Selective oxidations with hydrogen peroxide and titanium silicalite catalyst

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Abstract

Titanium silicalite (TS-1) samples with increasing amount of titanium incorporated into the silicalite framework (from 1 to 3.45 wt.% TiO_2) have been synthesized and characterized by UV-DRS spectroscopy. The samples have been tested on propylene epoxidation, cyclohexanone ammoximation and ammonia oxidation reactions. It has been found that the yield obtained with TS-1, expressed as turnover number, increases with the Ti content. The trend is common for all the reactions investigated. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Titanium silicalite (TS-1), a zeolitic material discovered by ENI researchers [1], is one of the first examples of a MFI structure in which the framework heteroatom is different from Al.

TS-1 catalyzes a variety of useful oxidation reactions. Such reactions include phenol hydroxylation [2], olefin epoxidation [3], cyclohexanone ammoximation [4], alkane oxidation [5], oxidation of ammonia to hydroxylamine [6], secondary alcohols to ketones [2], secondary amines to dialkylhydroxylamines [7].

TS-1 catalyzed processes are advantageous from the environmental point of view as the oxidant is aqueous hydrogen peroxide, which turns into water, and the reactions, operated in liquid phase under mild conditions, show very high selectivities and yields reducing problems and costs of by-product treatment.

The confinement of the metal species in the well defined silicalite pore system endows TS-1 with shape selectivity properties analogous to enzymes. For these features the application of the terms 'mineral enzyme' or 'zeozyme' to TS-1 is appropriate [8].

The outstanding catalytic activity and selectivity of TS-1 have made it a commercial catalyst for the manufacture of catechol and hydroquinone from phenol. Enichem is now developing the propylene epoxidation and the ammoximation of cyclohexanone as low-salt by-production alternatives to the conventional processes for propylene oxide (PO) and cyclohexanone oxime.

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The ammoximation reaction proceeds according to a mechanism involving two steps [9].

1. In the first step, ammonia is catalytically oxidized by hydrogen peroxide to hydroxylamine, the reaction intermediate:

$$NH_3 + H_2O_2 \overset{TS-1}{\rightarrow} NH_2OH + H_2O$$
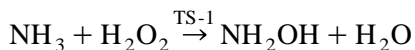
2. In the second step, hydroxylamine reacts with cyclohexanone to give cyclohexanone oxime:

$$C_6H_{10}O + NH_2OH \overset{TS-1}{\rightarrow} C_6H_{10}NOH + H_2O$$
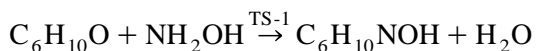
Cyclohexanone and other ketones small enough to diffuse into the zeolite channels can immediately react with hydroxylamine inside the TS-1 pores. Bulky ketones, which are not able to penetrate the zeolite channels, can react only with the hydroxylamine migrated to the external surface [9].

For epoxidation reaction a mechanism involving a solvent assisted transition state is proposed and detailed in Ref. [10]. A protic solvent, actually methanol, stabilizes hydroperoxo Ti species with a five member cyclic configuration suitable for the approach of the olefin to the oxygen farther from Ti atom.

The unique activity and selectivity of TS-1 is believed to be due to isolated sites of tetrahedral titanium atoms inserted in vicariant position of silicon in the silicalite framework. The isolated and tetracoordinated Ti centres are able to expand their coordination sphere up to six by interaction with extra ligands (i.e., water, ammonia). It has also been demonstrated that Ti centres interact with hydrogen peroxide to form hydroperoxo species [9].

The framework composition of TS-1 can be defined as: $xTiO_2 \cdot (1-x)SiO_2$, and the upper limit for x (the Ti mole fraction) is around 0.025 [12]. Attempts to produce TS-1 with significantly higher Ti content fail, as the excess titanium segregates as TiO_2. The catalytic activity of TS-1 is affected by the presence of extra framework Ti, which can promote extensive side reactions including decomposition of hydrogen peroxide.

In order to elucidate the structure of the Ti centre in vacuum and in the reaction conditions several techniques have been used, such as UV–Vis, EPR, IR and Raman spectroscopies, as well as XRD, XANES and EXAFS [9,12–15].

Tetrahedral titanium atoms located in the framework sites are characterized by the 960 cm^{-1} band in the IR spectra and the 48 000 cm^{-1} band in the UV–Vis spectra [9–15].

The unit cell parameters of TS-1 were found to increase linearly as a function of Ti content (XRD) [1,12].

Recently it has been found that the coordination number of Ti, in a dehydrated TS-1 sample, is larger than 4. EXAFS data analysis gives a value of 4.44 ± 0.25 [15]. This result indicates the presence of Ti species different from the perfect 'closed', four-fold coordinated $Ti(OSi)_4$ species. In full agreement with the EXAFS results, from photoluminescence spectroscopy two bands have been observed in both emission and excitation scans, so indicating the presence of two slightly different families of framework Ti species which differ for their local environment [15].

In this paper we present and discuss new results on TS-1 reactivity as a function of the Ti content. TS-1 samples with increasing amount of titanium incorporated into the silicate framework have been synthesized and characterized.

The samples have been tested in ammonia oxidation, cyclohexanone ammoximation, and propylene epoxidation.

The aim of this work is to provide new information on the catalytic behaviour of the active sites. In particular, very useful information have been obtained from the comparison of the behaviour of the catalyst used in the different investigated reactions.

2. Experimental

TS-1 samples were synthesized and characterized according to Ref. [1].

Ammoximation runs were performed in a semibatch apparatus. Details of the method of operation and analytical procedures have been provided previously [4].

Different amounts of catalyst were used in order to have the same amount of Ti [0.228 g (TiO_2)/l] in each experiment. Hydrogen peroxide (30 wt.%) was fed over 1 h to the reaction suspension [cyclohexanone 9.8 g: *t*-butanol (25 ml): H_2O (12 ml):NH_3 (30 wt.%, 13 ml)] at 78°C.

On completion of the H_2O_2 addition the suspension was cooled, filtered and analyzed.

Ammonia oxidation experiments were carried out as described in detail in Ref. [6]. Hydrogen peroxide was added over 20 min, at 70°C, to the reaction suspension [*t*-butanol (25 ml): H_2O (12 ml): NH_3 (30 wt.%, 13 ml)].

The NH_3/H_2O_2 mole ratio was 20, the Ti concentration was 0.335 g(TiO_2)/l.

Propylene epoxidation was performed in a Mettler RC1 calorimeter (1 l CSTR reactor). The procedure is described in Ref. [3].

The reaction conditions were: $T = 40$°C, P 4 atm. The reaction solvent was MeOH:H_2O (92:8 wt.%), the H_2O_2 concentration in the reaction mixture was 1 M/Kg, the Ti concentration was 0.135 g (TiO_2)/Kg.

3. Results and discussion

3.1. TS-1 synthesis and characterization

The composition of the catalysts used, in terms of Ti content are reported in Table 1.

The Ti mole fraction range from 0.0073 (sample A) to 0.0262 (sample H).

In Fig. 1 the DRS UV–Vis spectra of samples A ($x = 0.0073$), C ($x = 0.0152$) and H ($x = 0.0262$) are reported. They exhibit only the characteristic 48 000 cm^{-1} band of tetracoordinated Ti species, which confirms that no extra framework Ti is present in the TS-1 samples.

Anyway it is possible to see that the band shape changes: the band becomes more struc-

Table 1
List and composition of TS-1 samples

TS-1 sample	Crystalline product	
	x (Ti mole fraction)[a]	TiO$_2$ (wt.%)[a]
A	0.0073	0.97
B	0.0105	1.39
C	0.0152	2.01
D	0.0192	2.54
E	0.0220	2.90
F	0.0226	2.99
G	0.0229	3.02
H	0.0262	3.45

[a]Determined by chemical analysis (XRF).

tured and broader towards lower wavenumbers upon increasing the Ti content.

This suggests the presence of slightly different framework Ti species, in agreement with what found with photoluminescence spectroscopy [15].

3.2. Activity test

The TS-1 samples were tested in ammonia oxidation, cyclohexanone ammoximation and propylene epoxidation reactions.

As the Ti content of the samples was not constant, different amounts of catalyst were used in order to have the same amount of Ti in each series of experiments.

The yield is expressed as turnover number (TON), given as moles of product (oxime, hydroxylamine or propylene oxide [PO]) per Ti site per hour.

All reported data (TON, conversion and selectivity) are expressed as a percentage of the maximum value observed, i.e. for the turnover number:

$$TON\%_{\text{sample } i} = (TON_{\text{sample } i}/TON_{\text{maximum}})100$$

Lines in the plots are an aid for visualization and do not represent any mathematical interpretation.

3.2.1. Ammonia oxidation to hydroxylamine

The results are reported in Fig. 2. The TON% is plotted vs. the molar fraction of Ti in the TS-1 sample.
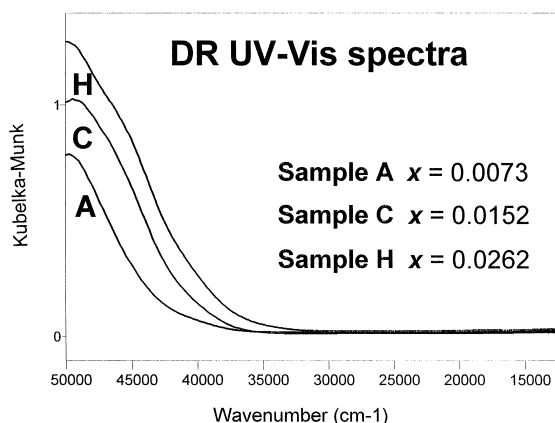
Fig. 1. DRS UV–Vis spectra of TS-1 samples A, C and H.

In the ammonia oxidation reaction almost all the TS-1 but sample A ($x = 0.0073$) show a similar yield.

The hydrogen peroxide conversion is almost complete (> 98 mol%) in all the experiments.

The lower yield of sample A is due to a lower selectivity to hydroxylamine, based on hydrogen peroxide.

3.2.2. Cyclohexanone ammoximation

In the cyclohexanone ammoximation the yield increases by increasing the Ti content up to x about 0.020 (Fig. 3a), with an almost linear relationship between the two variables. A remarkable scattering of values (larger than the experimental error) is observed in the region of high x.

The increase of the catalyst yield is due to an increase of both conversion and selectivity to
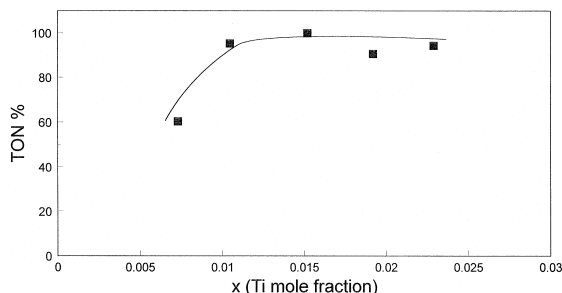

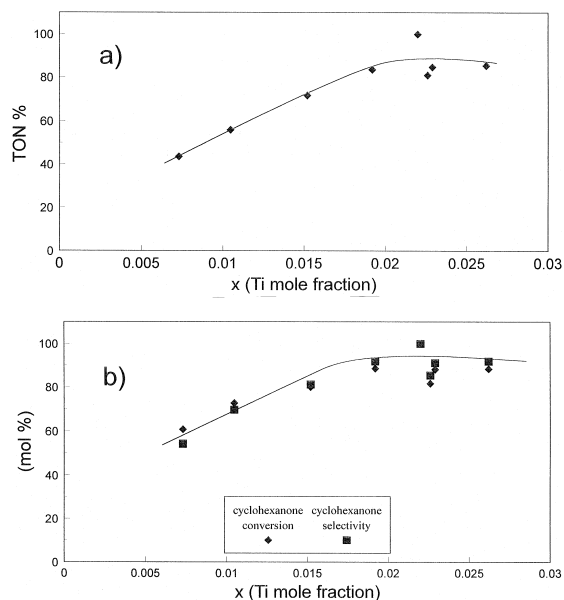Fig. 2. Ammonia oxidation. Activity data as a function of the Ti mole fraction in the TS-1 samples.

Fig. 3. Cyclohexanone ammoximation. (a) Activity data, (b) cyclohexanone conversion and selectivity to oxime as a function of the Ti mole fraction in the TS-1 samples.

oxime, based on cyclohexanone, as shown in Fig. 3b.

Therefore, in the two related reactions, ammonia oxidation and overall ammoximation reaction, an apparently different trend is observed as a function of Ti content.

3.2.3. Propylene epoxidation

As depicted in Fig. 4, the effect of Ti content in the propylene epoxidation shows a similar trend as in the ammoximation reaction.
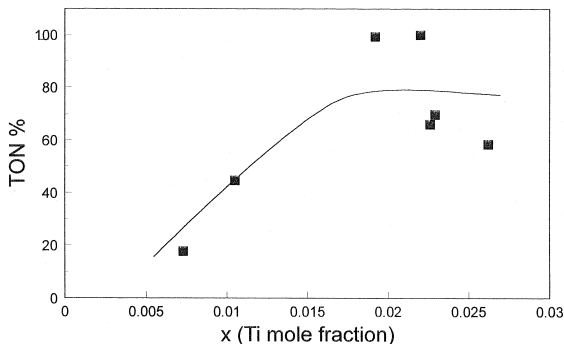

Fig. 4. Propylene epoxidation. Activity data as a function of the Ti mole fraction in the TS-1 samples.

As in ammoximation, the increase of the catalyst yield is due to an increase of both propylene conversion and selectivity to the epoxide. The scattering of values in the region of high x is here even more evident.

3.3. Discussion

Attempting to explain the different catalytic results on increasing Ti content, two evidences from characterization should be taken into account:

1. the unit cell parameters of TS-1 increase linearly with Ti content (XRD) [1,12]
2. at least two different framework Ti species can be detected in TS-1 [15], one of which seems to increase with Ti content

On the basis of the above evidences two hypotheses can be proposed.

a) Ti content affects the catalytic activity by affecting the unit cell parameters.

In fact the first evidence implies an increase in the micropore diameter, which can influence the diffusion rate of reagents inside the channels.

It was already reported that channels dimension is affected by framework Ti and that molecules with large kinetic diameter (*m*-xylene) are sensitive probe for slight changes in micropore diameter [16].

This could explain the differences found in the three test reactions. Low or no effect has been found in ammonia oxidation, the smallest reagent. The effect is well evident in propylene epoxidation and becomes remarkable in cyclohexanone ammoximation, the reagent with the largest molecular size. In fact it has been reported that cyclohexanone reacts with the hydroxylamine intermediate in the TS-1 channels [9].

b) The different framework Ti species have a different catalytic activity.

This hypothesis appears difficult to support since no correlation has been drawn out as the two species are only qualitatively recognized but not quantitatively measured. Moreover ammonia oxidation doesn't show a very evident trend by increasing Ti concentration, which makes *b)* less likely.

However it cannot be excluded that both hypotheses play a role in the overall activity of TS-1. Indeed, the observed scattering of activity data at similar (high) Ti content, cannot be explained by taking into consideration only the first hypothesis.

4. Conclusion

A dependence of the activity of Ti site upon framework Ti content in TS-1 for cyclohexanone ammoximation and propylene epoxidation has been found. In ammonia oxidation all the samples (except at very low Ti content) show a similar activity.

Two explanations for this behaviour are possible on the basis of the available characterization data. The first deals with morphological parameter, actually the pore diameter, which increases with increasing Ti content. The second, merely chemical, suggests a different activity for the slightly different Ti species observed in TS-1.

The trend found for the catalytic activity highlights the paramount importance of producing well structured TS-1 with the highest loading of framework titanium.

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