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Clean synthesis of furfural oxime through liquid-phase ammoximation of furfural over titanosilicate catalysts

Xinging Lu, Yejun Guan*, Hao Xu, Haihong Wu and Peng Wu*

Clean synthesis of furfural oxime (FO) has been realized through titanosilicate-catalyzed liquid-phase ammoximation of furfural with ammonia and hydrogen peroxide. A detailed investigation of furfural ammoximation over three representative titanosilicates of Ti-MOR, TS-1 and Ti-MWW reveals that the reaction involves the hydroxylamine route and the imine route. The hydroxylamine route answers for the formation of objective product (FO), while the imine route leads to the formation of undesired products such as 2-furylamide and 2-furoic acid. With a high effeciency for the hydroxylamine formation, Ti-MOR proves to be superior to TS-1 and Ti-MWW. The catalytic performance of Ti-MOR depends greatly on the operating conditions of the reaction, which is closely related to its activity in catalyzing hydroxylamine decomposition. The decomposition of hydroxylamine and the non-catalytic oxidation of furfural can be effectively suppressed in Ti-MOR-catalyzed ammoximation when employing water as the solvent and adding H₂O₂ dropwise into the reaction system. Under optimized conditions, Ti-MOR is capable of providing furfural conversion and oxime selectivity both above 97%.

1. Introduction

Renewable biomass resources have the potential to serve as a sustainable and alternative carbon supply of modern chemical industry that is currently based on fossil resources to large extent.¹ Furfural, produced by acid-catalyzed dehydration of cellulose biomass, have attracted much attention recently for the production of biofuels and downstream chemicals.²⁻¹⁰ The annual global production of furfural can be amounted up to 300 Kton according to a report in 2008.⁴ A number of valuable chemicals and biofuels can be produced from furfural, such as furfuryl alcohol, tetrahydrofuran, methyl-tetrahydrofuran, pentanediol, and cyclopentanone.¹¹ Besides these oxygenates, furfural derivatives containing nitrogen atom have also attracted remarkable interest. For instance, furfurylamine, produced by the selective reductive amination of furfurals with ammonia, possesses many potential applications in pharmaceutical synthesis or resin industry.¹²⁻¹⁵ Another furfural derivative, furfural oxime (FO) is also an important intermediate with a constantly increasing world market for the production of biologically active compounds with a wide range of medicinal properties. Moreover, FO has gained attention as a versatile platform chemical for the production of 2furvlamide. 2-furonitrile, 2-furfurylamine, tetrahydro-2furfurylamine (Scheme 1). In addition, FO and its derivatives are used in agronomy as nitrification inhibitors that are effective against nitrobacteria species, thereby retarding the nitrification rate.^{16, 17}

The conventional processes for manufacturing FO are of multi-steps including the synthesis of hydroxylamine derivatives like $(NH_2OH)_2 \cdot H_2SO_4$, the non-catalytic oximation of furfural with hydroxylamine sulfate and the recovery of FO by distilling after neutralizing the formed acid with ammonia. These processes are encountering serious disadvantages, such as using poisonous hydroxylamine salts and producing large amounts of ammonium sulphate byproducts together with nitrogen oxides, leading to environmental problems. Thus, it is urgent to develop environmentally friendly routes for synthesizing FO as well as economically. In this regard, one-pot production of FO using NH₃ and H₂O₂ as the ammoximation agents shows obvious advantages compared with conventional methods.



The ammoximation of several carbonyl compounds such as cyclohexanone has been widely studied and has been commercialized by EniChem based on the $TS-1/H_2O_2$ system since 1990s.^{18, 19} Many other titanosilicates, such as TS-2,²⁰ Ti-

ARTICLE

Beta,²¹ Ti-MOR and Ti-MWW,²²⁻²⁸ have been developed for the aldehydes or ketones ammoximation. These titanosilicates show structure- and substrate-dependent activities and selectivities due to the varying hydrophilic/hydrophobic characteristics of the reaction system. In this sense, environmental and selective synthesis of furfural derived oxime remains to be a challenging task because furfural contains several reactive functional groups.

In this study, the clean synthesis of FO has been attempted from the ammoximation of furfural on three representative titanosilicates, Ti-MOR, TS-1 and Ti-MWW. By thoroughly investigating the furfural ammoximation in particular the parameters controlling the oxime selectivity, Ti-MOR is found to be the best catalyst with the highest reaction activity and FO selectivity in the presence of green solvent of water. The preliminary study on the reaction mechanism of furfural ammoximation suggests that the unique performance of Ti-MOR is due to the highly efficient production of hydroxylamine, which does not undergo significant decomposition on Ti-MOR but quickly reacts with furfural when it forms. Our report undoubtedly provides a much cleaner process for FO production.

2. Experimental

2.1.Catalyst preparation

According to the procedures reported previously,²⁹ Ti-MOR was post-synthesized through a solid-gas reaction between dealuminated mordenite (Si/Al = 196) and TiCl₄ vapor at elevated temperature. A dealuminated MOR sample (2 g) placed in a quartz tube reactor (Ø 3 cm) was pretreated at 773 K for 4 h in a dry N₂ stream (50 mL min⁻¹). The TiCl₄ vapor was carried by N₂ flow into the reactor, which contacted the zeolite bed to induce Ti incorporation. After TiCl₄ treatment at 773 K for 2 h, the sample was purged with pure N₂ at the same temperature for 1 h to remove any residual TiCl₄ species from the zeolite powder. After cooling down to the room temperature under N₂ atmosphere, the TiCl₄-treated sample was washed with deionized water and dried at 353 K overnight (denoted as Ti-MOR).

Ti-containing MWW lamellar were hydrothermally synthesized using boric acid and piperidine (PI) as crystallization-supporting agent and structure-directing agent (SDA), respectively. The gels, with a molar composition of 1.0 $SiO_2 : 0.05 TiO_2 : 1.4 PI : 0.67 B_2O_3 : 19 H_2O$, was crystallized under rotation (10 rpm) at 443 K for 7 days in a Teflon-lined stainless-steel autoclave. After crystallization, the obtained precursor was refluxed with 2 M aqueous HNO₃ solution at a solid-to-liquid weight ratio of 1:30 with the purpose of removing extra-framework Ti species as well as part of framework boron. The acid-treated products were filtered, washed with deionized water and dried at 353 K overnight. Subsequently, the sample was calcinated at 823 K for 6 h, denoted as Ti-MWW. TS-1 was hydrothermally synthesized from the gel with a molar composition of 1.0 SiO₂ : 0.03 TiO₂ : 0.18 TPAOH : 18 H_2O under rotation (10 rpm) at 443 K for two days.³⁰

2.2.Characterization methods

The X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Ni-filtered Cu K α radiation (λ = 0.1541 nm) in a scanning range of $2\theta = 5 - 35^{\circ}$ to confirm the structure and crystallinity of the titanosilicates. Morphologies and crystal sizes were examined by a Hitachi S-4800 scanning electron microscope. The coordination states of Ti species were examined by UV-visible spectroscopy on a Shimadzu 2700PC spectrophotometer using BaSO₄ as a reference. Infrared spectra were collected by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm⁻¹. The spectra were obtained using a KBr pellet technique (3 wt. % diluted in KBr). In order to avoid the influence of absorbed water, the KBr diluted wafer placed in a quartz IR cell sealed with KBr windows, was evacuated at 723 K for 2 h before measurement. The amounts of Si, Ti, B and Al were determined by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP after the samples were dissolved in aqueous HF solution. The textural properties of the titanosilicates were determined by N₂ adsorption at 77 K using a BEL SORP instrument. Prior to the adsorption measurements, the samples were degassed in vacuum at 573 K at least for 6 h.

2.3.Catalytic reactions

Furfural with a purity of 99 % was procured from J & K Chemicals and it was used without further purification. The ammoximation of furfural to FO was carried out under vigorous stirring in a three-neck flask equipped with a condenser. The catalyst (50 - 150 mg), solvent (12 g), furfural (20 mmol), and NH₃ (25 wt. % aqueous solution, 20 - 40 mmol) were added into the flask, and the mixture was heated to the desired temperature (303 - 343 K). The reaction was then initiated by adding 20 - 40 mmol of H_2O_2 (31 wt.% aqueous solution) into the reactor at once or feeding at a constant rate continuously with a micropump for a certain period of time (15 - 60 min).

The hydroxylamine formation reactions were also proceeded in the above-mentioned three-neck flask. In a typical run, a mixture of Ti-MOR (0.1 g), H₂O (12 g), NH₃ (25 wt. % aqueous solution, 30 mmol) was added in the flask and heated to 323 K. Then, 25 mmol of H_2O_2 (31 wt. %) was fed into the slurry at once or dropwise at a constant rate with a micropump for a certain period of time (0.25 - 1 h). After the catalyst solid was removed by filtration, an excessive amount of furfural was added into the filtrate and stirred at 323 K for 1 h. FO thus formed under non-catalytic conditions was determined by gas chromatography, and its amount was taken as that of hydroxylamine formed in the catalytic oxidation step of ammonia with H₂O₂ over Ti-MOR catalyst. With respect to the hydroxylamine decomposition reaction, commercially available hydroxylamine chloride was used instead of free hydroxylamine considering the safety to handle. A mixture of Ti-MOR (if used, 0.1 g), H₂O (12 g), and hydroxylamine chloride (20 mmol) was added in the flask and heated to 323 K. Then, a certain amount of H₂O₂ (31 wt. %) was fed into the slurry at

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once or dropwise at a constant rate with a micropump for a certain period of time (1 - 5 min). After the catalyst was removed by filtration, an excessive amount of furfural was added into the filtrate and stirred at 323 K for 1 h. From the amount of furfural converted, the amount of remaining hydroxylamine was then determined.

The products were separated from the reaction mixture by centrifugation and determined by a gas chromatograph (Shimadzu 2014) equipped with an Rtx®-Wax capillary column (30 m \times 0.25 mm \times 0.25 μm) and FID detector. The amounts of H₂O₂ and NH₃ remaining in the mixture were determined by iodometry and acid-base titration method, respectively. In case of water solvent, the reaction mixture was converted into a homogeneous phase by adding 15 g of ethanol, and then it was subject to GC analysis. The products formed were identified by a GC-MS (Agilent 6890 series GC system, 5937 network mass selective detector). The result of the furfural ammoximation reaction was given using these criteria:

moles of furfural comsumed ×100% Furfural conversion = moles of furfural in the feed moles of FO produced FO yield = moles of furfural in the feed moles of a defined product ×100% Product selectivity = moles of furfural comsumed

3. Results and discussion

3.1. Characterization of titanosilicate catalysts

Fig. 1 shows the SEM images and XRD patterns of the titanosilicates. It can be seen that all materials show characteristic morphology of MOR, MFI and MWW structures. Ti-MOR and TS-1 crystals were aggregates of nanocrystals while Ti-MWW crystals showed a typical platelet-shaped morphology with the thickness of ~50 nm. The XRD patterns clearly suggest that these materials are of high crystallinity and no impurities of other zeolite phase or amorphous phase are detected. The specific surface areas (Langmuir) determined from N₂ adsorption at 77 K were in the range of 537 - 552 m² g⁻ ¹ (Table 1). As shown in Fig. 2, the band at 210 nm and 963 cm⁻ ¹ in UV-vis and IR spectra, respectively, indicating the incorporation of the tetrahedral Ti species in the zeolite framework. $^{\rm 29,\ 31}$ Meanwhile, the band around 330 nm was nearly negligible, indicating the absence of anatase-like phase in these titanosilicates.



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Fig. 1. SEM images of Ti-MOR (a), TS-1 (b), Ti-MWW (c) and XRD patterns of titanosilicates (d).

Table 1 Physi	2 1 Physicochemical properties of various titanosilicates.					
Catalyst	Structure	Ti content ^a	Crystal size ^b	SA ^c		
		(mmol g⁻¹)	(µm)	(m ² g ⁻¹)		
Ti-MOR	MOR	0.31 (53)	0.2 - 0.4	552		
TS-1	MFI	0.33 (50)	0.2 - 0.3	537		
Ti-N/\\/\//	N/1\A/\A/	0 37 (44)	06×06×01	545		

^a Determined by ICP analysis. The values in parentheses indicate the Si/Ti molar ratios.

^b Evaluated by SEM

² Specific surface area (Langmuir) measured by N₂ adsorption at 77 K



MWW (c).

3.2.Comparison of furfural ammoximation among various titanosilicates

Table 2 shows the results of ammoximation of furfural over various titanosilicate catalysts in different solvents. It should be noted that all the furfural converted goes to the detected products in all cases. The reaction of furfural in the absence of heterogeneous catalysts is also listed for comparison. To exclude the effect of un-catalysed reactions, we started the blanks tests by following the conversion of furfural with either NH₃ or H₂O₂ in the homogeneous conditions and the results suggested that no reaction occurred in neither case. For

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ARTICLE

homogeneous oxidation in solution containing both NH₃ and H₂O₂ in the absence of titanosilicate catalysts, 15.5% of furfural conversion was found, producing 2-furylamide and 2furoic acid with selectivity of 86.9% and 13.1%, respectively (Table 2, Entry 1). It is well known that imine can be easily formed when ketones react with ammonia, which is shown as imine route in Scheme 2. However, the formed imine is unstable and tends to decompose back to a ketone through the reverse reaction in the absence of $H_2 O_{27}^{22}$ resulting in no visible conversion of furfural with NH_3 . In presence of H_2O_2 , the formed imine can then be oxidized to 2-furylamide and 2furoic acid. It should be noted that no FO was detected in these non-catalyzed reactions. We then tried the non-catalytic oximation of furfural with hydroxylamine chloride. This time we observed a good FO yield of 92.3%, with selectivity of 97.6% at a high furfural conversion of 94.6% (Table 2, Entry 2). The main byproduct was 2-furonitrile that formed due to acidcatalyzed dehydration of FO (Scheme 2). 2-furylamide and 2furoic acid were not detected in this non-catalytic oximation, confirming that they are produced through the imine route.

In Table 2, entries 3-17 show us the furfural conversion and product distribution in the presence of titanosilicate catalysts. It can be seen that in all cases FO was formed with yield range from 5.1 to 94.8% depending on the catalysts and solvents used. Byproducts such as 2-furonitrile, 2-furamide, and 2-furoic acid were also found in all cases. These results suggest Table 2 A comparison of ammoximation of furfural in various solvents^a

that the catalytic ammoximation of furfural to FO occurred simultaneously or competed with the non-catalytic oxidation of furfural to 2-furylamide and 2-furoic acid, meanwhile the dehydration of FO to 2-furonitrile was inevitable. It was found that a higher furfural conversion tended to be accompanied by a higher FO selectivity, similar to the common phenomena well observed in the processes of titanosilicate-catalyzed ammoximation of various ketones and aldehydes.^{18, 19, 22-28} Two findings can be drawn from the data shown in Table 2. On the one hand, the catalytic ammoximation and the noncatalytic oxidation takes place in parallel and compete with each other. On the other hand, the product distribution shows clear structure-dependent and solvent-dependent trend. Generally, reactions in methanol whatever the catalyst used always gave moderate furfural conversion about 40% while low selectivity to FO (<30%). When the solvent is water, isopropanol or t-BuOH, the FO selectivity after reaction for 5 min on Ti-MOR is all higher than 92% (entries 3, 6 and 7) at furfural conversion around 20%. These results suggest that Ti-MOR shows much better performance than TS-1 and Ti-MWW in ammoximation of furfural. Under similar reaction conditions, Ti-MOR showed the highest FO yield of 94.8 % together with the highest FO selectivity of 96.1 % in water. These results suggest that the undesired byproduct formation pathways can be effectively retarded by choosing a highly active titanosilicate such as Ti-MOR for catalytic ammoximation.

Entry Cat.	Solvent	Furfural conv. (%)	FO yield (%)	Products selectivity (%)				
				FO	2-furonitrile	2-furylamide	2-furoic acid	
1	None	H ₂ O	15.5	-	-	-	86.9	13.1
2	None ^b	H ₂ O	94.6	92.3	97.6	2.4	-	-
3	Ti-MOR	H ₂ O	98.6 (24.7) ^c	94.8 (24.0)	96.1 (97.0)	2.4 (1.5)	1.3 (1.2)	0.2 (0.3)
4		MeOH	45.0	9.0	19.9	1.4	75.5	3.2
5		EtOH	46.5	32.9	70.7	2.2	25.0	2.1
6		iso-propanol	90.9 (22.0) ^c	84.5 (20.4)	93.0 (92.8)	6.2 (6.5)	0.5 (0.7)	0.0 (0.0)
7		t-BuOH	83.8 (21.3) ^c	79.1 (20.1)	94.4 (94.2)	4.2 (4.1)	1.2 (1.7)	0.0 (0.0)
8	TS-1	H ₂ O	28.5	7.0	24.6	1.9	64.9	8.6
9		MeOH	47.9	13.7	28.6	0.8	65.8	4.8
10		EtOH	43.4	10.6	24.4	0.5	69.4	5.7
11		iso-propanol	28.6	12.2	42.6	2.6	52.7	2.1
12		t-BuOH	25.1	6.8	27.1	0.1	66.1	6.7
13	Ti-MWW	H ₂ O	23.9	5.1	21.4	1.6	65.2	11.8
14		MeOH	43.1	6.9	16.1	7.0	72.8	4.1
15		EtOH	40.3	5.8	14.4	1.0	83.1	1.5
16		iso-propanol	25.6	7.1	27.9	1.2	68.1	2.8
17		t-BuOH	24.2	6.3	26.1	1.0	68.0	4.9

^a Reaction conditions: cat. (if), 0.1 g; solvent, 12 g; furfural, 20 mmol; H₂O₂ (31 wt. %), 25 mmol; NH₃ (25 wt. %), 30 mmol; temp., 323 K; total time, 1 h. H₂O₂ added dropwise at a constant rate within 1 h.

^b Reaction conditions: NH₂OH·HCl, 25 mmol; solvent, 12 g; furfural, 20 mmol; temp., 323 K; time, 1 h.

^c The values in parentheses are results from studies at the reaction conditions as follows: Ti-MOR, 0.1 g; solvent, 12 g; furfural, 20 mmol; H₂O₂ (31 wt. %), 2.08 mmol; NH₃ (25 wt. %), 30 mmol; temp., 323 K; total time, 5 min. H₂O₂ added dropwise at a constant rate within 5min.

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ARTICLE



Scheme 2. Possible reaction pathways in furfural ammoximation.

Early studies have systematically investigated the ammoximation of ketones (e.g. cyclohexanone and methyl ethyl ketone) on TS-1, Ti-MWW and Ti-MOR.^{18, 19, 22, 26-28} These catalysts have been proved to be effective and selective for the ammoximation of these commonly-used ketones. For furfural, it shows rather high reactivity for imine formation and thus readily results in byproducts other than oxime. In this regard, selective ammoximation relies on a good choice of titanosilicate to a huge extent.

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

Our preliminary results have undoubtedly shown that Ti-MOR serves as an appropriate and efficient catalyst for the selective formation of FO in the furfural ammoximation when H_2O is chosen as a solvent. We next investigated the effect of reaction parameters such as the reaction time, the adding method of substrates, the catalyst amount, the reaction temperature and H_2O_2 /furfural and NH_3 /furfural molar ratios, on the ammoximation behaviour over Ti-MOR.

3.3.1. Effect of reaction time and adding method of substrates

The effect of reaction time on the performance of furfural ammoximation over Ti-MOR was investigated while H_2O_2 was fed at once into the reactor. As shown in Fig. S1A, both the furfural conversion and the FO selectivity increased with prolonging the reaction time on stream, however, a large amount of the byproducts of 2-furylamide and 2-furoic acid (> 20 %) were by-produced from the non-catalytic oxidation of furfural due to the presence of excess free H_2O_2 .

Fig. S1B compares the results of furfural ammoximation over Ti-MOR with various H_2O_2 feeding rate. When H_2O_2 was fed at once into the reactor, the reaction gave a furfural

conversion of 78.5 % along with a FO selectivity of 72.6 %. While prolonging the feeding time of H_2O_2 periodically, both the furfural conversion and the FO selectivity increased and finally reached 98.6 % and 96.1 % at a feeding time of 1 h, respectively. In our earlier work, it has been demonstrated that the ammoximation of cyclohexanone over Ti-MWW depended greatly on the method of adding substrates.²⁷ We believe that when H_2O_2 was charged into the reactor too quickly the unreacted H_2O_2 would accelerate the consecutive oxidation and decomposition of hydroxylamine to nitrogen oxides before it participates the oximation of ketone to corresponding oxime. Thus, a high conversion of ketone to oxime is only achieved when H_2O_2 is fed slowly. In the case of furfural ammoximation, the addition of H₂O₂ not only played a significant role on the furfural conversion but also obviously altered the product distribution.

3.3.2. Effect of catalyst amount

Fig. S1C shows the effect of catalyst amount on the ammoximation of furfural over Ti-MOR. Reasonably, the furfural conversion increased gradually with an increasing Ti-MOR amount, and it reached the maximum of 98.8 % at 0.125 g catalyst loading. Additionally, the effect of catalyst amount on the FO selectivity has also been investigated. As shown in Fig. S2A, the FO selectivity increased with the increase of catalyst amount. The above results imply the reaction should be operated using a sufficient amount of catalyst to fasten the main catalytic step of ammoximation while suppressing the step of non-catalytic oxidation.

3.3.3. Effect of reaction temperature

The effect of the reaction temperature on the performance of furfural ammoximation was investigated in the temperature range of 303 - 333 K (Fig. S1D). With increasing the reaction temperature from 303 to 323 K, the furfural conversion increased and reached a maximum, and they remained almost unchanged from 323 to 333 K. The byproducts of 2-furylamide and 2-furoic acid were hardly detected, only a small amount of 2-furonitrile (< 3 %) was by-produced in the temperature range of 323 - 343 K (Fig. S1D). The effect of reaction temperature on the FO selectivity has also been shown in Fig. S2B. It can be seen that the FO selectivity increased with the increase of reaction temperature, indicating that the non-catalytic oxidation could also be suppressed by increasing the reaction temperature.

3.3.4. Effect of H₂O₂/furfural and NH₃/furfural molar ratios

As shown in Fig. S1E, the effect of H_2O_2 /furfural ratio on the performance of furfural ammoximation was investigated in the range from 1 to 2 while fixing the NH₃/furfural molar ratio at 1.5, reaction temperature at 323 K and total reaction time at 1

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h. The H₂O₂/furfural ratio was varied by changing the added H₂O₂ amount. The stoichiometric furfural ammoximation requires equal moles of H₂O₂ and furfural. However, when the reaction performed at a H₂O₂/furfural molar ratio of 1, the furfural conversion was only 90.7 % due to the unproductive decomposition of H₂O₂. The furfural conversion increased to 98.8 % at a H₂O₂/furfural ratio of 1.25, and almost leveled off at the ratios > 1.25. The FO selectivity reached a plateau (> 97 %) at H₂O₂/furfural ratio of 1 - 1.5. When further increasing the H₂O₂/furfural ratio, the FO selectivity decreased slightly due to the acceleration of the non-catalytic oxidation of furfural to 2-furylamide and 2-furoic acid with the existence of excess amount of free H₂O₂ in the reaction system.

The effect of NH₃/furfural ratio on the furfural ammoximation was also investigated while fixing the H_2O_2 /furfural ratio at 1.25 (Fig. S1F). The furfural conversion and turnover number (TON) per Ti site increased with increasing the NH₃/furfural ratio and reached 98.7 % and 510 at 1.5, respectively, while the utilization efficiencies of H_2O_2 and NH_3 were always > 79.0 % and 66.7 %, respectively, along with a FO selectivity of > 97.0 %. No further changes in either furfural conversion or oxime selectivity were observed at NH₃/furfural ratios > 1.5. The high furfural conversion obtained in an excessive amount of NH_3 was probably due to a partial loss of NH₃ via vaporization and the fact that a suitable basic environment benefits the ammoximation. A similar phenomenon has already been discovered in the ammoximation of other aldehydes or ketones over titanosilicate catalysts.^{23, 24, 26, 27}

3.4. Stability and regeneration of Ti-MOR

The stability and reusability of a heterogeneous catalyst was the essential factor for actual application in industrial processes. We have checked the stability and reusability of Ti-MOR in the ammoximation of furfural (Fig. 3). The used Ti-MOR was regenerated by washing with acetone and by further calcination at 823 K for 6 h, and then it was subjected to repeated ammoximation of furfural at a constant ratio of catalyst-oxidant-NH₃-solvent. After five recycle of reactionregeneration, the catalyst maintained high furfural conversion and FO selectivity of 98.7 % and 97.3 %, respectively. ICP analysis indicated that Ti leaching was within 5% after the repeated cycling. Furthermore, no significant difference was found in XRD patterns, N₂ adsorption isotherm and UV-vis spectra between the fresh Ti-MOR and the regenerated one (Fig. S3), indicating that Ti-MOR is extremely stable and serves as a reusable catalyst for the ammoximation of furfural.

3.5 Investigation into the reaction mechanism of furfural ammoximation

According to the hydroxylamine route (Scheme 3), the furfural ammoximation includes several reaction pathways: (1) the hydroxylamine formation by the catalytic oxidation of ammonia with H_2O_2 on the Ti sites inside the zeolite channels, (2) subsequent non-catalytic oximation of furfural with hydroxylamine intermediate to FO, (3) the nonproductive oxidation of hydroxylamine by H_2O_2 on Ti sites to NO_x , and (4)

other side reactions.^{32, 33} The non-catalytic oximation of ketone with hydroxylamine rate constant (k₃) is independent of the type of titanosilicate used, but the hydroxylamine formation rate constant (k₁) and the hydroxylamine decomposition rate constant (k₂) relies closely on the catalytic ability of the Ti species.^{27, 34}

The kinetics was firstly studied for the formation of hydroxylamine with H₂O₂ over Ti-MOR, TS-1 and Ti-MWW in the presence of water (Fig. S4). It is well reasonable to assume that the hydroxylamine formation pathway proceeds always along with that of the hydroxylamine decomposition. As shown in Fig. S4, the hydroxylamine yield over Ti-MOR is comparable to the added H_2O_2 amount, indicating that the decomposition of hydroxylamine was effectively retarded when H₂O₂ was supplied controllably under dropwise conditions. Thus, the reaction rate constant (k₁) of Ti-MOR in the hydroxylamine formation determined by the C_{NH2OH} versus reaction time is estimated to be 27.7 mmol L^{-1} min⁻¹ (Table 3). As the hydroxylamine yield over TS-1 or Ti-MWW is far below the added H_2O_2 amount, its reaction rate constant (k₁) in the hydroxylamine formation could not be accurately determined. As shown in Fig. S5, the kinetics were also studied for the decomposition of hydroxylamine (chloride salt) with H₂O₂ in the presence of water. The reaction rate constant (k_2) of TS-1 in the decomposition of hydroxylamine is about 13.9 mmol L⁻¹ min^{-1} , which is far below the reaction rate constant (k₃) of noncatalytic furfural oximation with hydroxylamine chloride (69.1 mmol L^{-1} min⁻¹) (Fig. S6, Table 3). It means that the formed hydroxylamine prefers to react with furfural rather than being decomposed by H_2O_2 or TS-1/ H_2O_2 . Hence, the low activity of TS-1 in the catalytic furfural ammoximation is possibly due to the weak ability for the formation of hydroxylamine. With respect to Ti-MWW, it showed the highest reaction rate constant (k_2) of 69.8 mmol L^{-1} min⁻¹ in the decomposition of hydroxylamine, which is comparable to the reaction rate constant (k₃) of the furfural ammoximation with hydroxylamine (69.1 mmol L^{-1} min⁻¹) (Fig. S6, Table 3). Thus, the high hydroxylamine decomposition activity could account for the low activity of Ti-MWW in the furfural ammoximation. Based on the above results, we propose that the best catalytic performance of Ti-MOR in the production of FO among these titanosilicates is due to its high hydroxylamine formation efficiency and low hydroxylamine decomposition rate.

In order to prove whether the above assumption works or not for furfural ammoximation over Ti-MOR, we have studied the dependence of FO yield and hydroxylamine yield as the function of H_2O_2 amount added in the furfural ammoximation and the hydroxylamine formation reaction, respectively. As seen in Fig. 4, when the amount of H_2O_2 added was less than 10 mmol, the FO yield obtained in the furfural ammoximation reaction well equalled to hydroxylamine yield in the hydroxylamine formation reaction, both of which are equivalent to the amount of H_2O_2 added. This result firmly agrees with our previous finding that the crucial step in this process is the catalysed formation of hydroxylamine on Ti-MOR, while the next ammoximation step proceeds very fast. We can safely conclude that FO is formed from the Published on 30 August 2017. Downloaded by Gazi Universitesi on 30/08/2017 12:55:35.

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Journal Name

hydroxylamine route and the decomposition of hydroxylamine could be effectively retarded at the initial reaction stage when the amount of H_2O_2 fed dropwise was consumed off. Further increasing the amount of H_2O_2 , the FO yield and the hydroxylamine formation reaction both increased but was lower than the added H_2O_2 amount.



Fig. 3. Changes of furfural conversion and products selectivity with the reaction-regeneration cycles on Ti-MOR. Reaction conditions for the first run: Ti-MOR, 1.25 g; H_2O , 120 g; furfural, 0.2 mol; H_2O_2 (31 wt. %), 0.25 mol; NH_3 (25 wt. %), 0.3 mol; temp., 323 K; total time, 1 h. H_2O_2 was added within 1 h. The used catalyst was regenerated after every catalytic run. All the catalytic runs proceed at a constant ratio of catalyst-oxidant-NH₃-solvent. Regeneration condition: washed with acetone and dried at 353 K for 8 h, and further calcined at 823 K in air for 6 h.



Scheme 3. The reaction steps involved in furfural ammoximation.

Catalyst	st Reaction rate constant (mmol ⁻¹ min ⁻¹)				
	k ₁ ^a	k ₂ ^b	k ₃ ^c		
Ti-MOR	27.7	31.3	69.1		
TS-1	_ ^d	13.9	69.1		
Ti-MWW	_ ^d	69.8	69.1		

 a The formation of hydroxylamine. Reaction conditions: cat., 0.1 g; NH₃, 30 mmol; H₂O₂, 2.4 mmol; H₂O, 12 g; temp., 323 K. H₂O₂ was dropwise added at a constant rate within 6 min.

 $^{\rm b}$ The decomposition of hydroxylamine. Reaction conditions: cat., 0.1 g; NH₂OH·HCl, 20 mmol; H₂O₂, 2.4 mmol; H₂O, 12 g; temp., 323 K. H₂O₂ was dropwise added at a constant rate within 6 min.

 c The furfural oximation with hydroxylamine. Reaction conditions: NH2OH+HCl, 20 mmol; H2O, 12 g; temp., 323 K.

^d Hardly detectable for TS-1 and Ti-MWW.



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ARTICLE

Fig. 4. Hydroxylamine yield in ammonia oxidation with H_2O_2 (left) and FO yield in furfural ammoximation with NH_3 and H_2O_2 (right) as the function of H_2O_2 amount added. Hydroxylamine formation condition: Ti-MOR, 0.1 g; H_2O , 12 g; NH_3 (25 wt.%), 30 mmol; H_2O_2 (31 wt.%), 24 mmol; temp., 323 K; total time, 1 h. Furfural ammoximation condition: Ti-MOR, 0.1 g; H_2O , 12 g; furfural, 20 mmol; NH_3 (25 wt.%), 30 mmol; H_2O_2 (31 wt.%), 24 mmol; temp., 323 K; total time, 1 h. H_2O_2 was dropwise added at a constant rate within 1 h.



Fig. 5. The decomposition of hydroxylamine in the presence of Ti-MOR but without H_2O_2 (a), with H_2O_2 but without Ti-MOR (b), and in the presence of both Ti-MOR and H_2O_2 (c). Reaction conditions: Ti-MOR (if added), 0.1 g; H_2O_2 (if added), 25 mmol; H_2O_1 2 g; NH_2OH ·HCl, 20 mmol; temp., 323 K; time, 1 h.

In addition, the decomposition of hydroxylamine by oxidation with H_2O_2 was further investigated by using a common hydroxylamine derivative of hydroxylamine chloride instead of free hydroxylamine that is commercially unavailable and not easy for safe handling. Hydroxylamine hardly decomposed over Ti-MOR while in the absence of H_2O_2 (Fig. 5a). For comparison, ca. 30% decomposition of H₂O₂ was found in the presence of H_2O_2 without catalyst (Fig. 5b), indicating that the decomposition took place partially by the noncatalytic route. However, the Ti-MOR/H₂O₂ system showed a much higher activity for hydroxylamine decomposition (74.4 %) than the non-catalytic reaction (Fig. 5c). We surmise that Ti-OOH species formed through interaction of H₂O₂ molecules with Ti species in the framework may account for the above result, as Ti-MOR solely is inactive in the hydroxylamine decomposition when H₂O₂ is absent. This phenomenon well explains that a lower yield of hydroxylamine is noticed than that of FO at high H₂O₂ amount in Fig. 4. Therefore a relative low H₂O₂ concentration benefits to the clean synthesis of FO in this process.

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4. Conclusions

Clean synthesis of furfural oxime can be achieved by using titanosilicate-catalyzed liquid-phase ammoximation. Ti-MOR is capable of converting furfural to corresponding oxime at a conversion and selectivity both above 97 % in aqueous solution under optimized reaction conditions, and it proves to be a stable and reusable catalyst. The hydroxylamine route and the imine route are both found in the furfural ammoximation, with the former one leading to formation of furfural oxime while the latter one resulting in formation of 2-furylamide and 2-furoic acid. The key role of Ti-MOR in this process is that it efficiently catalyse the formation of hydroxylamine, thereby greatly accelerates the hydroxylamine route. Though the decomposition pathway of hydroxylamine in H_2O_2 on Ti-MOR is inevitable, feeding H_2O_2 dropwise into the reaction system can effectively retard this undesired step.

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