RSC Advances

Journal Name

ARTICLE TYPE

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

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The Lewis acidity of titanosilicates decides the selectivity of oxime in ammoximation. Higher Lewis acidic strength of Ti active sites could promote free H_2O_2 to participate into the high-efficient formation of NH_2OH via lowering the reaction
10 activation energy of forming Ti-OOH species and thus fundamentally suppress the side reactions of deep oxidation.

Finding a selective catalyst to desired product is very often at the beginning of catalysis in industry.[1] The successful manufacture of cyclohexanone oxime via liquid-phase ammoximation over TS-
15 1(MFI) is considered as a new milestone in the field of zeolite catalysis.[2] However, applying this green chemical process to high-value fine oximes producing (*e.g.* methyl ethyl ketone oxime, acetone oxime and acetaldehyde oxime) is hampered due to the relative lower selectivity to target product.[3] The typical side
20 reaction in ammoximation can be concluded as the deep oxidation of reactant or oxime, which depends greatly on the free H_2O_2 oxidation behaviors.[3,4] It is well accepted that ammoximation reaction proceeds via NH_2OH intermediates (S2 ESI†),[5] and it was proved that a higher concentration of NH_3
25 favors NH_2OH formation so that can inhibit side reaction of oxidation.[4] Hence, promoting the high-efficient formation of NH_2OH and thus suppress free H_2O_2-induced oxidation reactions would contribute to the high selectivity of oxime.

It is confirmed that the active site of titanosilicates is
30 tetracoordinated framework Ti^{IV},[6] and many publications have supported that the catalytic nature of titanosilicates is attributed to Lewis acidic sites related to these framework Ti species.[7] So it is reasonable to employ Lewis acidity of Ti active sites to represent catalytic activity of titanosilicates. In ammoximation, the
35 ammonia oxidation by free H_2O_2 over titanosilicates can be divided into two parts:[8] firstly, the activation of H_2O_2 on framework tetrahedral Ti^{4+} to form the oxygen donating-intermediates of Ti-OOH species, which depends on catalytic activity of titanosilicates, has been proven to be the most crucial
40 step in titanosilicate-catalyzed oxidation reactions;[6b,9] then the surrounding NH_3 would capture the active oxygen in Ti-OOH

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† Electronic Supplementary Information (ESI) available: synthesis, characterization methods and Figure S.DOI: 10.1039/b000000x/ 2.

Table 1 A comparison of product selectivity in different ammoximation
50 processes.[a]

No.	Catalyst	DMK(mol%)[b]			MEK(mol%)[c]		
		Conv.	Sel.	Sel.[d]	Conv.	Sel.	Sel.[e]
1	Ti-MWW	99.6	99.8	0.2	99.7	99.7	0.3
2	TS-1	99.3	94.9	5.1	99.7	95.9	4.1

[a]Reaction conditions: catalyst 0.15 g; ketone 10 mmol, H_2O_2 12 mmol; NH_3, 21 mmol; temp. 335 K for Ti-MWW (Si/Ti = 42) and 345 K for TS-1 (Si/Ti = 38); time 2h. [b]DMK for Dimethyl ketone or Acetone. [c]MEK for Methyl Ethyl ketone. [d]The selectivity of 2-nitropropane. [d]The selectivity of 2-nitrobutane.

species to give NH_2OH intermediates (S3 ESI†). Thus, in order to fundamentally promote the highly efficient formation of NH_2OH, it is important to accelerate the activation of free H_2O_2 via
55 lowering reaction energy barrier of Ti-OOH species. Furthermore, it also well-known that reaction activation energy would be strongly reduced with the increase of acid strength in hydrocarbon conversion over zeolites.[10] Reasonably, titanosilicate catalyst equipped with stronger Lewis acidity of Ti active sites is
60 inclined to remarkably reduce the reaction activation energy of Ti-OOH species, thereby activating free H_2O_2 to produce NH_2OH more efficiently and further cutting off the side reaction of oxidation. Therefore, we infer that the Lewis acidity of titanosilicates would decide oxime selectivity in ammoximation
65 by controlling reaction path of free H_2O_2 to NH_2OH intermediates.

In this communication, to demonstrate that the Lewis acidic strength of Ti active sites is the decisive factor on the highly selective synthesis of oxime, a series of ammoximation reactions
70 of linear ketones and acetaldehyde over representative titanosilicates with varied strength of Lewis acidity (TS-1 < Ti-MWW < F-Ti-MWW) (S4 ESI†) have been carried out. As anticipated, a titanosilicate catalyst with stronger Lewis acidity means a better selectivity to oxime.

75 Table 1 shows the results of ammoximation of linear ketones (acetone and MEK) over Ti-MWW and TS-1, respectively. For focusing on the issue of product selectivity, the ketone conversion was maintained over 99% by optimizing the reaction conditions, such as supplying sufficient catalyst concentration (15g/mol) and
80 loading the free H_2O_2 dropwise in case of further oxidation decomposition of NH_2OH intermediates (S2 ESI†).[5a,11] Ti-MWW was proved as a selective catalyst for linear ketones ammoximation, the selectivity of DMKO and MEKO both were
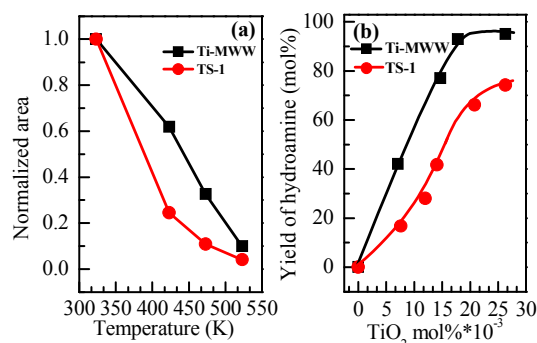
Fig. 1 Correlation between the formation of NH_2OH (b) and the Lewis acidic strength of titanosilicates (a). Reaction conditions: catalyst 0.05 g; cyclohexanone 20mmol; H_2O_2 10 mmol; NH_3 10 mmol, others see Table 1.

higher than 99.5% (Table 1, no 1). When it comes to TS-1, the oximes selectivity were reduced in certain extent because of the existence of 2-nitropropane and 2-nitrobutane that originated from the consecutive oxidation of oxime (Table 1, no 2).[3a] Although Song et al attributed the decline in linear oxime selectivity to diffusion constrains induced by TS-1 catalyst,[3a] our further study demonstrates that the diffusion constrains of catalyst merely intensify the side reaction of deep oxidation instead of deciding the oxime selectivity (S5 ESI†). Thus, combined with the ammoximation of linear ketones of different carbon chains (S6 ESI†), the oxime selectivity differences existed between Ti-MWW and TS-1 quite conform to our assumption, namely, Ti-MWW possessing higher Lewis acidic strength displays superior oxime selectivity than that of TS-1 with relatively weaker Lewis acidity.

In order to further clarify that the effect of Lewis acidity of titanosilicates on the improvement of oxime selectivity derives from promoting the formation of NH_2OH intermediates, we have correlated the Lewis acidic strength of Ti-MWW and TS-1 with their corresponding abilities of producing NH_2OH. Fig. 1b compares the yield of NH_2OH obtained by Ti-MWW and TS-1 in different Ti contents according to the relevant results of cyclohexanone ammoximation. Ti-MWW kept a much better yield of NH_2OH than TS-1 under the same Ti content, and the maximum yield gained by Ti-MWW was close to 95% which is nearly 25% higher than that of TS-1. Thus, the catalytic ability of forming NH_2OH between Ti-MWW and TS-1 are consistent with their order of Lewis acidic strength (Fig. 1a), and also agreeable to the change of oxime selectivity (Table 1). These positive correlations fully verify our inference that titanosilicates with higher Lewis acidic strength are beneficial to accelerate the reaction path of NH_2OH. Therefore, the above results well support our opinion that the Lewis acidity of titanosilicates decides the highly selective synthesis of oxime via affecting the high-efficient formation of NH_2OH intermediates.

In order to better demonstrate the decisive relations between the Lewis acidity and oxime selectivity, a series of linear ketones ammoximation reactions over mixing catalysts of TS-1/Ti-MWW have been further conducted. It has showed that TS-1 possesses weaker Lewis acidity than that of Ti-MWW (Fig 1a), so it is feasible to prepare a catalyst sample with adjustable Lewis acidic strength by mixing these two types of titanosilicates in different proportions. Reasonably, with increasing the weight

proportion of Ti-MWW, the Lewis acidic strength of mixing catalysts is enhanced simultaneously. If oxime selectivity is decided by Lewis acidity of titanosilicates, then the selectivity would be changed along with acid strength. Fig. 2 reports the results of DMK and MEK ammoximation over the TS-1/Ti-MWW mixing catalysts. As expected, the oxime selectivity was improved gradually with the increase of Ti-MWW proportion. This gradual change in selectivity also excludes that the positive effect on oxime selectivity enhancement merely caused by the introduced Ti-MWW. No further variation of oxime selectivity was noted when the Ti-MWW proportion is higher than 30%, which means this specific composition of mixing catalysts have enough Lewis acidic strength to prepare oxime in high selectivity. These findings show that the Lewis acidic strength of titanosilicate catalyst is able to regulate the oxime selectivity in ammoximation. Correspondingly, 2-nitroalkane selectivity also decreased with increasing the proportion of Ti-MWW, and the by-product was nearly eliminated when adopting the mixing sample consisting of 30% Ti-MWW and 70% TS-1 as catalyst. It implies that the deep oxidation of oxime, even in the presence of diffusion constrains caused by TS-1, can be mostly suppressed by strengthening the Lewis acidity of catalyst. Furthermore, the variation of residual free H_2O_2 also supports that titanosilicates with stronger Lewis acidity prefer to activate more free H_2O_2 molecules to form NH_2OH. Thus, it is well confirmed that the Lewis acidity of titanosilicates is the decisive factor on the synthesis of oxime in high selectivity.

In comparison to linear ketones, acetaldehyde (AA) is chemically more active, so that selectivity issue in the AA ammoximation becomes more complicated.[3b,12] On one hand, it was shown that AA would be further oxidized to acetic acid by Ti-OOH species,[3a] while it may be hard to happen in an actual ammoximation due to the existence of excess NH_3. On the other hand, it has been proved that lots of acetic acid and acetamide can be generated from homogenous deep oxidation of AA or oxime with free H_2O_2 under alkaline condition (S7 ESI†), which also closely rely on the free H_2O_2 oxidation actions. Consequently, in order to achieve an excellent selectivity of acetaldehyde oxime (AAO), a selective titanosilicates with much stronger Lewis acidity is required based on our present opinion. Table 2 compares the results of linear ketones and AA ammoximation over titanosilicates with different Lewis acidic strength. TS-1 exhibited much poorer selectivity to AAO than linear oximes
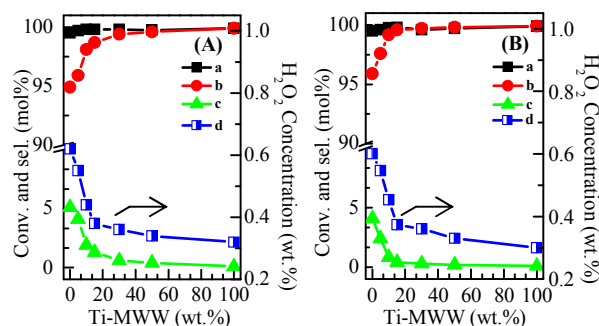

Fig.2 The ammoximation of DMK (A) and MEK (B) over the TS-1/Ti-MWW mixing catalysts. (a) Ketone Conv., (b) Oxime sel., (c) 2-nitroalkane sel., (d) H_2O_2 residual concentration. Reaction conditions: catalyst 0.45 g; ketone 30 mmol; H_2O_2 36 mmol; NH_3 63 mmol; sol. 10 g, temp. 341 K; time 2 h.

Table 2 A comparison of acetaldehyde and ketone ammoximation over titanosilicates with different Lewis acidic strength.[a]

No.	Reactant	Catalyst	Conv. (mol%)	Sel.(mol%)		
				Oxime	By-product	
					I[c]	II[d]
1[b]	MEK	TS-1(38)	99.7	95.9	4.1	
2[b]	DMK	TS-1(38)	99.3	94.9	5.1	
3	AA	TS-1(38)	99.1	86.6	5.0	8.4
4	AA	Ti-MWW(42)	99.3	98.5	0.5	1.0
5	AA	F-Ti-MWW(29)	99.3	99.6	0	0.4

[a]Reaction conditions: see Table 1. [b]The main by-product was 2-nitroalkane. [c]By-product I was acetic acid. [d]By-product II was acetamide.

(Table 2, nos.1~3), which means a higher chemical activity of AA. Then AAO selectivity was significantly increased to 98.6% when adopting Ti-MWW as catalyst because of the notable enhancement of Lewis acidity. Nevertheless, the AAO selectivity still fails to reach the parallel level of linear oximes obtained under the same reaction conditions (Table, no.1). These consequences fully sustain our speculation that with regard to the chemically more active AA, achieving high oxime selectivity becomes much harder than linear ketones by choosing titanosilicates with considerable strength of Lewis acidity. Hence, a titanosilicate catalyst with more superior Lewis acidity than Ti-MWW is needed in the AA ammoximation.

Recently, the Lewis acidic strength of Ti active site in F-Ti-MWW has been proved to be further enhanced than Ti-MWW due to the strong electron-withdrawing effect of incorporated fluorine species.[13] So F-Ti-MWW was applied to the AA ammoximation to further verify our inference about Lewis acidity controlling the oxime selectivity. Expectantly, Table 2 (no. 5) shows that the AAO selectivity was further increased up to 99.6% and it equals to the linear oximes selectivity gained by Ti-MWW (Table 1, no. 1). Hence, the titanosilicates investigated for AA ammoximation displayed the following order of oxime selectivity, F-Ti-MWW > 99.5% > Ti-MWW > 90% > TS-1, which also entirely conforms to their relevant Lewis acidic strength. It indicates that to highly selective obtain chemically more active oxime needs stronger Lewis acidity of titanosilicates. Moreover, by comparing the by-products selectivity between acetic acid and acetamide, we find that acetic acid selectivity is lower than that of acetamide. It proofs that Ti-OOH species would not promote the deep oxidation of AA in the presence of excess NH_3, and the side reactions are still mainly ascribed to those deep oxidations induced by free H_2O_2. These phenomena further indicate that the fundamental role of Lewis acidity in oxime selectivity is controlling the oxidation behaviors of free H_2O_2. This role was also supported by the apparent activation energy of Ti-OOH active species formed among TS-1 (32.29 kJ/mol), Ti-MWW (24.72 kJ/mol) and F-Ti-MWW (10.02 kJ/mol) (S8 ESI†), which demonstrates that the increase of Lewis acidic strength can remarkably lower the activation barrier of free H_2O_2 and thus promote free H_2O_2 molecules to participate into forming NH_2OH intermediates.

In summary, the Lewis acidic strength of Ti active sites is well confirmed as responsible for the high selectivity of oxime based on catalytic nature of titanosilicates and ammoximation mechanism. The stronger Lewis acid promotes the formation of NH_2OH, while the weaker acid strength is hard to suppress the free H_2O_2-induced side reactions. Therefore, regulating the Lewis acidity of titanosilicates could become a crucial guideline for designing or modifying catalysts for highly selective synthesis of oxime or even other oxygenated fine chemicals.

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