

Synthesis and characterization of TS-48, a titanium containing silica analog of ZSM-48

K. Madhusudan Reddy, S. Kaliaguine, A. Sayari¹

*Department of Chemical Engineering and CERPIC, Université Laval, Ste-Foy, Quebec,
Canada G1K7P4*

A.V. Ramaswamy

National Chemical Laboratory, Pune 411008, India

V. Saraswathi Reddy and L. Bonnevot

*Department of Chemistry and CERPIC, Université Laval, Ste-Foy, Quebec,
Canada G1K7P4*

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Crystalline titanium containing silica analog of ZSM-48 (TS-48) samples were synthesized using soluble peroxytitanate, fumed silica and diamino octane. All samples were characterized using a variety of techniques including XRD, IR, AAS, SEM, UV-Vis, XANES and catalytic testing in hydroxylation of phenol. Data suggest that titanium in these materials is linked to the framework. However, it was impossible to incorporate more than about 2 wt% Ti in the zeolite lattice. TS-48 samples prepared by this method had no activity for hydroxylation of phenol in the presence of hydrogen peroxide. The lack of activity of this material even though it showed all of the regular characteristics of other catalytically active titanium silicalites (i.e., TS-1 and TS-2) could be due either to diffusional limitations or to subtle differences in titanium environment.

Keywords: Titanium silica-ZSM-48; TS-48; diamino octane; titanium incorporation

1. Introduction

The presence of transition metals in the framework of a zeolite lattice can impart oxidation activity which can be combined with shape selective properties of the molecular sieve. Titanium silicalite molecular sieves of MEL and MFI structures,

¹ To whom correspondence should be addressed.

i.e., TS-1 and TS-2, have been studied extensively because of their remarkable performance as selective catalysts in the presence of diluted H_2O_2 [1–4]. TS-1 is used industrially in the hydroxylation of phenol. Several reports have dealt with the physico-chemical characterization of such materials. Different types of sites with different environments were put forward as active sites in the selective oxidation of organic substrates [5–12].

Based on XRD and IR data, it was first believed that in titanium silicalites, Ti occupies a tetrahedral position and was therefore isomorphously substituting Si in the zeolite lattice. Recently, Behrens et al. [9] showed from XANES and EXAFS investigations of TS-1 that a large fraction of the Ti is octahedrally coordinated and probably occupies framework positions; a local environment that provides an explanation for the extraordinary catalytic properties of this material. On the other hand, Lopez et al. [10] found from XANES and EXAFS analyses that titanium is incorporated into the framework by substitution for silicon, but a significant amount of titanium can also be present in the form of extra crystalline or intracrystalline inclusions of TiO_2 depending on the Si/Ti ratio in the synthesis mixture. According to Lopez et al. [10], in the absence of water, framework titanium is essentially tetrahedrally coordinated while in the presence of water its coordination becomes octahedral. Both investigations concluded that Ti is incorporated into framework positions. However, based on our EXAFS data we suggested earlier that the TiO_x units and SiO_4 tetrahedra are linked through an edge rather than via the usual corner sharing mode [11,12]. Framework Ti species thus described as structural defects rather than tetrahedral atoms isomorphously substituted for Si in zeolite lattice [11,12]. Van Hooff et al. [13] recently investigated the differences in activity of different TS-1 samples. Their studies led to the conclusion that not only the environment of titanium but also the particle size and morphology influence the activity.

Recently, the synthesis of yet another titanium containing silica analog of a zeolite having the ZSM-48 structure (TS-48) has been reported by Davis et al. [14]. Later, we have established a new synthesis method for the same TS-48 zeolite using hexamethonium hydroxide as the template [15]. ZSM-48 is a unidimensional, medium pore high silica zeolite, the topology of which was first determined by Kokotailo et al. [16]. The synthesis of ZSM-48 was reported to take place in the presence of a number of organic templates [17–20]. Data reported by Davis et al. [14] showed that in TS-48, titanium must be associated to the framework in a manner similar to its grafting in TS-1 and TS-2. Indeed, as in TS-1 and TS-2, the TS-48 zeolite exhibits an IR band at 960 cm^{-1} and lattice parameters that are dependent on Ti content. However, no catalytic properties were reported. In the present work we report a detailed study of the physico-chemical properties of TS-48 samples synthesized following the method of Davis et al. [14]. The focus will be on a comparison of the properties of these TS-48 samples with the properties of the only other two known titanium silicalites, namely TS-1 and TS-2.

2. Experimental

2.1. SYNTHESIS

A series of TS-48 samples containing increasing amounts of titanium was synthesized hydrothermally following the procedure described by Davis et al. [14]. In a typical synthesis, the gel was prepared by stirring a slurry of fumed silica, water soluble peroxytitanate and diamino octane in water. The water soluble peroxytitanate was formed upon stirring the freshly prepared hydrous titanium oxide with aqueous H_2O_2 . The hydrothermal synthesis was carried out in teflon coated stainless steel autoclaves at 473 K for 10 days. The autoclaves were rotated at 40 rpm during crystallization. The solid material was filtered, washed with deionized water and dried at 373 K. The diamino octane occluded in the zeolite was decomposed in air at 873 K for 16 h. Samples were also acid leached in order to remove alkali metal impurities, whenever present, and part of the extra framework titanium oxide formed during the synthesis. Acid treatment was carried out with 1 N HCl solution overnight at room temperature under agitation. After acid leaching, the samples were again calcined at 823 K for about 8 h.

2.2. CHARACTERIZATION

Chemical analysis of all samples was performed by atomic absorption using a Perkin-Elmer 1100 B spectrometer. The samples were dissolved in a 20% HF and 20% HCl solution at 323 K for atomic absorption. X-ray diffraction patterns of the samples were recorded on a Rigaku D-MAX III VC X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ ($\lambda = 1.506 \text{ \AA}$) radiation and a graphite crystal monochromator. The unit cell parameters were calculated from XRD spectra using silicon as an internal standard. IR spectra were recorded on a self supporting wafer prepared by pressing 2 mg of sample in 100 mg of KBr using a Digilab FTS-60 spectrometer with 2 cm^{-1} resolution. Diffuse reflectance UV-Vis spectroscopy was performed on a Perkin-Elmer Lambda 5 spectrophotometer interfaced with an IBM computer and using MgO as a standard. Scanning electron microscope (SEM) pictures were taken using a JEOL-840A instrument.

BET experiments were carried out using an Omnisorp 100 sorption analyzer operating in the continuous mode. About 0.1 g batches were used after a vacuum pretreatment at 300°C . The adsorption capacity for *n*-butane was measured at room temperature using a Setaram microbalance.

X-ray absorption experiments were performed in the transmission mode at LURE, (France) with a monochromatized ($\text{Si}(311)$ two-crystal channel cut) radiation emitted by DCI. The XANES spectra were analyzed using a set of computer softwares developed by Michalowicz [21]. The absorption edges were analyzed, using a classical edge normalization procedure and energy calibration to the first peak of the K-edge of a titanium foil.

Catalytic runs were carried out batchwise. Prior to the catalytic reactions, samples were treated with 1 N ammonium acetate solution and then calcined again at 823 K in air for about 8 h. The oxidation of phenol to dihydroxy-benzene using H_2O_2 (30% aqueous solution) was carried out in a batch reactor. In a typical reaction, 100 mg of the catalyst was dispersed in a solution containing 1 g of phenol and 10 g of solvent (water). The mixture was vigorously stirred before adding, in one lot, the required amount of 30% hydrogen peroxide corresponding to a molar ratio phenol/ H_2O_2 of 3. Reactions were carried out at 353 K for 16 h. The products were analyzed by high resolution capillary GC (HP 5890).

3. Results and discussion

3.1. SYNTHESIS

Data of bulk chemical analysis and unit cell volume from XRD patterns for the various TS-48 samples are recorded in table 1. All samples were crystalline and phase-pure. It was observed that the crystallinity of the zeolites increases with the increase in silicon content in the synthesis mixture. The crystallinity of the pure silica analog of ZSM-48 was higher than the crystallinity of the TS-48 samples (fig. 1), which is a common observation for framework modified high-silica molecular sieves [22].

The silicon to titanium ratios in the solids were found to be lower than those in the initial gels. Moreover, dissolved silica (unreacted) was detected in the mother liquor after crystallization but not titanium, which indicates that not all silicon precursors were involved in the crystallization process. High pH may be responsible for this phenomenon, explaining the lower yield of Si during the hydrothermal synthesis, which was also observed with other titanium silicalites (TS-1 and TS-2) [3,4].

Table 1
Properties of TS-48 samples

| Sample | Si/Ti ^a (gel) | Si/Ti ^a (product) | Si/Ti ^{a,b} (product) | Unit cell ^c volume (\AA^3) | Nitrogen adsorption | | <i>n</i> -butane (ml/g) |
|--------|-----------------------------|---------------------------------|-----------------------------------|---|---------------------|-----------------------|----------------------------|
| | | | | | BET ^d | mesopore ^e | |
| 0TS-48 | — | — | — | 2407 | 152 | 0.128 | 0.089 |
| 1TS-48 | 100 | 82 | 111 | 2418 | 177 | 0.443 | 0.105 |
| 2TS-48 | 50 | 39 | 53 | 2420 | 223 | 0.490 | 0.082 |
| 3TS-48 | 33 | 25 | 34 | 2417 | 189 | 0.445 | 0.079 |
| 4TS-48 | 25 | 19 | 24 | 2413 | 220 | 0.433 | 0.085 |

^a Molar ratio calculated from bulk chemical analysis.

^b Molar ratios after the acid leaching treatment.

^c Calculated from XRD.

^d BET surface area in m^2/g .

^e Mesopore volume in ml/g .

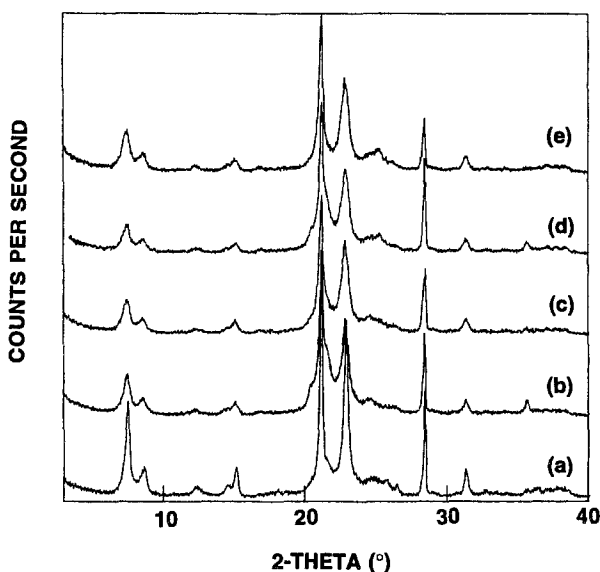


Fig. 1. X-ray powder diffraction patterns of (a) pure silica ZSM-48, (b) 1TS-48, (c) 2TS-48, (d) 3TS-48 and (e) 4TS-48. Peak marked is from a silicon internal standard.

3.2. CHARACTERIZATION

XRD. The X-ray diffraction patterns of TS-48 samples were similar to that of silica ZSM-48 (fig. 1). ZSM-48 is a high silica zeolite with orthorhombic or pseudo-orthorhombic symmetry, the X-ray pattern of which was indexed on the basis of a Pmma-orthorhombic cell [16]. The grafting of Ti in the framework is expected to bring about an increase in the lattice parameters and hence in unit cell volume. Table 1 confirms the increase in the unit cell volume of TS-48 samples as compared to the pure silica ZSM-48, i.e., 0TS-48, which indicates the titanium incorporation in TS-48. However, it can be noticed that the unit cell volume increase is not proportional to the increase of Ti content, especially in samples containing more than about 2 wt% titanium indicating the formation of extralattice titanium species.

SEM. All the samples of TS-48 examined by scanning electron microscopy were composed of spherical random agglomerates of small needle shaped crystals (figs. 2b and 2c). The balls were from 5 to 15 μm in diameter and the constituent needles were 0.2 to 1.0 μm long. They had a maximum diameter of about 0.1 μm . This unusual morphology is responsible for the observed low bulk density. Similar results were observed in the case of (Al)ZSM-48 prepared using diamino hexane as template [23]. However, the silica analog of ZSM-48 (fig. 2a) prepared by a similar method was in the shape of needles of 0.5 to 4 μm long with about 0.2 μm in diameter.

Framework IR. Fig. 3 illustrates the framework IR spectra of TS-48 samples and their silica analog. An absorption band at about 960 cm^{-1} was observed in the

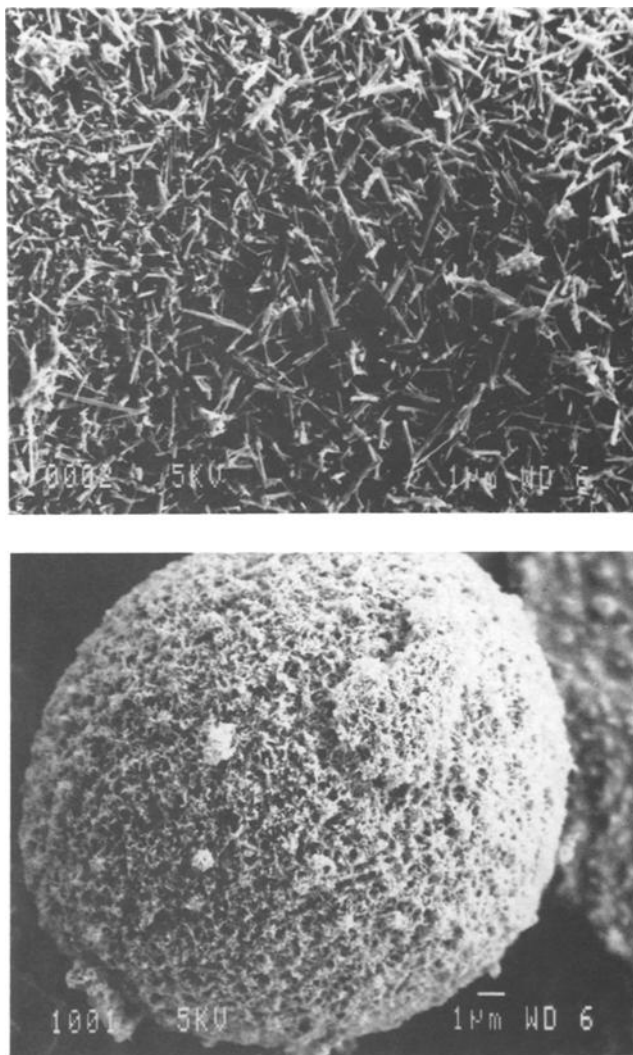


Fig. 2. Scanning electron micrographs of samples (a) pure silica ZSM-48, (b) 1TS-48 and (c) 2TS-48.

case of all TS-48 samples. No such band appeared in the IR spectrum of silica ZSM-48, which is in agreement with similar observations for other titanium silicates [5–8]. The band at 960 cm^{-1} in titanium silicalites (TS-1 and TS-2) was attributed to a vibrational mode involving a silica tetrahedron perturbed by interaction with a Ti atom linked to the framework [5]. Recently, Corma et al. [24] assigned this band to the presence of $\text{Si}-\text{O}^-$ defect groups formed upon Ti incorporation. However, for our samples the intensity of this band was not correlated with the bulk Ti content, which is again an indication of the presence of extralattice titanium species.



Fig. 2. (continued).

UV-Vis spectroscopy. Diffuse reflectance UV-Vis spectra of all the TS-48 samples are shown in fig. 4. As seen each spectrum exhibits two strong transitions around 212 nm (47000 cm^{-1}) and 312 nm (32000 cm^{-1}). The pure silica sample did not show such transitions. Pure TiO_2 (anatase) absorbs at 312 nm (32000 cm^{-1}) [5]. Boccuti et al. [5] have observed a transition around 210 nm (48000 cm^{-1}) in TS-1 and assigned it to an electronic transition with charge transfer character from oxygen to empty d orbitals of isolated framework Ti(IV) in tetrahedral coordination. The presence of both transitions in our samples further confirms the presence

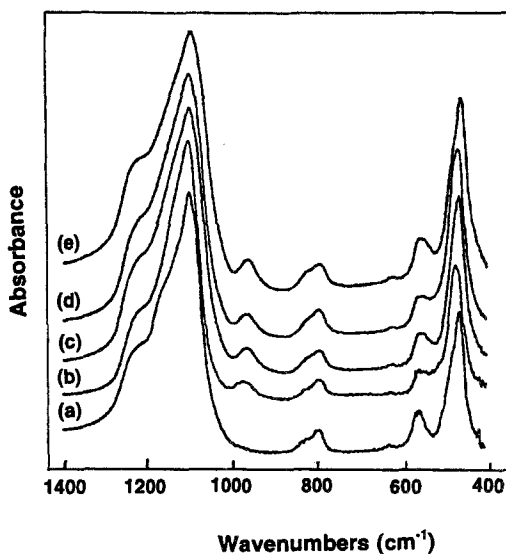


Fig. 3. IR spectra of (a) pure silica ZSM-48, (b) 1TS-48, (c) 2TS-48, (d) 3TS-48 and (e) 4TS-48.

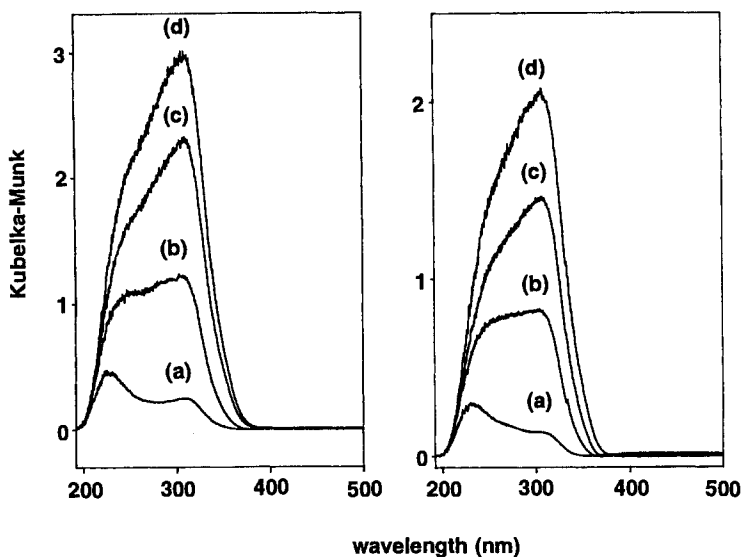


Fig. 4. Diffuse reflectance UV-Vis spectra of before (left) and after (right) acid leaching of samples (a) 1TS-48, (b) 2TS-48, (c) 3TS-48 and (d) 4TS-48.

of both octahedral and tetrahedral Ti species. The relative intensity of the band at 312 nm due to octahedral Ti increased with the titanium content in both the as-prepared and acid leached samples suggesting an increase in the extralattice titanium content.

On acid leaching, the relative intensity of the band at 312 nm decreased (fig. 4), probably because of selective extraction of extralattice titanium, which is in agreement with the observed increase in Si/Ti ratio upon acid leaching (table 1).

Nitrogen and *n*-butane adsorption. As shown in table 1, the BET surface area of Ti containing samples is of ca. 200 m²/g. The surface area of the pure silica ZSM-48 is somewhat lower probably because of the residual carbon. The difficulty of freeing pure silica ZSM-48 from organic materials as compared to its Ti containing counterparts has been demonstrated by Davis et al. [14]. In addition, it is seen from table 1 that the pure silica sample has a smaller mesoporous volume than the Ti modified samples. This may also be related to the different morphologies of both types of zeolites. As shown in fig. 2a, silica ZSM-48 appears as needles separated from each other, thus the mesoporosity is mostly related to local crystal defects. On the other hand the primary crystals of Ti containing samples tend to agglomerate into spherical secondary particles, thus creating mesopores [25].

The micropore volume of all samples as measured by *n*-butane adsorption was of 0.9 ± 0.1 ml/g. Based on geometrical considerations [26], a theoretical micropore volume of 0.104 ml/g was calculated. This volume in close agreement with experimental data indicating that the micropore structure of our samples remains fully accessible despite the presence of some extraframework titanium species.

XANES. The normalized pre-edge X-ray absorption spectra are given in fig. 5. The spectrum (fig. 5 (a)) of Ba_2TiO_4 was considered as a standard for titanium in tetrahedral coordination. The anatase spectrum (fig. 5 (f)) shows a triplet structure which is characteristic of titanium in a distorted octahedral environment. The TS-48 pre-edges exhibit intermediate intensities and positions (table 2) compared to purely tetrahedral and purely octahedral titanium in the two model compounds. Similar behavior was already observed in other titanium silicates [9–12,27]. This suggests the presence of a mixture of sites in agreement with previous findings for TS-1 and TS-2 [9,11].

The results in fig. 5 also show that as the Ti content increases the XANES peak heights and positions shift towards the values observed for the anatase structure (see also table 2). Thus the octahedral Ti symmetry becomes predominant.

Fig. 5 allows also a comparison between the pre-edge X-ray absorption of the TS-48 samples recorded before (left) and after (right) dehydration. The increase in intensity of the 2.5–2.7 eV line upon dehydration, specially observed at low Ti content (sample 1TS-48 in fig. 5 and table 2) clearly indicates a change in Ti coordination yielding more tetrahedral Ti. In the case of TS-1, Lopez et al. [10] observed a similar change upon dehydration which they ascribed to a change in coordination from octahedral to tetrahedral. However, a more extensive study [11,12] of low Ti content TS-2 samples gave no indication of the presence of octahedral Ti. A recent EXAFS study of TS-1 suggested that this change in coordination is a result of the opening of one out of two Ti-O-Si bridges upon hydration [28].

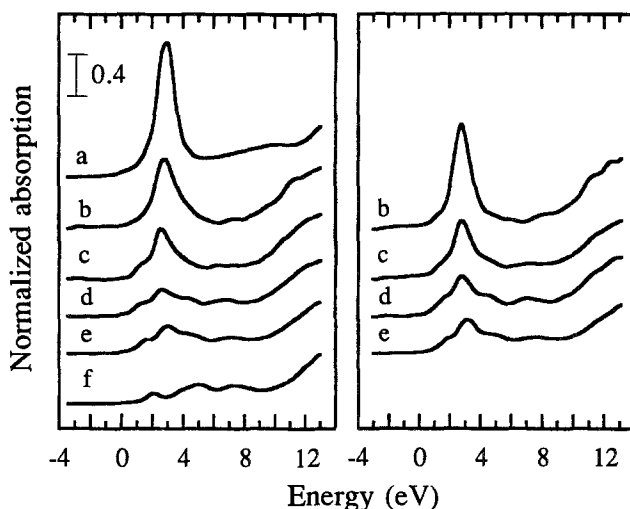


Fig. 5. Pre-edge X-ray absorption spectra (XANES) of samples (a) Ba_2TiO_4 , (b) 1TS-48, (c) 2TS-48, (d) 3TS-48, (e) 4TS-48 and (f) anatase before (left) and after (right) dehydration. For the TS-48 samples, the edge position was taken at the maximum of the highest peak.

Table 2
Pre-edge characteristics of TS-48 samples ^a

| Samples | Position (± 0.2 eV) | Height ($\pm 5\%$) |
|---|-----------------------------|-------------------------|
| Ba ₂ TiO ₄ anatase | 2.50 | 1.06 |
| | 2.30 | 0.13 |
| | 4.70 | 0.22 |
| | 7.80 | 0.21 |
| 1TS-48 | 2.65 | 0.53 |
| 1TS-48 dehydr. | 2.70 | 0.80 |
| 2TS-48 | 2.60 | 0.40 |
| 2TS-48 dehydr. | 2.80 | 0.48 |
| 3TS-48 | 2.50 | 0.22 |
| 3TS-48 dehydr. | 2.90 | 0.31 |
| 4TS-48 | 3.00 | 0.20 |
| 4TS-48 dehydr. | 3.27 | 0.30 |

^a The zero of the energy scale was taken at 4964.2 eV, the titanium foil K edge.

3.3. CATALYSIS

Hydrogen peroxide can be used for the hydroxylation of the aromatic ring, as well as for a variety of other oxidation reactions over titanium silicalite catalysts. In the present study the oxidation of phenol to dihydroxy benzenes was chosen as a test for catalytic activity of TS-48 because it is industrially important and known as a characteristic reaction for titanium silicalites TS-1 and TS-2.

Hydroxylation of phenol in the presence of hydrogen peroxide was performed over all the TS-48 samples reported in table 1, as well as over their silica analog. Neither pure silica ZSM-48 nor any TS-48 sample was found to be active in this reaction and the conversion of phenol over all samples was less than 1%. Under the same conditions for the same reaction over titanium silicalites, TS-1 and TS-2 with similar Si/Ti ratios, about 30% phenol conversion and 70% hydrogen peroxide selectivity were reported [29]. This difference in catalytic activity is quite intriguing, because all the characterization techniques reported above indicate a striking similarity between TS-48 samples on one hand and TS-1 and TS-2 on the other. Van Hooff et al. [13] recently studied the catalytic activity of different TS-1 samples for the hydroxylation of phenol with H₂O₂ and found significant differences in activity for samples showing large differences in particle size and morphology. These studies also led to the conclusion that it is not possible on the basis of only XRD, IR and UV-Vis measurements to differentiate between active and almost inactive samples. The reason for this is that in samples with large size particles this reaction is strongly limited by internal diffusion. The effectiveness factor was found to be decreased from 0.90 to 0.04 as particle size is increased from 0.2 to 10 μ m. Our scanning electron micrographs revealed that TS-48 samples are composed of spherical balls of 5–15 μ m in diameter. These balls are comprised of ran-

dom agglomerates of small needle shaped crystals (fig. 2). Such needle shaped morphology may impede the diffusion of organic substrates. Moreover, TS-48 has a non-interpenetrating linear channel system which is more prone to plugging than the three-dimensional intersecting channel systems of TS-1 and TS-2. The presence of non-leachable octahedral titanium (fig. 4) even at low loading, suggests that the pore system may be partially blocked by extra framework titanium oxide phases. Therefore the hypothesis that the lack of activity of TS-48 may be due to diffusional limitations, as suggested by van Hooff et al. [13] in the case of TS-1, cannot be excluded.

The lack of activity of TS-48 may also be due to a particular local environment of Ti. Indeed, even for other titanium silicalites (TS-1 and TS-2), Jacobs et al. [30] found that the presence of an IR absorption band at 960 cm^{-1} is a necessary but not sufficient condition for the sample to be catalytically active. Our recent investigations of the titanium environment in TS-1 and TS-2 based on XANES and EXAFS data [11,12,28] established that titanium and silica tetrahedra are linked through an edge rather than via the usual corner-sharing mode. Titanium is therefore located in a framework defect and not in a regular tetrahedral site. It is not yet possible to confirm whether this also applies for tetrahedral Ti in TS-48 as a detailed EXAFS study at the Ti K-edge is not yet available. The techniques used in the present work do not seem to probe the structural features of the Ti environment which are responsible for the catalytic activity of Ti in phenol hydroxylation by H_2O_2 . It is therefore of interest to reach a more precise characterization of the local environment of the Ti grafted to the TS-48 lattice. In particular a comprehensive EXAFS study of TS-48 may reveal features that would help delineate the problem as to why TS-1 and TS-2 are active oxidation catalysts while TS-48 is not.

4. Conclusions

Titanium containing silica analog of ZSM-48 (TS-48) samples with varying titanium contents have been synthesized using soluble peroxytitanate, fumed silica and diamino octane. Evidence for the Ti being involved in the zeolite structure was obtained by XRD, IR, UV-Vis and XANES. However, the data also indicated that it is impossible above a total titanium content of 2 wt%, to incorporate all of the titanium into the framework. Inefficient reaction between fumed silica and peroxytitanate during the gel making process could be the reason that limits the incorporation of titanium. It seems that once diamino octane is added to the gel, the unreacted peroxytitanate undergoes hydrolysis. Hence, the level of incorporation depends on the extent of reaction that takes place between fumed silica and peroxytitanate before the addition of the organic template.

TS-48 was found to be inactive for hydroxylation of phenol in the presence of H_2O_2 , even though it exhibited the characteristics of other titanium silicalites, TS-1

and TS-2, which are active for the same reaction. This behavior could be due to subtle differences in titanium environments or to different morphology.

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