

Synthesis of TS-1 Molecular Sieves Using a New Ti Source

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Received: February 2, 2006; In Final Form: June 9, 2006

The incorporation of Ti in the MFI structure using a cheap and easy to handle source, the hexafluorotitanic acid, was successfully achieved without the formation of contaminant phases. The TS-1 samples with 1%, 2%, and 2.5% Ti present a linear increase in the cell parameters. This indicates that the Ti present in the solid is incorporated into the framework, and this is confirmed by infrared analysis. The TS-1 particles present morphology that is typical of the MFI structure. The UV–vis diffuse reflectance results indicate the existence of tetra- and hexacoordinated framework Ti species. Independent of Ti content, all of the samples present similar activity for the oxidation of cyclohexene using hydrogen peroxide as an oxidant agent. Also, a high selectivity for the formation of the corresponding epoxide is observed.

Introduction

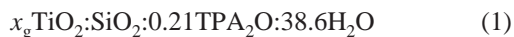
TS-1, a molecular sieve with an MFI structure, was discovered in 1983 by Taramasso et al.,¹ and it has become an important catalyst for the oxidation of organic compounds, making possible the use of the hydrogen peroxide as an oxidant agent. Since the original synthesis of TS-1,¹ other preparation methods and new reagents have been tested with the objective of increasing the catalytic activity and reducing the final cost of the catalyst. Also, the substitution of a reagent can make changes in the preparation method possible, such as modification of the gel aging time or the crystallization temperature.

In this study, the effect of the simultaneous substitution of two reagents originally used in TS-1 synthesis¹ was investigated. This was done with the objective of facilitating the preparation of the synthesis gel and reducing production costs. The following substitutions were made: (a) fumed silica was used as a substitute for tetraethyl orthosilicate (TEOS), and (b) hexafluorotitanic acid (HFTA), instead of tetraethyl orthotitanate (TEOT), was used as a Ti source. Some authors have already used fumed silica as a Si source for the synthesis TS-1.^{2–4} However, apparently HFTA has only been used successfully as a Ti source for the synthesis of Ti-BEA.⁵ Sulikowski et al.⁶ attempted to perform the synthesis of TS-1 using HFTA and fumed silica as Ti and Si sources, respectively, but TS-1 was always formed in the presence of other phases, quartz, cristobalite, and rutile (extraframework Ti).

Experimental Section

Material. TS-1 was synthesized using hexafluorotitanic acid (Aldrich, 60%) as the Ti source, amorphous silica (Aerosil 380, Degussa), and tetrapropylammonium hydroxide (20% aqueous TPAOH solution, Aldrich).

The composition of the gel for the synthesis of TS-1 is given by eq 1, where x_g is the Ti/Si molar ratio:



To verify the influence of Ti content in the gel, the syntheses were accomplished with values of $100 \cdot x_g = 0, 1, 2$, and 2.5.

The gels were prepared at 25 °C by the dropwise addition of the hexafluorotitanic acid to the tetrapropylammonium hydroxide solution. The amorphous silica was then slowly added to the solution, and later the necessary water was also added. During the gel preparation, the system was stirred to maintain homogeneity. When the addition of all of the gel components was completed, the solution was maintained under agitation for an additional period of 30 min. The final pH of the gels was between 12.0 and 12.5.

The crystallization was accomplished in PTFE cylinders of 30 mL, each one containing approximately 20 g of gel. The cylinders were placed in stainless steel autoclaves for crystallization at 170 °C for periods of 12, 24, 48, 72, and 120 h. The crystallization took place under autogenous pressure, maintaining the autoclaves in static conditions.

After the crystallization, the solid product was separated by centrifugation, washed with deionized water until the pH was equal to 9.5, and then was dried at 110 °C. For the characterization of the material, the template was removed by calcination, heating the solid at a rate of 1 °C/min up to 540 °C under an inert atmosphere, and maintaining this temperature for 8 h in air to burn off the coke formed.

The TS-1 samples were characterized by the following techniques: XRD, Rietveld, and chemical analysis, SEM, UV–vis, and IR diffuse reflectance spectroscopy.

X-ray Powder Diffraction. The MFI structure of the synthesized materials was confirmed by X-ray diffraction using a Cu K α radiation source (Miniflex). The calculation of the crystallinity of the samples was accomplished by calculating the ratio of the area under the three peaks formed at 2θ (between 23° and 24.5°), in relation to the sample with the largest area, which was designated as a reference and attributed a crystallinity of 100%. The XRD spectra were collected stepwise in the $20^\circ \leq \theta \leq 50^\circ$ angular region, with 0.02° step and 3 s counting time (Rigaku-Denki 2θ diffractometer). The refinements were accomplished considering the contribution of both K α_1 and K α_2 (2:1 intensity ratio) radiation to the pseudo reflection profile.

Chemical Analysis. The analysis of the solids was performed by induced plasma-atomic emission spectroscopy (ICP-AES) using a Varian Spectra AA640. Determination of the MFI unit

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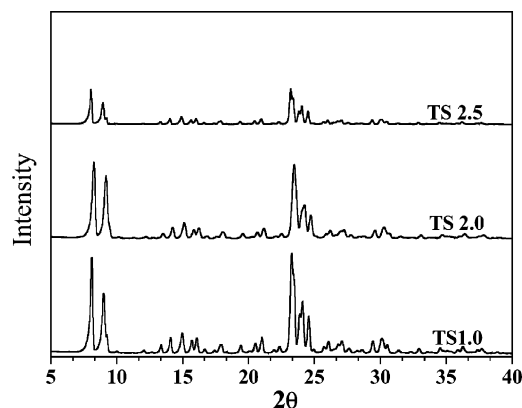


Figure 1. XRD patterns of TS-1 samples with 1%, 2%, and 2.5% of titanium.

cell parameter was accomplished by pattern Rietveld analysis using the pseudo Voigt peak profile function and DBWS program.

The IR spectroscopy was obtained on a Magna 750 Nicolet spectrometer, mixing the calcined samples with dry potassium bromide (98% of KBr and 2% of sample).

The UV–visible diffuse reflectance spectroscopy was achieved using a Varian Cary 5 spectrometer equipped with a diffuse reflectance and using BaSO₄ as a reference. Original or calcined samples, the latter in dried or humidified form (in equilibrium with an atmosphere of 35% relative humidity), were used. The SEM images were obtained using a Zeiss DSM 960 microscope.

Catalytic Experiments. The oxidation reactions were carried out in a round-bottomed flask immersed in an isothermal bath and equipped with a condenser, a thermometer, and a magnetic stirrer. In a typical experiment when using H₂O₂ as oxidant, 20 mmol of cyclohexene, 25.5 g of acetonitrile as solvent, and 5 mmol of diluted (30 wt %) hydrogen peroxide are mixed in the flask and heated at 60 °C under vigorous agitation. At this point, 0.1 g of catalyst is added to reaction mixture, and after 2 min the reaction started (time zero). Aliquots were taken at selected reaction times and catalyst particles separated by centrifugation. The products were separated and analyzed by gas chromatography in a capillary column (methylphenylsilicone, 50 m length) using an FID detector. The amount of unreacted hydrogen peroxide was determined by iodometric titration.

Results and Discussion

Figure 1 shows the XRD patterns of TS-1 samples with 1%, 2%, and 2.5% titanium, which shows that all of the samples have the MFI structure. The XRD patterns of TS-1 samples show that they are pure titanium silicalite free of the impurities phase.

Figure 2 presents the degree of crystallinity and the solid yield for 100 g of gel, as a function of the crystallization time. The maximum crystallinity is reached in the first 24 h of crystallization. However, the yield increases only slowly up to 72 h. The variation of the Ti contents in the gel does not affect significantly the maximum yield or degree of crystallinity of the solids, and thus the amount of Ti added to the system is relatively low (2% of titanium). Sulikowski et al.,⁶ using the same Si and Ti sources, obtained very impure TS-1 samples that were contaminated with cristobalite, quartz, and rutile. In the present case, no other phase was observed to form simultaneously with TS-1. The explanation for these differences can be related to the different pH values of the gel. The gels prepared by Sulikowski presented pH values of 4.0–9.0 because

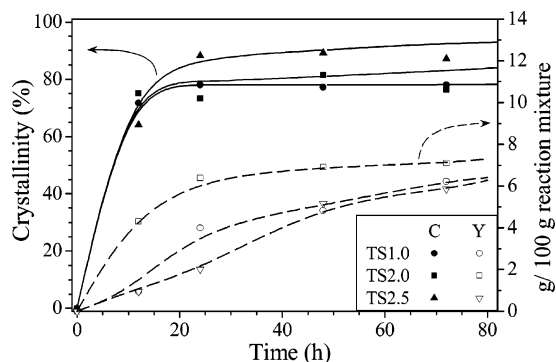


Figure 2. Crystallinity (C) and yield (Y) of TS-1 as a function of the crystallization time.

he employed TPABr as template agent, NH₄OH as base, and different amounts of hexafluorotitanic acid as Ti source. In the present study, the same Ti source was also used; however, the template was the strong base TPAOH. As a consequence, the pH of the gels was always around 12.0, which is more appropriate for the depolymerization of the silica and construction of the zeolite framework.

Figure 3 presents the values obtained for the unit cell parameters and the unit cell volume as a function of the Ti content in the solid (x_s), for samples that contained up to 2% Ti in the gel. The adjustments were satisfactorily linear (correlation coefficient > 98%). Millini et al. synthesized TS-1 using TEOS and TEOT as sources of Si and Ti,⁷ and the authors observed a linear increase in the cell parameters as a function of the Ti content in the solid. This result was interpreted as being evidence that the Ti present in the solid is incorporated in the MFI framework. Thus, HFTA was a satisfactory Ti source, as the unit cell parameters, as well as the unit cell volume, increase linearly with increasing Ti content in the gel, showing that the Ti present is proportionally incorporated in the zeolite framework. In the graphs presented in Figure 3, the unit cell parameters for Ti > 2% are not presented, due to the fact that above this value they remained constant. This result will be discussed later (Figure 4).

From the results presented in Figure 3D, the relationship between the unit cell volume, v , and the Ti content in the solid, x_s , is given by the following expression, the parameters of which are close to those of Millini et al.:⁷

$$v = 5345.6 + 19.7 \cdot x_s \quad (2)$$

The percentage of Ti in the solid, x_s , was obtained by chemical analysis, while, for all samples presented in Figure 3D, the framework Ti, $x_f = x_s$. Therefore, from eq 2, x_f can be deduced as:

$$x_f = 0.05 \cdot v - 271.35 \quad (3)$$

Figure 4 shows the percentage of Ti in the solid, x_s , and in the framework, x_f , as a function of the Ti percentage in the reaction mixture, x_g . As can be observed, there is no change in x_f for samples with $x_g > 2.0\%$. This indicates that, under the synthesis conditions used in this study, Ti values higher than 2% are not incorporated in the framework. The solid composition, x_s , for the sample prepared with $x_g = 3.5\%$ Ti in the gel exhibits a big difference as compared to the value in the framework, x_f . This difference is due to the presence of TiO₂ in the anatase form in the solid, as detected by the UV DRS band at 320 nm (see Figure 6).

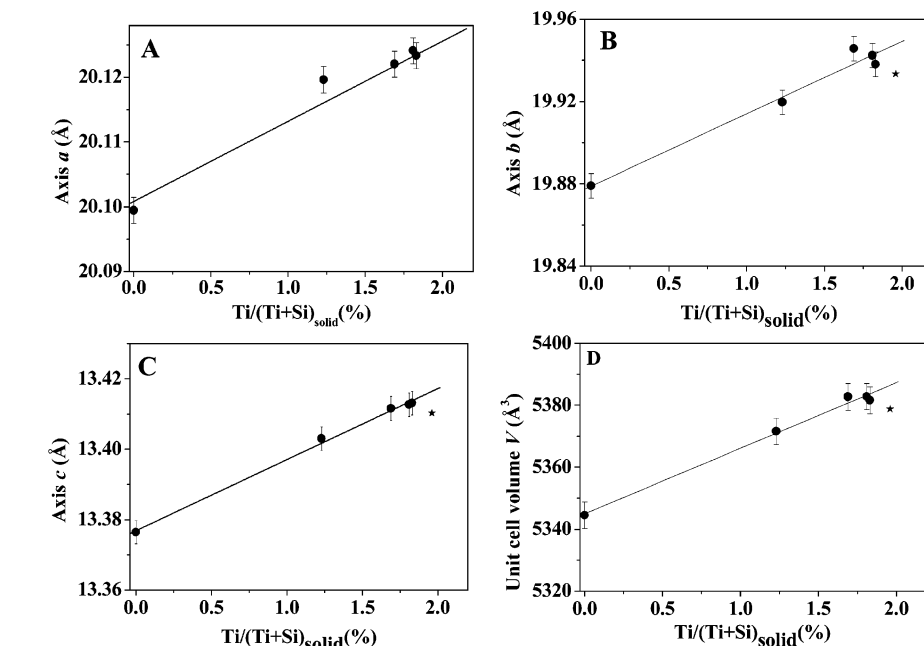


Figure 3. (A, B, and C) Unit cell parameters a , b , and c , and (D) cell volume v as a function of Ti content.

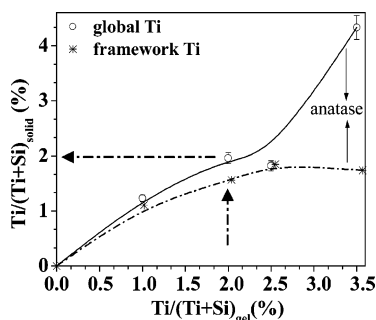


Figure 4. Ti content in the solid (x_s) and in the framework (x_f) as a function of the Ti % in the gel (x_g).

The scanning electron micrographs of TS-1 with 1%, 2%, and 2.5% Ti in the reaction mixture and 48 h of crystallization are shown in Figure 5.

The average crystal size is about 4–5 nm, and the crystallite shape of all samples follows the typical morphology of the MFI structure.⁸ There is no clear relationship between the crystal size and the Ti content in the synthesis gel.

The UV–vis diffuse reflectance spectra of TS-1 obtained after 48 h of crystallization, calcined and dried, are shown in Figure 6. All of the spectra show a strong absorption band at around 215 nm and a second less intense band at around 260 nm. To compare the relative intensities of the UV bands, the intensity of the peak at 215 nm was maintained constant. The results show that as the quantity of Ti in the reaction mixture and in the solid increases (see Table 1) the intensity of the second band increases (at around 260 nm). With increasing Ti content, a shift of the second band to higher wavelengths is also observed.

The band at 215 nm is attributed by various authors^{2,7,9} to the isolated tetraordinated Ti species. The attribution of the second band at about 260 nm is the subject of some controversy. Petrini⁹ and Blasco¹⁰ observed a broad band at approximately 270 nm, which comes from partially polymerized hexacoordinated Ti species that contain Ti–O–Ti bonds. However, Tuel² claims that the band at 270 nm is not due to hydrated hexacoordinated titanium species but rather to extra lattice species. According to the chemical analysis (Figure 4), the

sample synthesized with 3.5% Ti shows a very broad band centered at 320 nm, which is attributed to TiO₂ anatase.

Figure 7 shows the UV–vis spectra of the wet TS-1 samples presented in Figure 6, with 1%, 2%, and 2.5% Ti. Comparing the spectra of Figures 6 and 7, the band at 260 nm increases in the presence of adsorbed water. This increase becomes more accentuated as the Ti content in the solid increases and confirms that the band at 260 nm is related to hexacoordinated Ti in the presence of water molecules.

The fact that the intensity of the band at 260 nm, in the hydrated samples, increases when the Ti content is higher can be attributed to that the Ti generates hydrophilic regions. Consequently, there is a greater probability that these regions will interact with water.

The IR spectra of the TS-1 samples exhibit a band at 965 cm^{−1}, which is generally considered as a proof of the incorporation of Ti in the MFI framework.^{11,12} So, to estimate the amount of Ti incorporate in the BEA structure, Cambor¹² used the ratio of the areas under the peaks that appear at 965 and 800 cm^{−1}. Table 1 shows that also for TS-1 prepared in this work, the ratio of these peaks increases as the amount of Ti in the framework, x_f , also increases. This indicates once more that Ti is incorporated into the framework in quantities that are proportional to the amount of Ti in the gel. Table 1 also shows the global Ti content in the solid, x_s , which was presented in Figure 4.

Figure 8 shows the conversion of cyclohexene as a function of reaction time, using the TS-1 samples containing 1%, 2%, and 2.5% Ti. The conversion, under the conditions employed here, reaches a maximum value of 2% in 4 h, and this value is independent of the Ti content. Similar results, under analogous conditions, have been reported by Kwak et al. when testing TS-1 samples with 3% Ti synthesized using TEOT.¹³ According to Blasco and co-workers,¹⁴ the low (about 2%) activity of this reaction system could be due to the difficulty that cyclohexene (and its derivatives) encounters to diffuse through the narrow TS-1 pores.¹⁴ This result agrees with Tatsumi et al., who observed that cyclohexane presented a smaller conversion as compared to hexane¹⁵ attributed to a restricted diffusion of this substrate in the channels of TS-1, due to its channel dimensions.

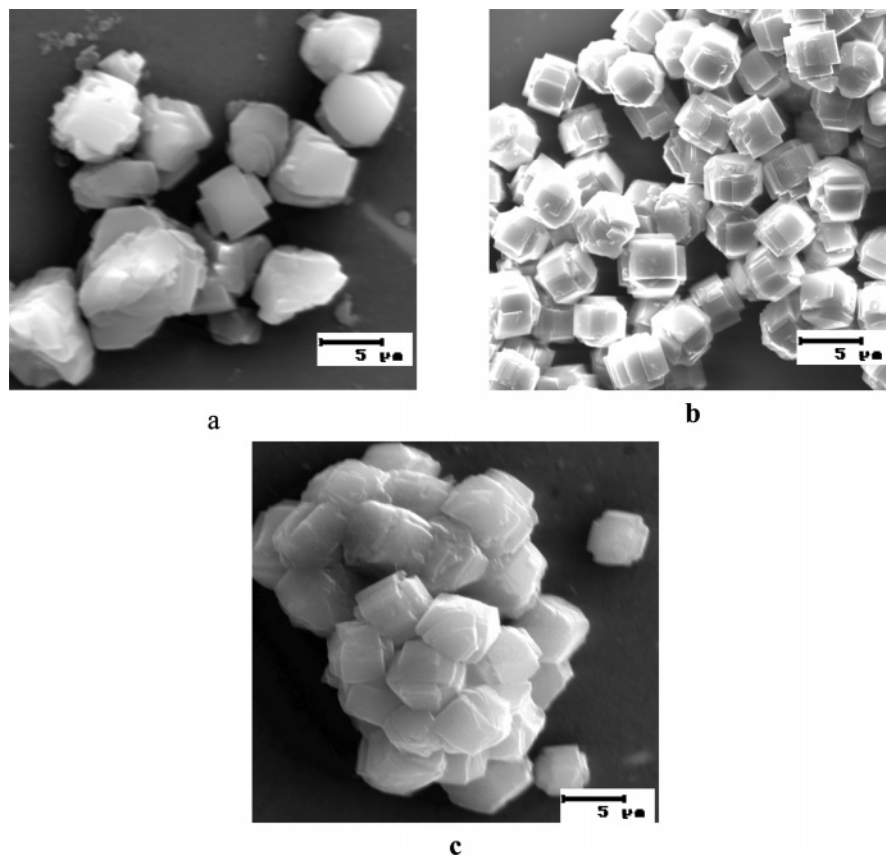


Figure 5. Micrographs of TS-1 with (a) 1.0%, (b) 2.0%, and (c) 2.5% Ti.

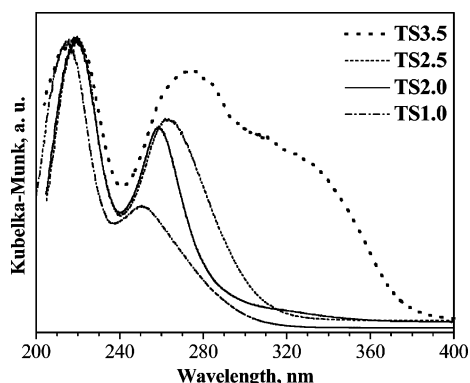


Figure 6. UV-vis diffuse reflectance spectra of calcined and dried TS-1 samples.

TABLE 1: Amount of Ti and Ratio among Bands of UV

sample	$100 \cdot x_g$ gel	$100 \cdot x_s$ solid	$100 \cdot x_f$ framework	I_{965}/I_{800}
TS1.0	1.0	1.32	1.31	0.732
TS2.0	2.0	1.96	1.68	0.761
TS2.5	2.5	1.90	1.88	0.946

Another factor that contributes to unchanged activity is the relatively large size of the TS-1 particles (approximately 5 μ m, Figure 4). The study of the effect of the particle size in the activity is under development, using TS-1 crystals of different sizes, synthesized with aging of the gel.

In the case of TS-1, the solvent could also be a factor that contributes to the low activity. Blasco¹⁴ observed that the activity of TS-1, when compared to [Ti, Al]- β , using acetonitrile was much lower and that this is due to differences in polarity and also to the intrinsic properties of each zeolitic structure.

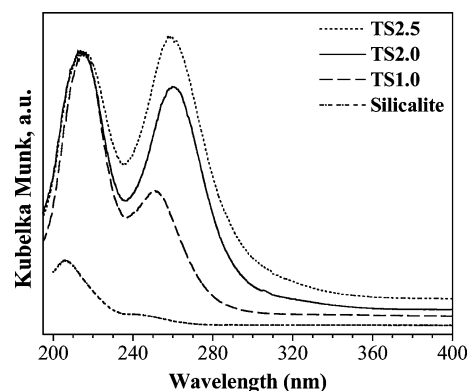


Figure 7. UV-vis diffuse reflectance spectra of calcined and wet TS-1 samples.

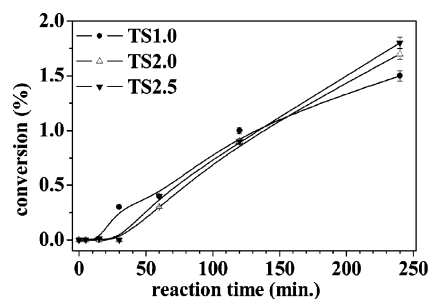


Figure 8. Conversion of cyclohexene using TS-1 samples.

Figure 9 shows the selectivity for the two oxidation products (cyclohexene oxide and 2-cyclohexene-1-ol) as a function of time. As can be observed, the selectivity is independent of the Ti content. Initially the main product is cyclohexene oxide. However, after 1.5 h, 2-cyclohexene-1-ol can also be considered

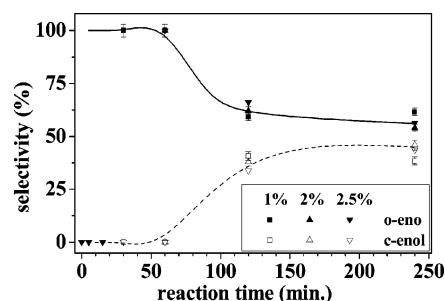


Figure 9. Selectivity of the oxidation products formed during the reaction.

as one of the primary products, being formed in a proportion similar to the epoxide. The two products are formed through different mechanisms: (1) the epoxide is formed at a Ti site that is in the form of hydroperoxide-species¹⁶ and (2) 2 cyclohexene-1-ol by a radical mechanism,¹⁷ which requires the presence of acidic Ti sites. The change in the predominant mechanism during the course of the reaction is possibly due to alterations in the Ti sites, which make them more acidic.

Conclusions

The results show that TS-1 can be synthesized using a new source of titanium, together with amorphous silica. In comparison with the traditionally used tetraethyl orthotitanate and tetraethyl orthosilicate, this method presents the advantages of low cost and stability of the reagents: they do not undergo hydrolysis when exposed to air. TS-1 is formed with high crystallinity at low crystallization times. The maximum TS-1 yield is obtained after approximately 48 h of crystallization. Unlike other authors who used hexafluorotitanic acid as a source of Ti, in this work the formation of extraframework titanium species was observed only for samples prepared with a relatively high Ti content.

Evidence for incorporation of Ti in the MFI framework was obtained by XRD, which indicated a linear increase in the unit

cell volume with increasing Ti content. Also, IR spectroscopy displayed an increase in the 960/800 cm^{-1} band ratio as the Ti content in the gel increased. UV-vis spectra presented an increase in the intensity of the band at 260 nm for wet samples. This suggests that there is an increase in the formation of Ti framework species hexacoordinated with water molecules. The SEM analysis indicates that the use of hexafluorotitanic acid as a source of Ti results in the formation of large crystals. All of the TS-1 samples display activity for the oxidation of cyclohexene using H_2O_2 , and this activity is independent of Ti content. The TS-1 samples present greater selectivity for the formation of cyclohexene oxide, independent of Ti content.

Acknowledgment. We wish to thank CNPq and PRONEX for financial support.

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