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CHARACTERIZATION AND CATALYTIC PROPERTIES OF TITANIUM SILICALITE-1 CATALYST

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Abstract – Titanium silicalite 1 (TS-1) catalyst was prepared by three different hydrothermal synthesis methods. XRD, elemental analysis, SEM, IR, ^{29}Si MAS NMR, UV-vis DRS, physical adsorption of nitrogen, and EXAFS analysis were then performed to evaluate its physical properties. For a test of catalytic activity, liquid phase 2-butanol oxidation and 1-hexene epoxidation using hydrogen peroxide as an oxidant were conducted. The crystal size of the TS-1 catalyst was shown to have a considerable effect on the 1-hexene epoxidation, and smaller crystals resulted in higher activity.

Key words: TS-1, Characterization, Morphology, Oxidation, Epoxidation

INTRODUCTION

With the growth of the interest in the utilization of zeolites as catalysts, considerable attention has been focused on the incorporation of various hetero-atoms as substitutes for silicon or aluminum in the zeolite framework. In this regard, titanium-substituted molecular sieves have received much attention in recent years in the field of liquid phase oxidation reactions.

Taramasso et al. [1983] first reported the hydrothermal synthesis of a titanium-containing zeolite, denoted as titanium silicalite-1 (TS-1). Titanium silicalite-1, like the aluminosilicate ZSM-5, is a zeolite with an MFI structure that can be synthesized by isomorphous substitution of Ti for Si in the framework of silicalite-1. TS-1 was found to be a very efficient catalyst for the preparation of many organic compounds with aqueous hydrogen peroxide used as oxidant under mild reaction conditions, and studies on the hydroxylation of aromatics and phenol [Kraushaar and van Hooff, 1989], epoxidation of olefins [Clerici and Ingallina, 1993], oxidation of paraffins to the corresponding alcohol and ketones [Tatsumi et al., 1990; Huybrechts et al., 1990], and oxidation of alcohols and amines [Esposito et al., 1984; van der Pol and van Hooff, 1993] have been reported. Several reactions catalyzed by TS-1 (phenol hydroxylation, cyclohexanone ammoximation and propylene epoxidation) are at present in different stages of industrial application [Notari, 1993]. It is generally believed that titanium atoms existing in TS-1 lattice positions, replacing silicon atoms, are the active sites in selective oxidation reactions using hydrogen peroxide as the oxidant.

In the original patent [Taramasso et al., 1983], TS-1 catalyst was synthesized with either tetraethyl orthosilicate (TEOS) or a colloidal silica sol (Ludox AS-40 from DuPont) as silica sources. The first recipe involved a hydrolysis of Si and Ti alkoxide mixtures (preferentially ethoxides) followed by hydrothermal treatment using tetrapropylammonium hydroxide (TPAOH) solution as the template. The second route differed considerably in that peroxotitanate species were first formed before addition of the colloidal silica sol. An alternative and simpler method for the synthesis of TS-1 was developed by Padovan et al. [1991], who reported the preparation of TS-1 by dry impregnation of a preformed microspheroidal porous SiO_2 with a solution containing TPAOH and the titanium alkoxide, and subsequent hydrothermal treatment in sealed SiO_2 tubes. A major problem often encountered during the synthesis of the TS-1 catalyst is the precipitation of the oxides of titanium outside the lattice framework. This gives rise to samples that, though they are highly crystalline, are inactive in oxidation reactions. It has also been widely reported that the presence of alkali cations in the synthesis mixture leads to extraframework TiO_2 species upon hydrolysis of the titanium source. Therefore, the usual synthesis routes involving NaOH or KOH as inorganic bases cannot be used to prepare the TS-1 catalysts.

Several studies have been conducted to elucidate the nature of the titanium environment in TS-1. A common feature observed in all samples showing catalytic activity was the presence of an absorption band at ~960 cm^{-1} in the IR spectra [Huybrechts et al., 1991; Lee et al., 1996]. Boccuti et al. [1989], using UV-VIS spectroscopy, showed that the titanium sites are tetrahedrally coordinated, and Tuel et al. [1990] provided further support for the tetrahedral coordination by investigating the EPR spectra of Ti^{+3} (obtained by reducing the Ti^{+4} in TS-1 with CO). Additionally, Schultz et al. [1992] showed by EXAFS measurements that the titanium sites in TS-1 are tetrahedrally coordinated. The XPS data of TS-1 show an identical binding energy to that of Ti(IV) in SiO_2-TiO_2 glasses suggesting that the oxidation state of the titanium in TS-1 is +4 [Trong On et al., 1992].

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This paper reports the synthesis of titanium silicalite-1 by various hydrothermal synthesis methods and the influence of synthesis parameters such as SiO_2/TiO_2 molar ratio and silica source on the morphology of TS-1 crystals. The TS-1 samples synthesized were extensively characterized by XRD, SEM, IR, UV-vis DRS, BET, ^{29}Si MAS NMR, and EXAFS-XANES spectroscopies, while the catalytic properties were tested by means of the 2-butanol oxidation and epoxidation of 1-hexene over TS-1 using hydrogen peroxide as an oxidant.

EXPERIMENTAL

1. Synthesis of TS-1 Catalyst

The synthesis procedures for TS-1 catalysts with tetraethylorthosilicate (first method), colloidal silica Ludox AS-40 (second method), and fumed silica Cab-O-Sil (third method) as silicon source are as follows, and these three synthesis procedures are schematically represented in Figs. 1, 2 and 3, respectively.

1-1. First Method

A pyrex beaker was placed in a glove box and nitrogen was flushed over to minimize the adverse effect of moisture. A calculated amount of tetraethylorthosilicate (Aldrich, 98 %) was transferred to the pyrex beaker and tetraethylorthotitanate (Aldrich, ~20 % Ti) was carefully introduced into the vigorously stirred solution. The reactants were mixed homogeneously for half an hour depolymerising titanate oligomers that may be present in tetraethylorthotitanate. The mixture was then cooled to about 0 °C. The TPAOH solution used as a template was also cooled to 0°C. After a few minutes, the calculated amount of TPAOH aqueous solution (Aldrich, 20 %) was very slowly added dropwise into the mixture. Stirring and cooling was maintained during this process. If a white, gelatinous precipitate is formed one should wait until this has disappeared. If the precipitate does not dissolve, amorphous TiO_2 has been formed and the synthesis is considered failed (TPAOH has been added too fast or TEOS and TEOT have not been mixed sufficiently). After addition of all TPAOH the synthesis mixture was kept for 5-6 hours at 70-80 °C in order to accelerate hydrolysis and evaporate the ethyl alcohol which was released. Make-up deionized water was then added to maintain the total volume of the mixture at its original value. The substrate prepared had the following composition ratios: SiO_2/TiO_2=32.7, TPA^+/SiO_2=0.46, H_2O/SiO_2=35. This clear homogeneous solution was then transferred to a teflon-lined stainless steel autoclave and placed in a convection oven at 175 °C under autogenous pressure. To investigate the crystallization process, autoclaves were taken out from the oven at different time intervals and were quenched immediately in cold water for identification. The solid products were separated by means of suction-filtration or centrifugation, washed several times with hot deionized water, and dried in an air oven at 110 °C overnight. The products were finally calcined at 550 °C for 6 hours.

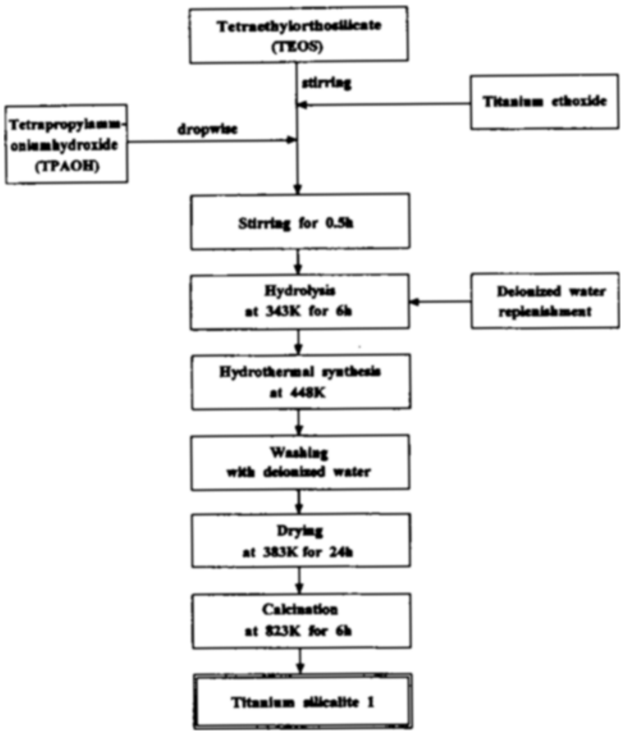

Fig. 1. Schematic diagram for the preparation of Ti-silicalite 1 using tetraethylorthosilicate as silica source.

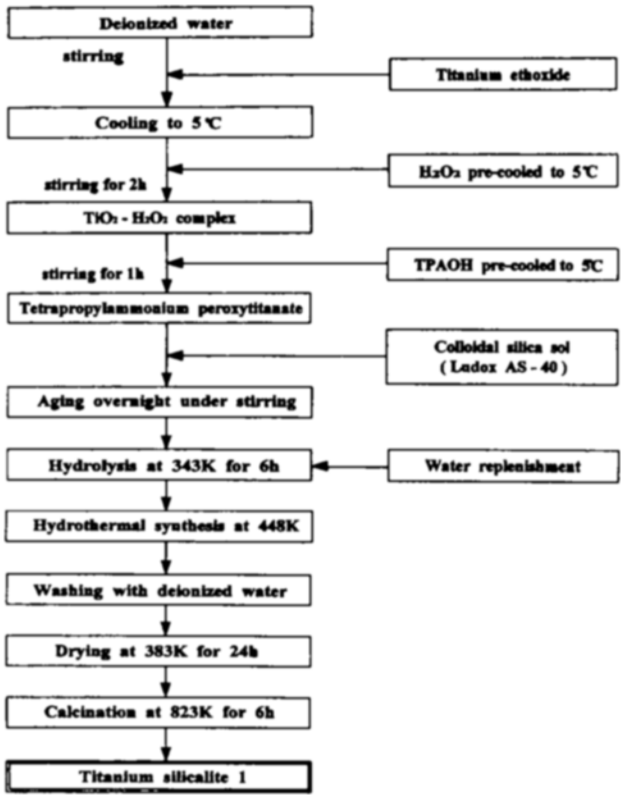

Fig. 2. Schematic diagram for the preparation of Ti-silicalite 1 using colloidal silica as silica source.

1-2. Second Method

This method utilizes tetrapropylammonium peroxytitanate as the titanium source. The pertitanates are known to be stable in a strongly basic environment. TS-1 samples were also prepared from substrates having the following composition ratios: SiO_2/TiO_2=32.7, TPA^+/SiO_2=0.46, H_2O/SiO_2=35.

A calculated amount of tetraethylorthotitanate was slowly

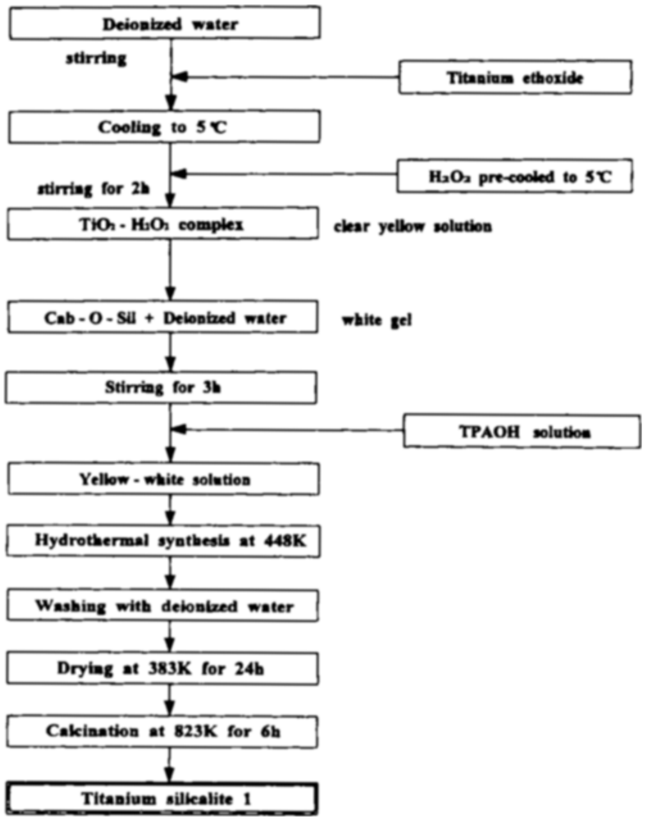

Fig. 3. Schematic diagram for the preparation of Ti-silicalite 1 using Cab-O-Sil as silica source.

added dropwise into the required amount of deionized water under stirring. A white gelatinous suspension was obtained. It was cooled to 5 °C and the calculated amount of hydrogen peroxide (Junsei Co., 30 %), also cooled to 5 °C, was added. It was then stirred occasionally over two hours while maintaining the temperature low. A clear orange-coloured solution resulted. At this point, an aqueous TPAOH solution (Aldrich, 20 %) pre-cooled to 5 °C was added under continuous stirring at 5 °C. After one hour, the calculated amount of Ludox AS-40 (Du Pont Co., 40 % SiO_2) was added, mixing being carried out carefully, and the resulting yellow solution was kept stirred overnight at room temperature. Finally, it was heated to 70-80 °C for 5-6 hours in order to remove the excess of hydrogen peroxide. The clear transparent solution thus obtained was transferred to an autoclave, and the same operations described in the first method were then followed.

1-3. Third Method

The reaction mixture was prepared with the composition of $10SiO_2 \cdot 0.3TiO_2 \cdot 657H_2O \cdot 1.1H_2O_2 \cdot 9TPAOH$. The TiO_2-H_2O_2 complex was obtained by mixing the calculated amounts of tetraethylorthotitanate, deionized water and hydrogen peroxide. The mixture was stirred two hours in order to obtain a clear yellow solution. The solution was then slowly dropped into the white gel formed from a silica source (Cab-O-Sil) and deionized water. After about 3 hours of stirring, the templating solution (TPAOH) was added. The yellow-white solution was then heated at 175 °C for 4 days, and the operations described in the first method were then carried out.

2. Characterization of TS-1 Catalyst

The synthesized samples were analyzed by X-ray diffraction (XRD) for qualitative and quantitative phase identification. The unit used was a powder X-ray diffractometer (Philips, PW-1700) with a scintillation counter and a graphite monochromator attachment, utilizing Ni-filtered CuKα radiation (40 kV, 25 mA). Unit cell parameters were obtained by a least-squares fit to the interplanar spacings measured in the 5-45° (2θ) angular region, using silicon as an internal standard. The morphology, i.e., crystal size and habit, of the different samples was examined with a scanning electron microscope (Hitachi, X-650) after coating with a Au-Pd evaporated film. Framework i.r. spectra of samples were recorded in air at room temperature on a Perkin Elmer 221 spectrometer (in the range of 400-4,000 cm^{-1}) with wafers of zeolites mixed with dry KBr. The chemical analysis of crystalline samples was performed by using ICP (Jobin Yuon JY-38 VHR) and XRF (Rigaku, 3070). The specific surface areas and micropore volumes were determined by nitrogen physisorption with the BET method at liquid nitrogen temperature using a Micromeritics ASAP 2000 automatic analyzer. UV-VIS diffuse reflectance spectroscopy was performed on a Varian CARY 3E double beam spectrometer connected to a computer and dehydrated MgO as a reference in the range of 190-500 nm. The solid state NMR spectra were obtained with a Bruker AM 300 spectrometer at a frequency of 59.6 MHz and spinning rate of 3.5 kHz with a pulse width of 3 μsec, a relaxation delay of 5 sec and 100-200 acquisitions. The chemical shift was referenced with respect to the ^{29}Si signal of tetramethylsilane (TMS). The X-ray absorption measurement was carried out above the Ti K edge (4966 eV) at room temperature using Beam Line 7C at the Photon Factory in Tsukuba. The injection beam energy was 2.5 GeV. The monochromator was a Si(111) double crystal with a typical resolution $\Delta E/E=1.1\times10^{-4}$ at the Ti K edge. The X-ray absorption data were analyzed by the standard method using the UWXAFS2 code distributed by the University of Washington [Frenkel et al., 1993].

3. Catalytic Reactions

For a catalytic activity test of TS-1, the oxidation of 2-butanol with aqueous H_2O_2 as oxidant was performed by using a 125 ml Pyrex reactor fitted with a reflux condenser and a magnetic stirrer. In a typical run, 10 ml of 2-butanol (Junsei, 99 %) and 10 ml of H_2O_2 aqueous solution (Junsei, 30 %) were mixed in the reactor and heated to the desired temperature in a sand bath. Then, 0.1 g of TS-1 catalyst was added to the reaction mixture, and the reaction was conducted at 50 °C for 3 hours with vigorous stirring. After the reaction, the catalyst and reaction mixture were separated and the products analyzed by a gas chromatograph (Shimastu, GC-14A) equipped with a 25 m capillary column (Supelco, CBP-M25-25) using a FID detector.

The epoxidation of 1-hexene with aqueous H_2O_2 as oxidant was also carried out using 0.1 g of TS-1 catalyst, 20 mmol of 1-hexene (Aldrich, 99 %), 7 mmol of hydrogen peroxide (Junsei, 35 %), and 100 mmol of 2-butanone (Junsei, 99 %) as the solvent. The reaction was conducted at 50 °C for 2 h with vigorous stirring in a 40 ml Pyrex reactor immersed in a constant temperature sand bath. In all cases, mesit-

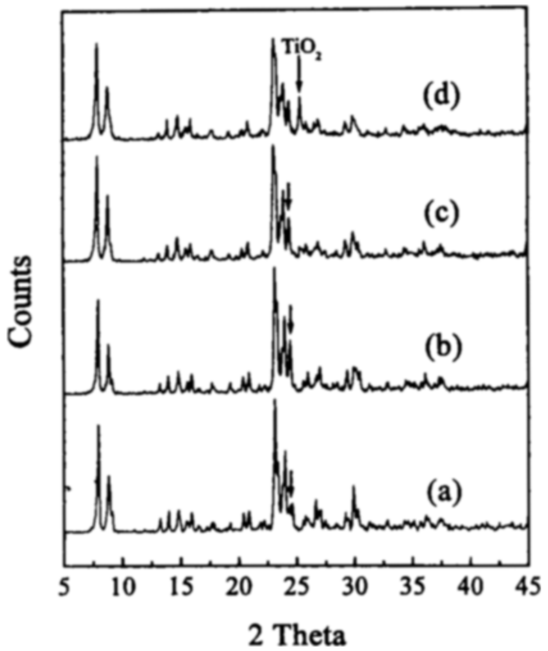

Fig. 4. XRD patterns of Ti-silicalite 1 and silicalite-1: (a) silicalite-1, (b) ZSM-5, (C) TS-1 (3 mol% Ti), and (d) TS-1 (8 mol% Ti).

ylene was used as an internal standard for gas chromatographic analysis. The unreacted hydrogen peroxide was determined by potassium permanganate titration.

RESULTS AND DISCUSSION

1. Characterization of Titanium Silicalite-1 Catalyst

The X-ray diffraction patterns of the TS-1, ZSM-5 and silicalite-1 prepared are shown in Fig. 4. The X-ray diffraction pattern of the calcined TS-1 zeolites was similar to that of ZSM-5 zeolites. The symmetry of the calcined TS-1 was orthorhombic, consisting of single reflections around 24.5° and 29.2° for 2θ. As expected, calcined silicalite-1 had monoclinic symmetry, which presents double reflections at the same 2θ. As the spectral differences between TS-1 and silicalite-1 are relatively small, particular care was required in the spectral determination. The persistence of the orthorhombic symmetry in the calcined state in the titanium silicalites is indicative of the location of Ti in the zeolite framework [Taramasso et al., 1983]. The XRD pattern of the sample (d) which contains 8 mole% Ti in the reaction mixture exhibited a peak around $2\theta=25.4°$, characteristic of crystalline TiO_2 (anatase). These observations suggest the presence of extra-lattice titanium in the sample (d).

The isomorphous substitution of Si^{4+} by the larger Ti^{4+} ions in the TS-1 framework can cause a slight expansion in the unit cell parameters and volume. Fig. 5 shows the variation of unit cell volume calculated for calcined TS-1 samples with different titanium contents. The unit cell volume increased almost linearly with the mole% of titanium in the reaction mixture up to 3 mol%. A linear increase in the unit cell volume, V, with the increase in the mole% of Ti suggests the presence of titanium in the framework. However, as the titanium content increased above 3 mol%, the linear correlation between titanium content and unit cell volume no longer held. It seems that the upper limit of titanium incorporated in the framework is about 3 mol% as reported [Taramasso et al., 1983].

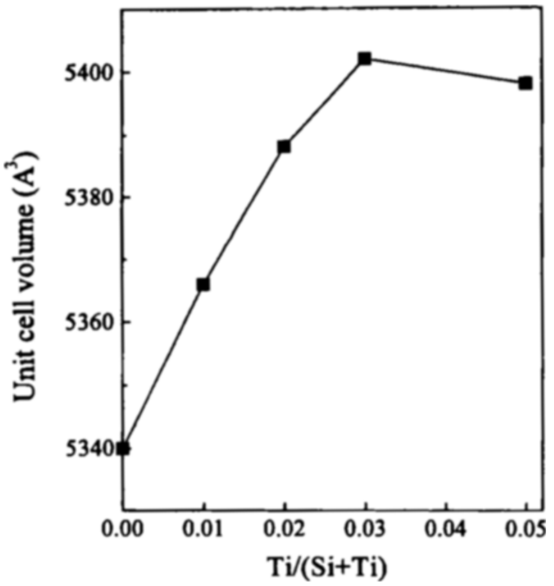

Fig. 5. Unit cell volume of TS-1 as function of titanium content.

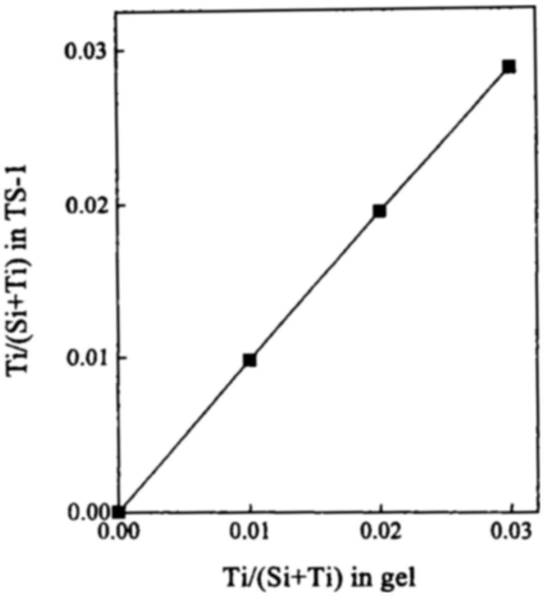

Fig. 6. Relationship between the titanium content of the TS-1 samples and of the gel mixtures.

In this study, a series of samples were prepared by varying the amount of titanium in the synthesis gel. Fig. 6 shows the bulk titanium contents of TS-1 crystals plotted against the titanium contents of their reaction mixtures. It is seen that the titanium contents of TS-1 crystals are linearly correlated with the titanium content of the reaction mixtures and almost equal to those in the reaction mixtures. This indicates that almost all of the Ti in the substrate mixture is incorporated into the framework within a concentration range of Ti less

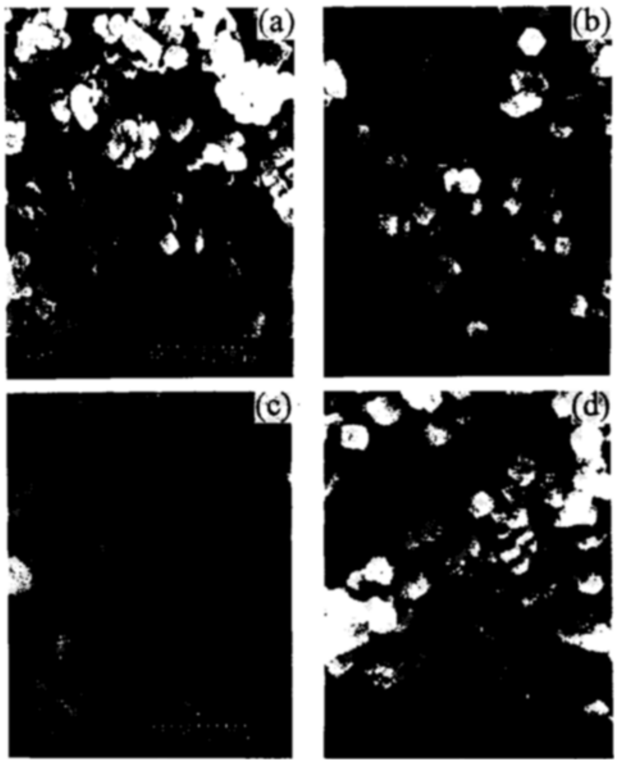

Fig. 7. SEM photographs of Ti-silicalite 1 synthesized with different SiO_2/TiO_2 molar ratios: (a) silicalite-1, (b) SiO_2/TiO_2=99, (c) SiO_2/TiO_2=49, and (d) SiO_2/TiO_2=32.7.

Fig. 8. SEM photographs of Ti-silicalite 1 synthesized with different silica source: (a) TEOS, (b) Ludox AS-40, and (c) Cab-O-Sil.

than about 3 mol%.

Fig. 7 shows the effect of SiO_2/TiO_2 ratio on the morphology of TS-1 crystals. All TS-1 samples were hydrothermally treated under static conditions for 5 days at 175 °C. As can be seen, the change in titanium content in the reaction mixture did not lead to significant modification in the morphology of TS-1, and all TS-1 crystals were about 0.3 μm. This result is in contrast to those of Thangaraj et al. [1991] who reported that the crystal size of TS-1 samples decreases with the amount of Ti in the substrate.

The scanning electron micrographs of TS-1 samples with different silica source are presented in Fig. 8. The TS-1 sample synthesized using TEOS as silica source is the smallest of all TS-1 products and consists of uniform size crystals of 0.3 μm and cuboid shape. An SEM photograph of TS-1 crystals obtained with colloidal silica Ludox AS-40 reveals crystals of approximately 7 μm in size which have twinned coffin shapes. In addition, the crystals are covered with very tiny irregular grains that did not exist in the batch synthesized with TEOS. The sample (c), prepared from Cab-O-Sil, resulted in elongated hexagonal plate shaped crystals of about 23 μm in size.

Fig. 9 shows the framework IR spectrum of calcined TS-1. The IR spectrum of TS-1 showed a characteristic absorption band at 960 cm^{-1}, while the band was not observed in the IR spectra of calcined ZSM-5, silicalite and TiO_2 (rutile, anatase). Kraushaar and van Hoof [1988] also observed the appearance of a new one at 970 cm^{-1} when they incorporated Ti in the framework of highly dealuminated ZSM-5 zeolites via vapor phase $TiCl_4$ treatment. This appearance IR band at 960 cm^{-1} is being interpreted as a stretching vibration of Si-O in $[SiO_4]^{4-}$ units which is perturbed by adjacent titanium such as, $Si\text{-}O^{\delta-}\cdots Ti^{\delta+}$ [Boccuti et al., 1989].

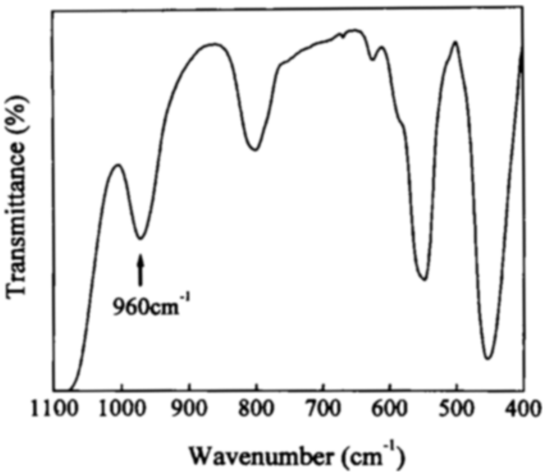

Fig. 9. Infrared spectrum of Ti-silicalite 1.

Fig. 10 shows the ratio of intensities of 960 normalized to 800 cm^{-1} bands with different mole% of Ti in the reaction mixture. For low titanium contents below 3 mol%, the ratio I_{960}/I_{800} increases proportionally with the Ti contents in the reaction mixture, in agreement with previously reported results [Taramasso et al., 1983]. For the two TS-1 samples

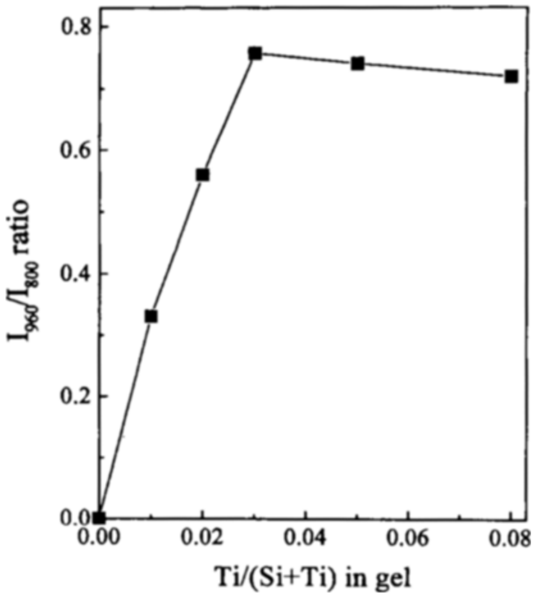

Fig. 10. Ratio of intensities of i.r. bands appearing at 960 and 800 cm^{-1} as a function of titanium content in the synthesis gel.

with relatively high titanium contents, 5 mol% and 8 mol%, however, the ratios of the intensities were lower than the expected values. These two TS-1 samples may contain extraframework titanium species. From these results, it can be speculated that it is difficult to incorporate the titanium above 3 mol% into the TS-1 framework. Similar results were reported by Perego et al. [1986].

Fig. 11 shows the UV-vis diffuse reflectance spectra of the calcined TS-1, pure silicalite-1 and TiO_2 (anatase). The UV-vis diffuse reflectance spectrum of the TS-1 exhibited a strong transition around 210 nm. The band around 210 nm has been assigned to isolated framework titanium in tetrahedral coordination [Boccuti et al., 1989], a broad shoulder around 270 nm has been attributed to the extraframework titanium, and the absorption of TiO_2 (anatase) is observed at 312 nm [Zecchina et al., 1991; Clark, 1968]. The pure silicalite-1 sample did not show such signals at all. The absence of a 270 nm band in the TS-1 samples further confirms the absence of occluded TiO_2 in the framework.

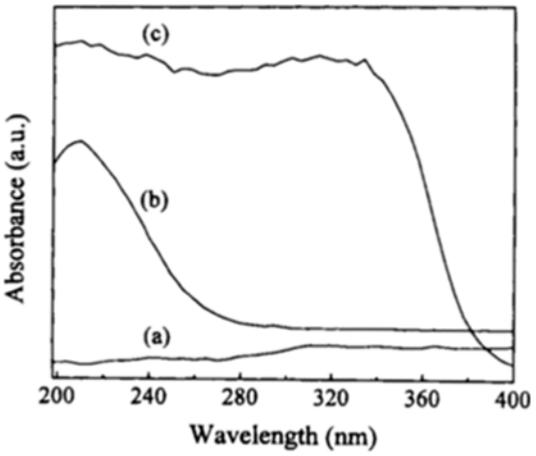

Fig. 11. UV-vis diffuse reflectance spectra of (a) silicalite-1, (b) Ti-silicalite 1, and (c) TiO_2 (anatase).

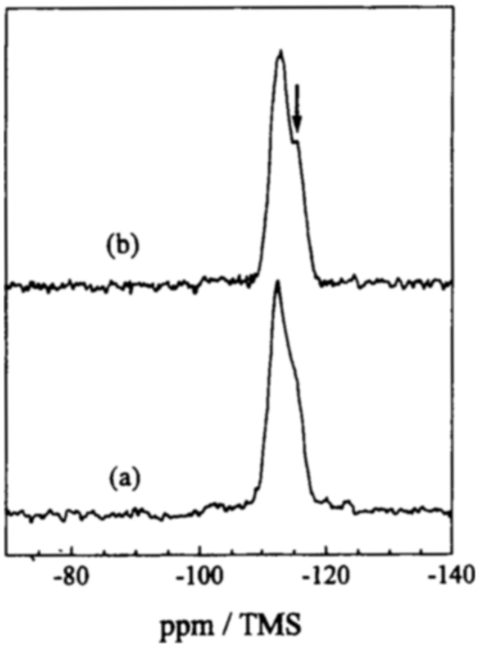

Fig. 12. ^{29}Si MAS NMR spectra of the calcined (a) silicalite-1 and (b) TS-1.

Fig. 12 shows the ^{29}Si MAS NMR spectra of the calcined TS-1 and silicalite-1 samples. The ^{29}Si MAS NMR spectrum of TS-1 showed a characteristic shoulder around $\delta = -116$ ppm that did not appear in the case of pure silicalite-1. The shoulder at -116 ppm had been attributed to arise from the distorted silicon environment in tetrahedra containing Si-O-Ti bonds [Reddy et al., 1990].

Fig. 13 shows XANES spectra for TS-1 and Ti standards. According to Bordiga et al. [1994], the pre-edge absorption of titanium in octahedral geometry is rather weak, while in tetrahedral geometry the strong pre-edge absorption occurs due to the considerable mixing of the 3d and 4p orbitals. The pre-edge absorptions of octahedral titanium, as in rutile and anatase, give rise to three pre-edge peaks usually denoted A_1, A_2 and A_3. A_2 and A_3 have been attributed to the 1s to t_{2g} and e_g electronic transitions, respectively, while the origin of A_1 is still controversial. The intensity of the central peak increases with the increase of site distortion owing to the relaxation of the inversion symmetry around titanium atoms, and there is only one peak for very distorted octahedral sites. A single and intense pre-edge feature is observed in tetra-coordinated titanium compounds because of the lack of inversion symmetry. The environment around Ti also affects the position of the main pre-edge feature (peak A_2), which is shifted to lower energy with decreasing coordination.

The anatase and rutile samples, used as standards in the present work, showed the same pre-edge features as other reports [Blasco et al., 1993; Behrens et al., 1991]. The TS-1 sample synthesized revealed a strong pre-edge absorption around 4968 eV, indicating that most titanium was in a tetrahedral configuration. This XANES spectrum for the TS-1 sample agrees with earlier reports [Schultz et al., 1992; Trong On et al., 1992].

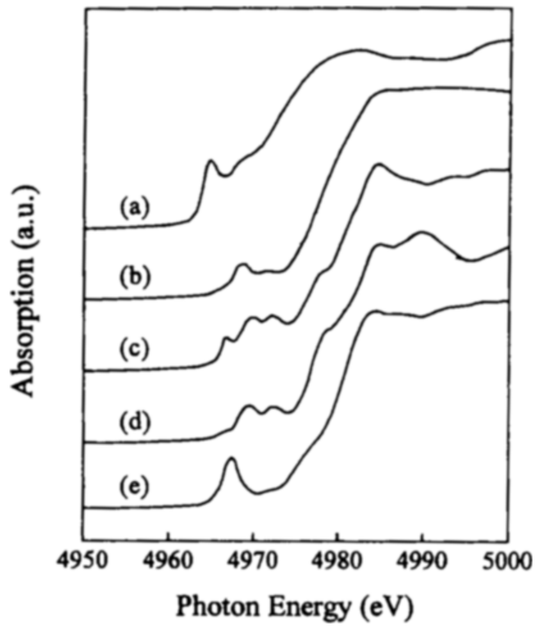

Fig. 13. XANES spectra of (a) Ti foil, (b) TiO_2 (anatase), (c) TiO_2 (rutile), and (d) TS-1.

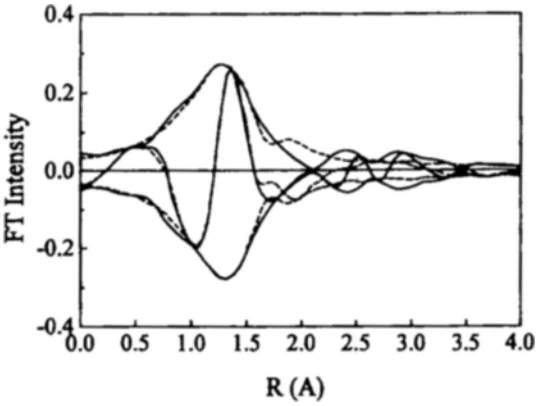

Fig. 14. K^1 weighted Fourier transform of TS-1. Its best fitted spectrum is shown as the dotted line.

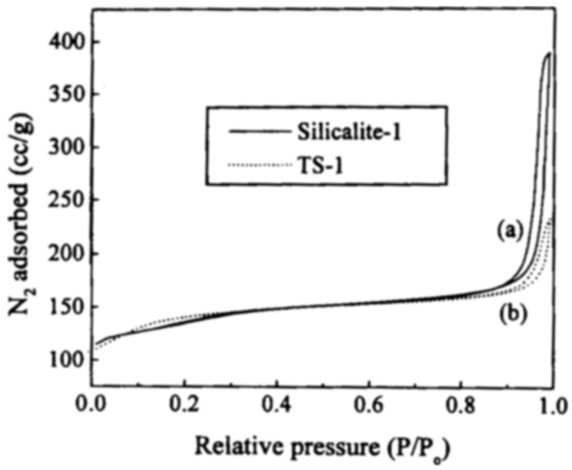

Fig. 15. N_2 adsorption isotherms of the calcined (a) silicalite-1 and (b) TS-1.

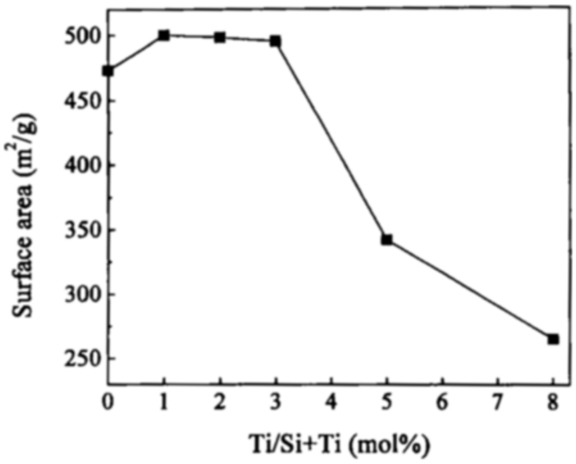

Fig. 16. Specific surface area (BET) of TS-1 with different titanium content.

Quantitative information on the local atomic structure of titanium can be obtained from EXAFS. Fig. 14 shows the results of Fourier transformation (FT) for TS-1 sample calcined in r-space. According to the EXAFS, the Ti-O distance and Ti-O coordination number for TS-1 sample calcined were 1.82 Å and 4.97, respectively. Babonneau et al. [1988] reported that the Ti-O distance for titanium alkoxide in four-fold coordination was 1.81 Å. Lytle and coworkers [Greegor et al., 1983; Yarker et al., 1986] reported that the Ti-O distance in four-fold coordination for titanium silicate glasses was shorter than that in six-fold coordination, 1.80 Å and 1.92 Å, respectively. They also showed that framework titanium in TS-1 adsorbed NH_3 or H_2O in the presence of these molecules, resulting in an increasing in the Ti-O coordination number. EXAFS studies carried out by Behrens et al. [1991] support the idea that the Ti^{+4} in TS-1 is tetrahedrally coordinated when the samples are dehydrated and octahedrally coordinated in the presence of water. Fig. 15 shows the nitrogen adsorption-desorption isotherms of TS-1 and pure silicalite-1, which were calcined at 550 °C in N_2, at liquid nitrogen temperature (77 K). As can be seen, the nitrogen adsorption capacity of TS-1 is similar to that of the pure silicalite-1. The shape of the two isotherms is also similar except for the presence of a large high-pressure hysteresis loop in silicalite-1, which results in a lower micropore volume. Both isotherms are of type I frequently found in zeolitic sorbents. Fig. 16 shows the specific surface area (BET) of TS-1 with different mole% of Ti in the reaction mixture. The specific surface area of TS-1 remained almost constant up to 3 mol% but exhibited a substantial decrease at a titanium content higher than 3 mol%. This is presumably due to the existence of extraframework titanium. From the results of N_2 adsorption measurements on TS-1 samples, it can be seen that the majority of the titanium up to 3 mol% in the reaction mixture is substituted isomorphously into the zeolite framework.

2. Catalytic Reaction Studies

Although various physicochemical techniques have been suggested to characterize titanium in a zeolite framework, it seems that the real fingerprint for this type of material is the catalytic activity for partial oxidation reactions [Blasco et al., 1993;

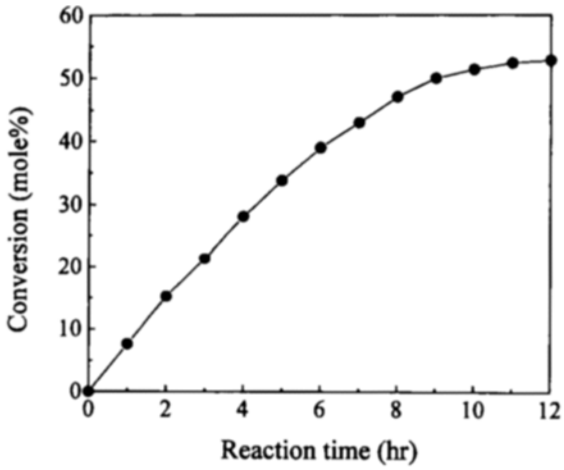

Fig. 17. Oxidation of 2-butanol with hydrogen peroxide on TS-1 catalyst: Reaction time: 323 K.

Reddy et al., 1994; Kim et al., 1993]. It is currently accepted that the zeolites with titanium only in the framework can be catalytically active for partial oxidation of organic compounds in the presence of H_2O_2. That is, if titanium is not in framework, the material is known to be inactive as an oxidation catalyst, regardless of the other physicochemical evidence.

Table 1 shows the results of the oxidation of 2-butanol with H_2O_2 over silicalite-1, HZSM-5, TiO_2 (anatase), TS-1 with varying amounts of titanium. The only product of the reaction is found to be 2-butanone. The conversion of 2-butanol to 2-butanone increased continuously with increases in titanium content of TS-1 up to 3 mol%. The high conversion of 54% was obtained over TS-1 with titanium content of 3 mol%. However, beyond 3 mol%, the conversion decreased slightly. It has been reported [Huybrechts et al., 1992] that a small amount of extraframework TiO_2 can reduce the catalytic activities dramatically, because H_2O_2 decomposes to H_2O and O_2 on the TiO_2 surface. Pure silicalite-1, HZSM-5 and TiO_2 (anatase), which were also examined as catalysts, were found to be inactive for the oxidation of 2-butanol. These results suggest that the Ti^{4+} present in the TS-1 framework is an active site for the oxidation of 2-butanol.

Table 1. Oxidation of 2-butanol with hydrogen peroxide over various catalysts

Samples	Ti/(Si+Ti) in reaction mixture	Conversion (%) of 2-butanol
TS-1	0.01	39
TS-1	0.02	46
TS-1	0.03	54
TS-1	0.05	51
TS-1	0.08	50
Silicalite-1	Si/Ti=∞	No reaction
HZSM-5	Si/Al=75	No reaction
TiO_2 (anatase)	–	No reaction
No catalyst	–	No reaction

Reaction conditions: 2-butanol : 10 ml; H_2O_2 : 10 ml; catalyst : 0.1 g; reaction temp.: 50°C; reaction time : 3 hr.

Table 2. Oxidation of alcohols with hydrogen peroxide on TS-1 catalyst

Substrate	Product yield (mole/g cat/h)		
	Aldehyde	2-Ketone	3-Ketone
1-Butanol	0.0373	–	–
2-Butanol	–	0.1600	–
1-Hexanol	0.0085	–	–
2-Hexanol	–	0.0733	–
3-Hexanol	–	–	0.0267

Reaction conditions: alcohol : 10 ml; H_2O_2 : 10 ml;
catalyst (Si/Ti=32.7): 0.05 g;
reaction temp.: 50 °C; reaction time : 3 hrs

Fig. 17 shows the conversion of 2-butanol as a function of reaction time. As expected, 2-butanol conversion increased steadily with the reaction time, and leveled off at about 53% in 10-12 hours. Based on the fact that the recovered catalyst exhibited its initial activity after calcination at 550 °C, and a substantial amount of hydrogen peroxide still existed in the solution, it is believed the levelling-off of conversion was not due to catalyst deactivation but due to a pore blocking mechanism, as suggested earlier [Kim et al., 1995a; Tatsumi et al., 1990].

Table 2 shows that the reactivity differs in alcohol oxidation depending on the position of the hydroxyl group, and the reaction rate in the same hydroxyl group position decreased following the order of increasing chain length. Between 1-butanol and 2-butanol, the latter showed higher reactivity possibly due to reduced mass transfer resistance in a homogeneous liquid phase, while the former resulted in an immiscible oil and aqueous phase.

Finally, the catalytic activity of the different TS-1 samples was examined for 1-hexene epoxidation using aqueous H_2O_2 as the oxidant. Table 3 presents the results of the epoxidation of 1-hexene over TS-1 catalysts synthesized with TEOS, Ludox AS-40, and Cab-O-Sil as a silica source, respectively. For the 1-hexene epoxidation, only 1,2-epoxyhexane was formed. TS-1(TEOS) catalyst synthesized hydrothermally using TEOS as silica source was much more active for the epoxidation of 1-hexene compared to that of the TS-1 sample which used Ludox AS-40 or Cab-O-Sil as a silica source. In addition to achieving the highest 1-hexene conversion, TS-1(TEOS) also resulted in the highest hydrogen peroxide efficiency. The

Table 3. Catalytic activity of different TS-1 catalysts for 1-hexene epoxidation

Sample	Crystal size (μm)	1-Hexene conversion (%)	H_2O_2 efficiency (%)^a
TS-1 (TEOS)	0.3	8.7	80.3
TS-1 (Ludox AS-40)	7	6.5	69.1
TS-1 (Cab-O-Sil)	23	3.7	47.5

Reaction conditions : catalyst: 1 g; 1-hexene : 20 mmol; H_2O_2 (35 %): 7 mmol; 2-butanol : 100 mmol; reaction temp.: 50 °C; reaction time : 2 hr.

a: Hydrogen peroxide efficiency=moles epoxide formed/moles H_2O_2 consumed.

increase in activity for TS-1(TEOS) over the other TS-1 samples is likely due to the smaller crystal size of TS-1(TEOS). This result is also consistent with our previously reported work which showed that differences in catalytic activity of TS-1 for the ammoximation of cyclohexanone was due to differences in the crystal size and morphology [Kim et al., 1995b]. It seems that the crystal size of TS-1 catalyst is a major factor in the ammoximation of cyclohexanone and epoxidation of 1-hexene. van der Pol et al. [1992] explained that the better reactivity with smaller particle catalyst was due to the differences in diffusion rates in the liquid phase hydroxylation of phenol over different TS-1 catalysts.

All TS-1 samples were active in the 2-butanol oxidation as well as in epoxidation of 1-hexene. However, the pure silicalite-1 was completely inactive in these reactions.

CONCLUSIONS

Titanium silicalite-1 with different titanium content has been synthesized by a hydrothermal method and extensively characterized. It was possible to prepare TS-1 samples using TEOS, Ludox AS-40 and Cab-O-Sil as the silicon source. Small crystals with 0.3 μm of diameter could be obtained with tetraethyl orthosilicate as the silica source.

The presence of a charge transfer at 220 nm in the UV-DRS spectrum of TS-1 indicated that the sample contained framework titanium. ^{29}Si MAS NMR of TS-1 exhibited a well-defined shoulder around $\delta = -116$ ppm due to the distorted Si environment. XANES obtained at the Ti K-edge of TS-1 showed a pre-edge peak at 4967 eV, which was characteristic of tetra-coordinated titanium in the framework. The curve fitting for EXAFS gave a Ti-O coordination number of 4.97 ± 1.0 with a distance of 1.82 ± 0.01 Å.

The TS-1 synthesized in this work showed good catalytic activity for the 1-hexene epoxidation and 2-butanol oxidation with hydrogen peroxide as the oxidizing agent. The chain length of the alcohol affected the oxidation rates, and the position of the hydroxyl group also had a strong effect on the activity of TS-1, such that yields were decreased, in order, as 2-hexanol $\gg$ 3-hexanol > 1-hexanol. The 1-hexene epoxidation activities of TS-1 catalysts were found to be dependent on the crystal size. The TS-1(TEOS) catalyst with smaller crystal size has been shown to be much more active than theh other TS-1(Ludox AS-40/Cab-O-Sil) samples for 1-hexene epoxidation with hydrogen peroxide as oxidant. Titanium present in the TS-1 framework was found to be the active site for the catalytic oxidation reactions.

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