Electronic Supplementary Information

Lewis acidic strength controlled highly selective synthesis of oxime via liquid-phase ammoximation over titanosilicates

Zuoxi Zhuo, Lizhi Wu, Lei Wang, Yichun Ding, Xiaoqian Zhang, Yueming Liu*, and Mingyuan He

Experimental section

1. The preparation of titanosilicate catalysts

1.1.1 Synthesis of Ti-MWW and F-Ti-MWW

Ti-MWW lamellar was synthesized in a boric acid system with piperidine (PI) as structuredirecting (SDA), following previously reported methods (P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, *J. Physic. Chem. B.* 105 (2001) 2897.). The starting gels with the molar compositions of 1.0 SiO₂:(0.0067-0.05) TiO₂:1.4 PI:0.67 B₂O₃:19 H₂O were crystallized in a 100-mL Teflon-lined autoclave under rotation (100 rmp) at 443 K for 7 days. The precursor was acid treated with 2 M HNO₃ at a solid-to-liquid weight ratio of 1:(30 or 50) to remove the extraframework Ti species and a part of framework Boron under the refluxed conditions. F-Ti-MWW was prepared from Ti-MWW precursor (Si/Ti = 25) according to the procedure reported recently (X. Fang, Q, Wang, A. Zheng, Y. Liu, L. Lin, H. Wu, F. Deng, M. He, and P. Wu, *Phys. Chem. Chem. Phys.*15 (2013) 4930.). All acid treatment samples were further calcined in air at 823 K for 8 h to obtain Ti-MWW with different Si/Ti molar ratios and F-Ti-MMW catalysts (Si/Ti = 29).

1.1.2 Synthesis of conventional TS-1, hollow TS-1 and lamellar TS-1

TS-1 was hydrothermally synthesized following the procedure reported in patent literature developed by ENI (M. Taramasso, G. Perego, B. Notari, *US Patent* 4410501. 1983.). By using tetraethyl orthosilicate (TEOS) and tetrabutyl orthotitanate (TBOT) as silicon and titanium source respectively, and tetrapropylammonium hydroxide (25 wt.%) was employed as SDA. The synthetic gel contains a molar composition of 1.0 SiO₂:(0.0067-0.033) TiO₂:0.18 TPAOH:18 H₂O, and was crystallized under 443 K for 48 h under static conditions. The product was recovered by filtration, drying, and calcinations (823 K) to gain TS-1catalyst, which has an average crystalline

size of around 300 nm, denoted as conventional TS-1 (CTS-1). Hollow TS-1 (HTS-1) (Si/Ti = 37) material was obtained by modifying the conventional TS-1 (CTS-1) with 0.06 mol/L tetrapropylammonium hydroxide under 443 K for 72 h based on the previous study (Y Zuo, W Song, C Dai, Y He, M Wang, X Wang, X Guo, *App. Catal. A: Gen.* 453 (2013) 272). Lamellar TS-1 (LTS-1) (Si/Ti = 58) was synthesized following the procedure proposed previously by Wang et al (J. Wang, L. Xu, K. Zhang, H. Peng, H. Wu. J. Jian, Y. Liu, P. Wu, *J. Catal.* 288 (2012) 16.).

2. Catalytic reactions

2.1 The ammoximation of linear ketones and aldehyde over titanosilicates

The ammoximation reaction was carried out by dispersing the catalyst in an ammonia-ketone or aldehyde aqueous-organic liquid phase and feeding the hydrogen peroxide to the well-mixed slurry. In a typical reaction, a 50-mL three-neck flask reactor equipped with a magnetic stirrer and a condenser was used as batch wise reactor, after loading 150 mg of catalyst, 10 mmol of ketone or acetaldehyde, 21 mmol of NH₃ (25 wt.%) aqueous solution, 5 g of solvent (water/*t*-BuOH cosolvent with a weight ratio of 0.15:0.85). Then the whole was vigorously stirred, and when the temperature raised to the desire value (335 K for Ti-MWW and F-Ti-MWW or 345 K for TS-1), the reaction was initiated by adding 12 mmol of H₂O₂ aqueous solution (27.5 wt.%) continuously at a constant rate with a micro pump. In order to better control the accuracy of feeding speed and avoid from inducing too much water into the reaction system if using the low concentration of H₂O₂, the 10 mmol of high concentration of H₂O₂ addition within 1.5 h, the mixture was further reacted for another 0.5 h. The catalyst solid was removed by centrifuging and the product was analyzed and quantified on a gas chromatography.

2.2 The ammoximation of cyclohexanone over Ti-MWW and TS-1

It's worth noting that to factually reflect the impact of Lewis acidic strength related to Ti active sites on the NH₂OH producing, the relevant ammoximation reactions were conducted in one pot rather than being separated into catalytic oxidation and oximation. The major reason is that the decomposition of NH₂OH in two steps can be almost inhibited in an actual ammoximation process by the timely contact of NH₂OH with ketone to give oxime, so that the corresponding ammoximation reactions were conducted directly to compare the forming ability of NH₂OH between Ti-MWW and TS-1. The ammoximation of cyclohexanone over Ti-MWW or TS-1

catalyst in varied Ti contents was carried out in a 50-mL three-neck flask equipped with a magnetic stirrer and a condenser. The catalyst (50 mmg), solvent (H₂O/*t*-BuOH, 5 g); cyclohexanone (20 mmol) and NH₃.H₂O (25 wt.%, 10 mmol) were well mixed in the flask, then the reaction mixture was heated to 335 K for Ti-MWW and 345 K for TS-1. When the temperature raised to desired value, 10 mmol of aqueous H₂O₂ (27.5 wt.%) pre-diluted by solvent was begin to feed into the slurry dropwise at a constant rate with a micropump. After finishing the addition of diluted H₂O₂ solution within 1.5 h, the mixture further reacted for another 0.5 h. The catalyst solid was removed by centrifuging and the product was analyzed and quantified on a gas chromatography. From the amount of cyclohexanone converted, the amount of cyclohexanone oxime as well as producing NH₂OH was then determined.

The yield of NH₂OH was calculated by the following equation:

Yield % (Hydro	oxylamine)		
_	n Hydroxylamine	_ n Cyclohexanone oxime	_ Conv. %(cyclohex
*	n Hydrogen peroxide 100%	n Hydrogen peroxide	10 m

2.3 The ammoxiamtion of linear ketones overTS-1/Ti-MWW mixing catalysts

The ammoximation of ketones (DMK and MEK) over TS-1/Ti-MWW mixing catalyst was performed in a similar way. In a typical run, 450 mmg of mixing catalysts, 30 mmol of ketone, 10 g of solvent (H₂O/*t*-BuOH), and 62 mmol of NH₃ added as a 25 wt.% aqueous solution were charged into the flask, and the mixture was heated to 341 K. The reaction was then initiated by adding 36 mmol of pre-diluted aqueous H₂O₂ continuously at a constant rate with a micropump for 1.5 h. After the reaction was performed for a desired certain time (120 min), the catalyst was removed and the analysis was performed on a gas chromatograph. The resident amount of H₂O₂ in the mixture was determined by iodometry titration with 0.1 M Na₂S₂O₃ solution.

2.4 The deep oxidation of acetaldehyde or acetaldehyde oxime with free H₂O₂

The oxidation reaction of acetaldehyde or acetaldehyde oxime with free H_2O_2 was carried out in 50-mL flask equipped with a magnetic stirrer and a condenser. In a typical reaction, 10 mmol of aldehyde or oxime, 10 g of solvent (H_2O /t-BuOH) and 20 mmol NH₃.H₂O aqueous solution (25 wt.%) were charged into the reactor. At once, 10 mmol of free H_2O_2 (27.5 wt.%) aqueous solution was added into the reaction mixture. After the oxidation at 335 K for a certain time (10-120 min), the mixture was cooled to room temperature and product was detected on a gas chromatograph.

2.5 The decomposition of free H₂O₂ over titanosilicates

The decomposition reaction of free H₂O₂ over TS-1, Ti-MWW and F-Ti-MWW was performed in a 250-mL three-neck flask reactor equipped with a magnetic stirrer and a reflux condenser. In a typical decomposition process, 5 g of catalyst and 40 mL solvent (CH₃OH) were well mixed in the reactor. When the temperature of slurry reached the desired value (318 K, 328 K and 333 K for TS-1; 333 K, 338 K and 343 K for Ti-MWW and F-Ti-MWW), the reaction was initiated by introducing 10 mmol H₂O₂ (27.5 wt.%). Then the reaction proceeded for another 5 min, and the residual free H₂O₂ concentration was determined by titration with 0.05 M Ce(SO₄)₂ solution. The relevant activation energy was calculation using Arrhenius equation ($k = \text{Aexp}(-\text{E}_a/\text{RT})$).

2.5 Characterization methods

The X-ray powder diffraction (XRD) patterns were measured on a Rigaku Ultima IV X-ray diffractometer using Cu-Karadiation (l = 1.5405 Å). The UV-visible diffuse reflectance spectra were recorded on a PerkinElmer UV/VIS Lambda 35 spectrophotometer using BaSO₄ as a reference. The amount of Si, Ti and B were quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The TEM images were taken on a JEOLJEM-2100 microscope. The IR spectra were collected on Nicolet Nexus 670 FT-IR spectrometer at a spectral resolution of 2 cm⁻¹. For pyridine spectra measurement (1000-4000 cm⁻¹ ¹), it was recorded as follows: a self-supported wafer (9.6 mg/cm⁻¹ thickness and 2 cm in diameter) was set in a quartz IR cell sealed with CaF₂ windows connected with a vacuum system. After the sample was evacuated at 723 K for 1 h, the pyridine adsorption was carried out by exposing the wafer to pyridine vapor (1.3 kPa) at 298 K for 20 min. The physisorbed and chemisorbed pyridine was then removed by evacuation at different temperatures (323 K-523 K) for 0.5 h. All the spectra were collected at room temperature. The product of reaction was analyzed on an Agilent GC-7890A gas chromatograph equipped with a DB-WAX capillary column (30 m \times 320 μ m \times 0.25 µm) and an FID detector. The side products formed during the ketones ammoximation were determined by using authentic chemicals on a GC-MS (Agilent 6890 series GC system, 5937 network mass selective detector).

Supplementary information caption

S1. Characterizations of titanosilicate catalysts

S2. NH₂OH reaction route in the ammoximation of ketones over titanosilicates

S3. Possible reaction pathway of forming hydroxylamine.

S4. Characterization of Lewis acidity and comparison of Lewis acidic strength among TS-1, Ti-MWW and F-Ti-MWW

S5. Effect of diffusion constrains on the product selectivity in the linear ketones ammoximation

S6. A comparison of oxime selectivity in the ammoximation of linear ketones with different carbon chains between Ti-MWW and TS-1

S7. Deep oxidation of acetaldehyde or acetaldehyde oxime with free H_2O_2

S8. Apparent activation energy (E_a) of formed active intermediates of Ti-OOH species over TS-1, Ti-MWW and F-Ti-MWW

S1. Characterizations of titanosilicate catalysts



Fig. S1. Representative XRD patterns (A) and IR, UV-visible spectra (B) of Ti-MWW (Si/Ti = 42) (a), TS-1 (Si/Ti = 38) (b), lamellar TS-1 (Si/Ti = 58) (c).

S2. NH₂OH reaction route in the ammoximation of ketones over titanosilicates



Scheme S1 The reaction route of NH₂OH in the ammoximation over titanosilicates

S3. The possible reaction pathway of forming hydroxylamine.



Lewis acidic Ti sites

Scheme 2 Possible reaction pathway of forming hydroxylamine.

S4. Characterization of Lewis acidity and comparison of Lewis acidic strength among TS-1, Ti-MWW and F-Ti-MWW

The FTIR spectra of pyridine after adsorption and desorption at different temperatures on Ti-MWW and TS-1 were collected. Fig. S2 confirmed that both Ti-MWW and TS-1 possessed 1446 cm⁻¹ and 1580 cm⁻¹ bands which are attributed to pyridine species interacting with Lewis acidic sites, while the Brønsted acidity is negligible as the 1540 cm⁻¹ which assigned to the pyridine ions was extremely weak in contrast to the others¹. Then a semiquantitative study of the strength of Lewis acidic sites was carried out following the procedure suggested by T Barzetti et al². The quantity calculating for Lewis (1446 cm⁻¹) sites absorption bands has been plotted as a function of evacuation temperature in Fig. 1a. Evidently, based on the tendency of reduction with increasing evacuation temperature, Ti-MWW shows stronger Lewis acidity than that of TS-1.

With respect to the relative Lewis acidic strength between Ti-MWW and F-Ti-MWW, it has been proved that F-Ti-MWW displays a higher of Lewis acidic strength due to the strong electronwithdrawing effect of the incorporated fluorine species³ (Fig. S3).

Therefore, the Lewis acidic strength of TS-1, Ti-MWW and F-Ti-MWW in present study follows the order: F-Ti-MWW > Ti-MWW > TS-1.



Fig. S2. FTIR spectra in the pyridine regions of Ti-MWW (Si/Ti = 42) (A), TS-1 (Si/Ti = 38) (B)



Fig. S3 ¹⁹F MAS NMR spectra of F-Ti-MWW (Si/Ti = 29).

References

1 G.A.H. Mekhemer, A.K.H. Nohman, N.E. Fouad and H.A. Khalaf, *Colloids. Surf. A.*, 2000, **161**, 439

2 T. Barzetti, E. Selli, D. Moscitti and L. Forni, J. Chem, Soc. Faraday. Trans., 1996, 92, 1401.

3 (a) X. Fang, Q, Wang, A. Zheng, Y. Liu, Y. Wang, X. Deng, H. Wu, F. Deng, M. He, and P. Wu,

Catal. Sci. Techonol., 2012, 2, 2433; (b) X. Fang, Q. Wang, A. Zheng, Y. Liu, L. Lin, H. Wu, F.

Deng, M. He, and P. Wu, Phys. Chem. Chem. Phys., 2013, 15, 4930.

S5. Effect of diffusion constrains on the product selectivity in the linear ketones ammoximation

In order to make clear the effect of diffusion constrains on the deep oxidation of oxime in the ammoximation of linear ketones, titanosilicates (MFI-type) with remarkably different abilities of diffusion have been designed carefully for exploring the effect of diffusion constrains on the oxime selectivity. The TEM images fully show the corresponding structural characters of varied titanosilicate catalysts with MFI-type (Fig. S4). As shown in Table S1, in spite of significant improvement of diffusion constrains¹, hollow TS-1 (HTS-1) with large intra-crystalline voids exhibited slightly higher linear oxime selectivity than the conventional TS-1 (CTS-1). Then the oxime selectivity was further enhanced when choosing lamellar TS-1 (LTS-1) as catalyst which featured as large intersheet mesopores and 2-nm nanosheets². These consequences indicated that the diffusion constrains can intensify the deep oxidation of oxime. Although the linear ketones ammoximation were catalyzed by LTS-1which is considered to be free of diffusion constrains for linear molecules, the oxime selectivity was still hard to reach that achieved by Ti-MWW (>99.7%). Thus, the diffusion constrains caused by catalyst is not crucial to selectivity differences in ammoximation.



Fig. S4. TEM images of CTS-1 (a), HTS-1 (b-1, b-2) and LTS-1 (c).

Table S1

A comparison of ammoximation of linear ketones over conventional TS-1, hollow TS-1 and lamellar TS-1, respectively.^a

No.	Catalyst ^c	Ketone	conv. (mol%)	Produc	t sel. (mol%)
				Oxime	Nitro-alkane
1	CTS-1(38)	Acetone	99.3	94.9	5.1
2	HTS-1(37)	Acetone	99.4	95.8	4.2
3 ^b	LTS-1(58)	Acetone	99.4	98.6	1.4
4	CTS-1(38)	MEK	99.8	95.9	4.1
5	HTS-1(37)	MEK	99.9	96.6	3.4
6 ^b	LTS-1(58)	MEK	99.8	98.8	1.2

^a Reaction conditions: the same as Table 1.

^b Reaction conditions: catalyst 0.25 g; ketone 3 mmol; NH₃ (25 wt.%) 6.2 mmol; H₂O₂ (27.5 wt.%)

3.6 mmol; others were the same as CTS-1 reaction conditions.

^c The value in the parentheses corresponds to the Si/Ti molar ratio.

References

- 1 (a) Y Zuo, W Song, C Dai, Y He, M Wang, X Wang, X Guo, App. Catal. A: Gen. 2013, 453,
- 272; (b) Y. Wang, M. Lin, A. Tuel. Micro. Meso. Mater., 2007, 102, 80.
- 2 (a) J. Wang, L. Xu, K. Zhang, H. Peng, H. Wu. J. Jian, Y. Liu, P. Wu, J. Catal., 2012, 288, 16;
- (b) K. Na, C. Jo, J. Kim, W-S. Ahn, R. Ryoo, ACS. Catal., 2011, 1, 901.

S6. A comparison of oxime selectivity in the ammoximation of linear ketones with different carbon chains between Ti-MWW and TS-1



Fig. S5 The linear oximes selectivity difference between Ti-MWW and TS-1. Reaction conditions: the same as Table 1.

S7. Deep oxidation of acetaldehyde or acetaldehyde oxime with free H_2O_2



Fig. S6 Deep oxidation of acetaldehyde (left) and acetaldehyde oxime (right) with free H_2O_2 . Reaction conditions: acetaldehyde or oxime 10 mmol; H_2O_2 (27.5 wt.%) 10 mmol; NH_3 (25 wt.%) 20 mmol; solvent, 10 g; temp. 335 K; time 10-120 min. H_2O_2 aqueous solution was added at once.

S8. Apparent activation energy (E_a) of formed active intermediates of Ti-OOH species over TS-1, Ti-MWW and F-Ti-MWW



Fig. S7 The apparent activation energy of formed Ti-OOH active species over TS-1 (a), Ti-MWW (b) and F-Ti-MWW (c); as well as a comparison of the calculation results of apparent activation energy among TS-1, Ti-MWW and F-Ti-MWW. Reaction conditions: the E_a was determined using the slurry reactor. Cat. 5g; CH₃OH 40 mL; H₂O₂ (27.5 wt.%) 10 mmol; time 5 min.

Table S2

A comparasion of apparent activation energy (E_a) among TS-1, Ti-MWW and F-Ti-MWW

No.	Catalyst	E _a (kJ/mol)
1	TS-1	35.29
2	Ti-MWW	24.72
3	F-Ti-MWW	10.02