; reaction time, 5 h. The reaction conditions were similar to those reported previously.<sup>13</sup> <sup>f</sup>No. 1 was reused for 5 times.



**Figure 1.** Dependence of cyclohexanone conversion on Ti content. Reaction conditions: cat., 50 mg; 338 K; time, 1.5 h; others, see Table 1.

version of cyclohexanone and the oxime selectivity reached as high as 99% in water solvent. Simultaneously, the utilization of both  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$  was reasonably high (>95%) as the reaction was performed under the conditions of almost stoichiometric molar ratios for the substrates. Despite being somewhat low in the conversion of cyclohexanone, a high performance was also achieved on Ti-MWW-HTS prepared by a hydrothermal synthesis (No. 5).

When the ammoximation was carried out on TS-1 under the same conditions as reported,<sup>1,13</sup> TS-1 catalyzed the ammoximation very actively and selectively in a cosolvent of water and *t*-BuOH (No. 6). However, in a single solvent of water the reaction retarded greatly (No. 7). It should be noted that not only in the solvent, the optimized conditions of TS-1 also differed in the amount catalyst used and the reaction time. To give a conversion of 97%, TS-1 required a catalyst amount of 20 wt% relative to cyclohexanone and a longer reaction time of 5 h. Other titanasilicates, Ti-MOR and Ti- $\beta$  were much less active (Nos. 8 and 9). Thus, considering the fact that Ti-MWW is capable of giving a conversion >99% at 5 wt% of catalyst relative to cyclohexanone, we claim that we have established a new ammoximation catalyst more effective than TS-1.

To further confirm this issue, a series of Ti-MWW and TS-1 both with various Si/Ti ratios have been synthesized, and they have been applied to the ammoximation. In order to fairly evaluate the catalytic activity of these two titanasilicates, the reactions have been carried out under optimum conditions for each catalyst but with the same catalyst amount relative to cyclohexanone substrate (Figure 1). The oxime selectivity was comparably high for Ti-MWW and TS-1 (>98%). The conversion of cyclohexanone increased with increasing amount of Ti for both Ti-MWW and TS-1. Obviously, the former is more effective from the viewpoint of catalytic activity.

The stability and reusability of Ti-MWW in the ammoximation have been investigated. The used Ti-MWW catalyst was regenerated by washing with acetone and drying at 393 K, and was subsequently subjected to repeated ammoximation at a constant ratio of catalyst-substrate-solvent. After five cycles of reaction-regeneration, the Ti-MWW catalyst maintained the activity and oxime selectivity (Table 1, No. 10). The quantification of Ti by ICP indicated that the Ti leaching was within 5% after the re-

peated reaction, and XRD patterns and UV spectra showed that the used Ti-MWW had the same crystallinity and coordination state of Ti as the fresh one. Thus, Ti-MWW possesses excellent stability and reusability in the ammoximation of cyclohexanone.

The activity of Ti-MWW greatly depends on the adding mode of reactants. In particular, adding  $\text{H}_2\text{O}_2$  into the reaction system rapidly decreased the oxime yield greatly. For example, when a desirable amount of  $\text{H}_2\text{O}_2$  was added all at once, the reaction resulted in only ca. 3% conversion of cyclohexanone, while the conversion of  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  reached 99 and 81%, respectively. This dramatic behavior is presumed to be related to the reaction mechanism of ammoximation. The titanasilicate-catalyzed ammoximation plausibly involves the formation of an intermediate of hydroxylamine formed through the catalytic oxidation of  $\text{NH}_3$  with  $\text{H}_2\text{O}_2$  on Ti active sites and a subsequent non-catalytic oximation of cyclohexanone with  $\text{NH}_2\text{OH}$  to oxime.<sup>5,14</sup> The latter oximation should compete with the consecutive oxidation of  $\text{NH}_2\text{OH}$  by  $\text{H}_2\text{O}_2$ . Ti-MWW with superior oxidation capability would accelerate the oxidation of  $\text{NH}_2\text{OH}$  before reacting with cyclohexanone to oxime particularly when an excess amount of  $\text{H}_2\text{O}_2$  exists. Thus, slow addition of  $\text{H}_2\text{O}_2$  would reduce its concentration in the reaction system, and hence avoid a deep oxidation of  $\text{NH}_2\text{OH}$ , which is then in favor of oxime formation.

As a result we have found that Ti-MWW deserves to be a promising catalyst for the greener synthesis of cyclohexanone oxime actively, selectively, and regenerably.

We thank the financial supports by NSFC (Nos. 20473027 and 20233030) and STCSM (03DJ14005). P.W. thanks Program for New Century Excellent Talents in University (NCET). T.T. thanks the support by Core Research for Evolutional Science and Technology (CREST) of JST Corporation.

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