Partial Oxidation of Hydrocarbons Using Titanium Containing Molecular Sieves

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Charles B. Khouw

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To my parents

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Abstract

The objective of this work is to investigate the reaction mechanism of alkane activation on titanium containing, aluminum-free ZSM-5 (TS-1) and to elucidate the relationships between the physicochemical properties of the catalyst and its reactivity. Samples of TS-1 have been synthesized using different methods. The activities of these catalysts for the oxidation of alkanes, alkenes and phenol at temperatures below 100 °C using aqueous H_2O_2 as oxidant are reported and compared to those from other titanium containing materials, e.g., anatase and an amorphous TiO_2-SiO_2 co-precipitate.

Comparisons between the activities of TS-1 and TiO_2-SiO_2 co-precipitate for alkane oxidation and alkene epoxidation using non-aqueous H_2O_2 indicate that the absence of water is crucial for the catalytic activity of silica-supported titanium oxide. Due to the hydrophobicity of TS-1, the concentration of water surrounding the titanium is maintained at low value so that aqueous H_2O_2 can be used as oxidant on this catalyst.

Issues of mechanism of the alkane oxidation on TS-1 are investigated by analyzing the stereoselectivity pattern of *cis*- and *trans*-1,3-dimethylcyclopentane, the "radical clock" rearrangement of ethyl- and isopropylcyclopropane and the effect of oxidants on the catalytic activity of TS-1. The stereoselective reaction pattern of *cis*- and *trans*-1,3-dimethylcyclopentane indicates that radicals are formed during alkane oxyfunctionalization with TS-1. The presence of stereoscrambling without any "radical clock"

rearrangement during alkane oxidation on TS-1 reveals that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur. A proposal for the mechanism of alkane oxidation on TS-1 is given and compared to a mechanism suggested for alkene epoxidation on TS-1 and the TiO_2-SiO_2 coprecipitate. Alkyl hydroperoxides are active as oxidants for alkene epoxidation on the TiO_2-SiO_2 coprecipitate but not for alkane oxidation reactions on both TS-1 and the TiO_2-SiO_2 coprecipitate. A plausible explanation for the above results is provided.

The presence of alkali metal ions in the synthesis mixture of TS-1 completely eliminates the catalytic activity of this material. However, the catalytic activity can be restored by washing the solid with acid solution prior to catalytic testing. The washing removes Na^+ ions from silanol groups adjacent to the framework titanium active centers. Thus, it is postulated that a silanol group in the neighborhood of the titanium atom is a necessary feature for catalytic activity. The acid treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali metal ions, e.g., TPAOH solutions. More importantly, this treatment opens the possibility of synthesizing other titanium containing silicate structures that require the presence of alkali metal ions in the synthesis mixture for their formation.

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CHAPTER ONE

Introduction and Objectives

Introduction

Background

The great abundance of alkanes makes them a very important source of energy and raw materials for the chemical industry. The partial oxidations of alkanes to the desired products, e.g., alcohols, aldehydes and carboxylic acids, have been a challenge for many chemists and chemical engineers for a long time. The difficulty lies in the fact that the partially oxygenated products are more easily oxidized than the alkanes themselves, so that some of the hydrocarbons are ultimately converted to CO and CO_2 unless the conversion is kept to a minimum.

Nature overcomes this difficulty by means of the monooxygenase enzymes that are able to catalyze the hydroxylation of relatively inert C-H bonds in various biogenic and abiogenic organic compounds at room temperature. These enzymes use dioxygen as the oxygen atom donor and with the consumption of two protons and two electrons, they insert one of the oxygen atom into the substrate and use the remainder to form water (Eq. 1).

$$RH + O_2 + 2e^- + 2H^+ \xrightarrow{\text{Monooxygenases}} ROH + H_2O \qquad (1)$$

The well-known monooxygenase enzyme of the cytochrome P-450 family *(1,2)* contains an iron porphyrin prosthetic group as the active site. It uses molecular oxygen and a reducing agent (NADH or NADPH) to oxidize alkanes to alcohols. The C-H bond hydroxylation mechanism is largely dependent upon the intrinsic reactivity of the iron-oxo active species that has been postulated to involve $Fe^{V}=O$ <-> $Fe^{IV}-O^{\bullet}$ species *(3)*. However, the regio- and stereoselectivities are mainly governed by the apoprotein structure. Depending upon the apoprotein structure, some cytochromes P-450 are highly stereoselective, e.g., those involved in steroid hormone biosynthesis, and some are not regioslective, e.g., the one involved in the detoxification of xenobiotics. Another monooxygenase enzyme, methane monooxygenase, is of particular interest since it can oxidize methane, which is the most inert alkane. The active site has been reported to contain a binuclear iron center *(4)* that has a similar structure to hemerithrine *(5)*. The rate determining step has been shown to be the hydroxylation of methane *(6)*, with a kinetic isotope effect (KIE) value of $k_H/k_D = 5$ *(7)*. It has also been demonstrated that methane is oxidized faster than other longer chain alkanes *(8)*. The remarkable selectivity of these enzyme systems is believed to be due to the specific binding sites of the enzymes for particular organic substrates.

Another class of enzymes that are able to activate C-H bonds of some substrates are dioxygenases. These enzymes are capable of inserting both oxygen atoms of dioxygen into the substrates (Eq. 2). With dioxygenases, substrates are oxidized by O_2 and without stoichiometric consumption of any reducing agent. Unfortunately, dioxygenases known so far only catalyze the oxidation of a few number of substrates (fatty acids or phenol) and none has been reported to be able to oxidize inert molecules like alkanes *(9)*.

$$RH + O_2 \xrightarrow{\text{Dioxygenase}} ROOH \qquad (2)$$

Many inorganic materials capable of oxidizing alkanes at relatively low temperature (<100 °C) have been developed *(10)*. The most well-known system is the Fenton reagent *(11)*. The hydroxylation of a wide variety of organic substrates, e.g., alkanes, alcohols, aromatics, at room temperature is accomplished using a ferrous salt as the catalyst and hydrogen peroxide as the oxidizing agent. Subsequent experiments *(12-14)* have shown that the reaction occurs through a hydroxyl radical (OH·) intermediate. The yields of the oxidized substrates are often low due to the nonproductive decomposition of H_2O_2 to water which severely limits the synthetic utility of Fenton's reagent. This is especially true for water-immiscible substrates like alkanes, since the production of hydroxyl radical occurs in the aqueous phase.

The Gif system (after the name of a place in France where this system was invented) that was first reported by Barton *et al.* *(15-20)* is another interesting oxidation system. Similar to Fenton's reagent, this system can oxidize alkanes at room temperature. It consists of iron salt, a reducing agent (usually metallic zinc or iron), pyridine, carboxylic acid (usually acetic acid) as solvent, a proton source and molecular oxygen. Although the acetic acid can be replaced by a number of other acids, pyridine is essential for the reaction to occur. It has been postulated that pyridine acts as an electron transfer agent during the reaction *(21)*. The unique feature of the Gif system is its high selectivity toward the oxidation of the secondary carbon atoms forming ketones as the major products and the high yields obtained compared to those from analogous systems *(22)*. The KIE value for the competitive oxidation of cyclohexane and its deuterated analogue was found to be $k_H/k_D= 2.5$ (18), which is comparable to values obtained from a number of non-porphyrin based systems *(23)* but not to those based on alkoxy or peroxy radical chemistry *(24).* The kinetic isotope measurement, combined with the results from the radical-trapping experiment strengthen the hypothesis that carbon radicals are not involved in the Gif system *(25,26).*

Another strategy that has been studied extensively is the mimicking of enzymatic systems in living organisms. For example, metalloporphyrins and phthalocyanines have been used as models for the active site of cytochrome P-450. These compounds are active catalysts for the oxidation of alkanes and epoxidation of alkenes as well as many other epoxidation reactions *(27-29).* J. T. Groves *et al. (30)* have reported that better results can be achieved by attaching several electron-withdrawing substituents (Cl or F) onto the Fe- and Mn-porphyrins. Besides the electron withdrawing effect of these halogen substituents on the porphyrin ring, they also provide some steric protection to the Fe=O or Mn=O active species that prevents rapid oxidative destruction of the porphyrin ring. Recently, more robust polyhalogenated metalloporphyrins that contain electron withdrawing substituents (Br, Cl, F or SO_3H) on the β-pyrrole positions have been shown to be efficient catalysts for hydrocarbon oxidations *(31).* It is reported that a very high yield of heptane hydroxylation can be obtained (about 80%) within a few minutes at room temperature using iodosylbenzene (PhIO) as the oxidant *(32).* Another interesting example, $Fe_2O(bpy)_4Cl_4$, has also been shown to mimic the binuclear active site of methane-monooxygenase and it is found to catalyze methane to methanol using anhydrous hydrogen peroxide *(33)*.

Additionally, to improve the performance of the aforementioned enzyme mimicking catalyst, immobilization of the metalloporphyrin complex into various supports has been accomplished. Such systems are easily separated from the reaction mixture and recycled. Moreover, they can provide some substrate shape-selectivity and regioselectivity due to specific interactions between the substrates and the inorganic matrix. Several methods for the immobilization of the metalloporphyrin complex have been reported, for examples: polymerization of the porphyrin itself *(34)*, simple adsorption of tetracationic or tetraanionic metalloporphyrins on silica or alumina *(35)* and covalent binding of metalloporphyrins to various supports *(36)*. Suspensions of supported Fe(III) or Mn(III) porphyrins have been reported to be efficient catalysts for the epoxidation of alkenes and the hydroxylation of alkanes by PhIO *(37)*. Another interesting approach to immobilization is the intercalation of the metalloporphyrins into layered minerals such as clays. Barloy *et al. (38)* have reported that tetracationic Mn-porphyrins can be intercalated into the interlayer space of layered minerals by simple ion-exchange with the already present cations. It is noteworthy that Mn-porphyrins supported in this manner give better yields for heptane hydroxylation (60%) than the same Mn-pophyrins simply adsorbed on silica (40%) although the origin of this enhancement is not well understood. Unfortunately, the use of PhIO as the oxidant is not economical for most practical purposes.

Alkane Activation using Zeolite Catalysts

Zeolites are crystalline aluminosilicates constructed from $TO_{4/2}$ tetrahedra (T = tetrahedral atom, e.g., Si, Al); each apical oxygen atom is shared with an adjacent tetrahedron. The tetrahedra are coordinated such that zeolites have open framework structures with high surface areas. Access to the cavities is possible through voids of various sizes. Approximately 70 distinct structures of zeolites and other molecular sieves are known with pore sizes range from 4 Å to 13 Å *(39)*.

The unique structure of zeolites has been proposed to be able to replace the protein portion of natural enzymes. As in natural enzymes, zeolites can modify the reactivity by imposing shape selectivity on the environment of the active complex. Metallophthalocyanines encapsulated in zeolites Y have been proposed as complete enzyme mimics *(3,40-47)*. For example, Parton *et al.* *(40,42)* reported that a mimic of cytochrome P-450 is constructed by *in situ* synthesis of iron phthalocyanine in the supercage of zeolite Y and in the channel of VPI-5. Both of these materials catalyze the formation of a mixture of secondary and/or tertiary alcohols and ketones using *tert*-butyl hydroperoxide as oxidant. The oxidation is regioselective at the outer positions of the carbon chain as a result of the shape selective effect. However, the oxidations rates tend to be low. Recently, Parton *et al.* *(43)* have improved the performance of the catalyst by embedding the zeolite Y that has been incorporated with iron phtallocyanine complexes into a polydimethylsiloxane membrane. The polymer is reported to act as a mimic of the phospholipid membrane in which cytochrome P-450 resides, acting as an interface between two immiscible phases so that no solvent or phase-transfer agent is necessary. It is also reported that this system oxidizes alkanes at room temperature at rates comparable to those of the enzyme *(3)*. The large KIE found on this catalyst suggests that the reaction proceeds through a similar mechanism to the enzymatic process.

The ability of zeolites to be ion exchanged with metal ions shows promise for the development of completely inorganic mimics of various enzymes. Herron prepared a mimic of cytochrome P-450 by exchanging Pd^{+2} and Fe^{+2} ions into different zeolite structures *(48)*. The Pd^{+2} was then reduced to Pd^{o} by reduction in hydrogen. Pd^{o} has been found to convert hydrogen and oxygen into hydrogen peroxide which is used by the Fe^{+2} ions to hydroxylate the organic substrates. Since it is believed that the oxidation actually proceeds via direct combination of hydrogen and oxygen over the Pd^{o} catalyst producing hydrogen peroxide, a direct feed of hydrogen peroxide into iron zeolites yields the same net oxidation effect. It is interesting that selectivity for oxidation toward the end of the octane chain is increased when using zeolite catalysts, especially at the terminal methyl group (unusual for alkane oxidation). It has been postulated that the conformation of the reactant approaching the active sites inside the zeolite framework dictates the selectivity *(48)*. In zeolite A, only the extended linear conformation of *n*-octane is capable of moving through the pores from cage to cage *(49)* where the Fe active sites are located so that the terminus of the molecule is preferentially exposed to the active sites. Moreover, Herron also reported that this catalyst system can oxidize methane to methanol with 0.5 turnovers.

The substitution of other ions for Al^{+3} and Si^{+4} in the zeolite frameworks may change the zeolite properties (although they still have the same topology and channel dimensions). These materials are no longer called zeolites (they are normally called metallosilicates if the Al^{+3} is replaced). Several metals have been claimed to be incorporated into zeolite frameworks, e.g., iron, boron, chromium, beryllium, gallium, germanium, cobalt, vanadium and titanium *(50)*.

Lyons *et al. (51)* have reported that iron sodalite (>10 wt% Fe), with iron both in the framework and exchange positions is an effective catalyst for the oxidation of alkanes. Methane is oxidized to methanol by vapor phase air oxidation at temperature around 400 °C over this catalyst. They also postulated that active iron centers might develop between an ion exchanged iron and a framework iron in the activated iron sodalite. This postulate suggests that these two iron sites might act cooperatively to catalyze methane oxidation to a methanol-rich product mixture via surface ferryl intermediates.

The discovery of titanium substituted ZSM-5 (TS-1) has led to a remarkable progress in new technology for the production of chemicals that are obtained through selective oxidation reactions; especially with aqueous hydrogen peroxide as the oxidant *(52)*. Aromatic hydrocarbons are hydroxylated to phenol or substituted phenols; phenol is hydroxylated to catechol and hydroquinone, olefins are oxidized to the corresponding epoxides, and primary and secondary alcohols are converted to aldehydes and to ketones, respectively. Moreover, Huybrechts *et al. (53)* and Tatsumi *et al. (54)* have also shown that n-alkanes can be oxidized to alcohols and ketones at 100° C over TS-1 with aqueous H_2O_2 as the oxidant. The interesting feature of these oxidations is that all of the reactions use aqueous hydrogen peroxide (40% aqueous H_2O_2 or less) as the oxidant with no loss in selectivity (in most cases is higher than 80% to the desired products).

Not very long after its discovery, TS-1 was used as a commercial catalyst for the production of catechol and hydroquinone from phenol and aqueous H_2O_2 *(52)*. The classical process for the synthesis of hydroquinone creates ~10 kg of salt for every kilogram of hydroquinone produced while the TS-1 catalyzed reaction forms water as the by-product. Hence, even though H_2O_2 is more expensive than O_2, H_2O_2 is often the oxidant of choice for the production of fine chemicals. This is especially true as increasingly stringent environmental constraints are enforced. Another advantage of using TS-1 is the ability of this catalyst to utilize aqueous H_2O_2 as the oxidant, since pure H_2O_2 is very reactive and difficult to handle.

Based on the outstanding results obtained from TS-1, isomorphous substitution of titanium into the molecular sieve framework other than ZSM-5 has been reported. For example, TS-2, which has the ZSM-11 (MEL) topology, has been synthesized and its catalytic activities have been examined *(55-57)*. It is shown that this catalyst has similar catalytic activities as TS-1. The isomorphous substitution of silicon by titanium in zeolite-ß has also been described *(58)*. Because of the large pore size of Ti-ß zeolite (pore dimensions ca. 6.8-7.3 Å), this catalyst is capable of oxidizing cyclododecane with 30% H_2O_2 as the oxidant giving a mixture that primarily consists of cyclododecanol and cyclododecanone. Another example, the mesoporous material Ti-MCM-41 has also been prepared by direct hyrothermal synthesis *(59,60)*. Due to the large pores of Ti-MCM-41, this catalyst is capable of activating norbornene to the corresponding epoxide using tert-butyl hydroperoxide as the oxidant *(59)* as well as converting 2,6-di-*tert*-butylphenol to the corresponding quinone using H_2O_2 as the oxidant *(60)*. More recently, Ti-SSZ-33 has been synthesized by post-synthetic method using $TiCl_4$ vapor *(61)*. Even though this catalyst is active for alkene epoxidation, it is not active for alkane activation. Even worse, on Ti-ZSM-48, although changes in unit cell dimensions and IR data are consistent with the incorporation of titanium into the framework positions, no catalytic activity is observed *(62)*.

Although several titanium containing silicates with various framework topologies have been successfully prepared, the features necessary for good catalytic performance remain unknown, e.g., how is TS-1 able to operate without deactivation in the presence of so much water ? Hence, information concerning the relationships between the physico-chemical properties and the reactivity of various titanium silicates when used in combination with clues on mechanism of the reactions will be necessary to guide further catalyst improvements and the design of new titanium silicate-based oxidation catalysts.

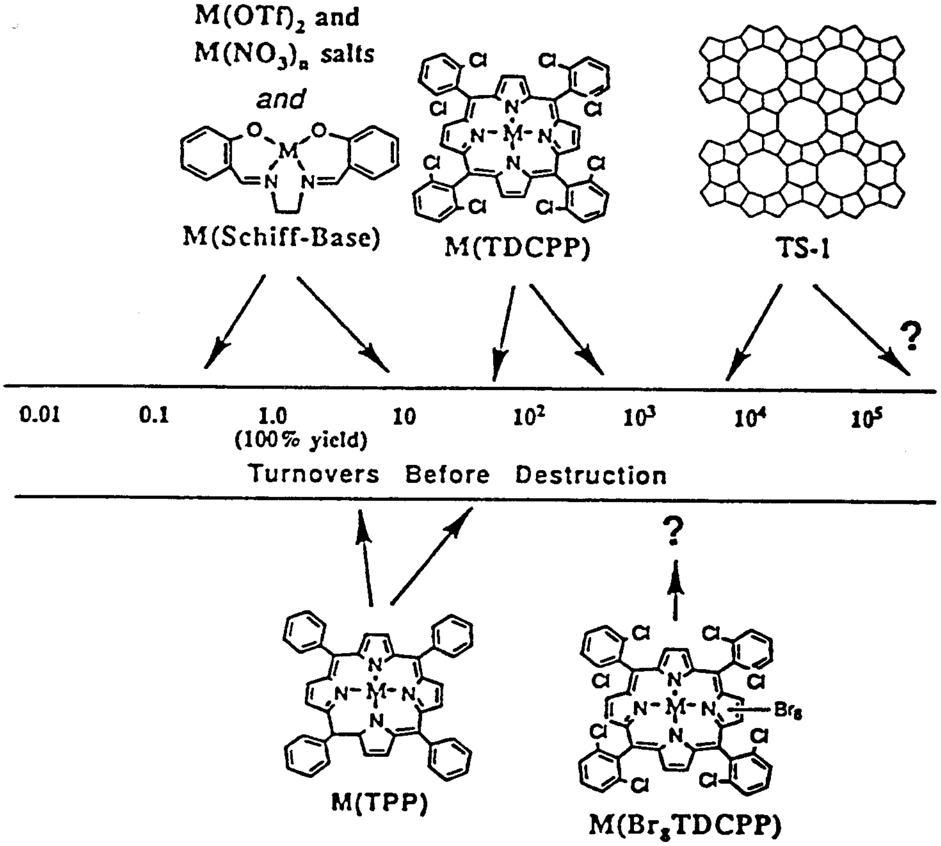
Objectives

The objectives of this work are to understand the reaction mechanism for alkane activation on TS-1 and the relationships between the physicochemical properties of this material and its catalytic activity. We believe that completely inorganic materials, when used as heterogeneous catalysts for partial oxidation reactions, provide several advantages over organic counterparts. Inorganic materials are robust and they do not compete with the reactant as potential substrates for oxidation. Figure 1.1 compares the turnover number (TON) before destruction of various organic and inorganic based catalysts for alkane oxygenations. It shows that TS-1 has the highest TON compared to the other catalysts at temperature below 100 °C (although the number reported for TS-1 is not the actual number of turnovers before destruction but the number when the reaction was stopped). Moreover, inorganic materials extend the possibility of running the reaction at higher temperatures. The use of zeolites as the catalyst provides another advantage, namely, shape selectivity. Based on the remarkable results obtained with TS-1, we envisage that catalysts based on the isomorphous substitution of silicon by titanium in the framework have a bright future. Hence, further study on these materials is merited

Although numerous papers have reported the isomorphous substitution of silicon by titanium in various molecular sieves and various oxidation reactions have been tested on TS-1, the mechanism of the reactions and the relationships between the physicochemical properties and the reactivity are still not well understood, especially for alkane activation.

In the first part (Chapter II) of this work, the physicochemical properties and catalytic activities of TS-1 synthesized by various methods and other titanium containing silicates are examined in order to understand what is necessary as far as the state of titanium in order to be an active catalyst. In Chapter III, the mechanism of alkane activation on TS-1 is studied and compared to the proposed mechanism for alkene epoxidation. The effects of water and alkali metal ions on the catalytic activities of titanium silicates are also discussed. In Chapter IV, the effect of alkali metal ions on the catalytic activity of TS-1 is investigated further. It is also shown here that it is possible to synthesize an active TS-1 by using alkali metal ions in the synthesis gel. Finally, Chapter V reports the synthesis and characterization of titanium silicates with various framework topologies prepared by the new synthesis method that is developed and reported in Chapter IV.

Figure 1.1. **Stability of organic and inorganic catalysts for alkane oxygenation (adapted form Ref. 63).**



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CHAPTER TWO

Selective Oxidation of Alkanes, Alkenes and Phenol with Aqueous H_2O_2 on Titanium Silicate Molecular Sieves

[Khouw, C. B., Li, H. X., Dartt, C. B. and Davis, M. E., *in "Catalytic Selective Oxidation"*

(Oyama, S. T. and Hightower, J. W., Eds.), p. 273. ACS, Washington, D.C., 1993]

Abstract:

Titanium containing pure-silica ZSM-5 (TS-1) materials are synthesized using different methods. The activity of these catalysts for the oxidation of alkanes, alkenes and phenol at temperatures below 100 °C using aqueous H_2O_2 as oxidant is reported. The relationships between the physicochemical and catalytic properties of these titanium silicates are discussed. The effects of added aluminum and sodium on the catalytic activity of TS-1 samples are described. The addition of sodium during the synthesis of TS-1 is detrimental to the catalytic activity while sodium incorporation into preformed TS-1 is not. The framework substitution of aluminum for silicon appears to decrease the amount of framework titanium.

Introduction

The discovery of titanium substituted ZSM-5 (TS-1) and ZSM-11 (TS-2) have led to remarkable progress in oxidation catalysis *(1,2)*. These materials catalyze the oxidation of various organic substrates using aqueous hydrogen peroxide as oxidant. For example, TS-1 is now used commercially for the hydroxylation of phenol to hydroquinone and catechol *(1)*. Additionally, TS-1 has also shown activity for the oxidation of alkanes at temperatures below 100 °C *(3,4)*.

Several preparation methods have been reported for the synthesis of TS-1. In this work, we have investigated the physicochemical properties of TS-1 samples synthesized by different preparation methods and tested these materials as catalysts for the oxidation of *n*-octane, 1-hexene and phenol using aqueous hydrogen peroxide (30 wt%) as oxidant at temperatures below 100 °C. For comparison, TiO_2 (anatase) and TiO_2-SiO_2 coprecipitate have also been studied. The effect of the presence of aluminum and/or sodium on the catalytic activity of TS-1 is also discussed.

Experimental

Samples

TS-1 samples were synthesized by modifications of the preparation methods reported in the patent literatures *(5,6)*. As shown in Table 2.1, samples TS-1(A) and TS-1(B) were crystallized from clear solutions prepared by mixing titaniumbutoxide (TNBT), tetraethylorthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH, 1 M) and double distillated water *(5)*. TNBT, TEOS and TPAOH were purchased from Aldrich. The reaction mixture for the crystallization of TS-1(A) was prepared in an ice-bath, while the one for TS-1(B) was mixed at room temperature. TS-1(C) was synthesized by wetness impregnation of a TiO_2-SiO_2 coprecipitate (Type III, no. 2, obtained from W.R. Grace) with the TPAOH solution *(6)*. Aluminum and/or sodium containing titanium silicate (Al-TS-1, Na-TS-1 and Na-Al-TS-1) were prepared by adding $Al(NO_3)_3$ and/or $NaNO_3$ (from Aldrich) into the TiO_2-SiO_2 coprecipitate/TPAOH mixture. All samples were calcined at 500-550 °C for 10 hours prior to physicochemical characterization and catalytic studies.

The TiO_2 used here was made by hydrolyzing TNBT in distillated H_2O with subsequent calcination at 500 °C. For comparison, pure-silica ZSM-5 was also synthesized in the absence of alkali metal cations. Its synthesis involves the use of tetrapropylammonium bromide (TPABr) and piperazine.

Characterization

X-ray powder diffraction (XRD) patterns were collected on a Scintag XDS-2000 diffractometer that is equipped with a liquid-nitrogen-cooled Germanium solid-state detector using Cu-K_α radiation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet System 800 Spectrometer using KBr pellets that contain 2 wt% of sample. Raman spectra were obtained on a Nicolet Raman accessory. Nitrogen adsorption isotherms were collected at liquid nitrogen temperature (77 K) on an Omnisorp 100 analyzer.

Catalytic Reactions

Phenol hydroxylation was carried out in a batch reactor using 30% aqueous H_2O_2 in acetone at reflux conditions at a temperature of ~80 °C. Hydrogen peroxide was introduced slowly via a syringe pump. The products were analyzed on a HP 5890 Series II Gas Chromatography (GC) equipped with a 50 m long HP-1 (non-polar) capillary column.

The oxidation of *n*-octane and the epoxidation of 1-hexene were performed in a 25 ml Parr reactor using 30% aqueous H_2O_2 as the oxidant and acetone as solvent at 100 °C and 80 °C, respectively, and stirred at 500 RPM. Prior to product analysis, the product mixtures were diluted with acetone in order to obtain a single liquid-phase. The products were analyzed on a HP 5890 Series II GC equipped with a 25 m long HP-FFAP (polar) capillary column.

Results and Discussion

Titanium Silicates

XRD data show that all the TS-1 samples are very crystalline and have the MFI structure. The TiO_2 obtained after calcination has the anatase structure.

Figure 2.1 shows the IR spectra of TS-1(A), TS-1(B), TS-1(C), TiO_2-SiO_2 coprecipitate and pure-silica ZSM-5. The absorption band at 960 cm^{-1} is characteristic of TS-1 *(7)*. All of TS-1 samples used in this study show this band. The band is not present in TiO_2 (not shown in the figure). However, this band is present in TiO_2-SiO_2 which is the precursor to TS-1(C). The relative intensities of the peak at 960 cm^{-1} are listed in Table 2.2.

The catalytic activity of the materials used in this study are shown in Table 2.2. The hydroxylation of phenol produces a mixture of catechol and hydroquinone. The oxidation of *n*-octane yields a mixture of 2-, 3- and 4-octanols and octanones. However, no terminal alcohol is observed. The epoxidation of 1-hexene gives 1,2-epoxy hexane without any hexanediol observed.

The activity data confirm that an IR absorption band at 960 cm^{-1} is a necessary condition for titanium silicates to be active for the selective oxidation of hydrocarbons with aqueous H_2O_2 as suggested by Huybrechts *et al. (8)*. However, this band is not a sufficient condition for predicting the activity of the TS-1 catalyst. Although TS-1(B) and TS-1(C) show intensities for the 960 cm^{-1} band similar to TS-1(A), their activities are different. First of all, the reaction data reveal that TS-1(A) is much more active than TS-1(B) for phenol hydroxylation, while both samples show similar activity for *n*-octane oxidation and 1-hexene epoxidation. Therefore, the presence of the IR band at 960 cm^{-1} in TS-1 catalysts may correlate with the activities for the oxidation of *n*-octane and the epoxidation of 1-hexene but not for phenol hydroxylation. However, note that the amorphous TiO_2-

SiO_2 also has an IR absorption band at 960 cm^{-1} and it does not activate either substrate.

Raman spectra of TS-1(A), TS-1(B) and anatase are shown in Figure 2.2. The spectrum for TS-1(A) (compared to the one for TiO_2 anatase) reveals that TS-1(A) contains anatase. No anatase is detected in TS-1(B) and TS-1(C) (not shown in the figure). The amount of TiO_2 in TS-1(A) is small and probably nanophase because 1) it is not observable by XRD; and 2) the nitrogen adsorption data from TS-1(A) and TS-1(B) indicate that they have pore volumes that are similar to that obtained from pure-silica ZSM-5. Figure 2.3 illustrates the diffuse reflectance UV (DR-UV) spectrum of TS-1(A). The spectrum shows two bands at ~220 nm and ~270 nm, which can be assigned to framework *(9)* and extraframework nanophase *(10)* titanium species, respectively. The other TS-1 samples do not show the band for extraframework titanium. From the catalytic activity data, it appears that the presence of TiO_2 anatase in a titanium silicate (TS-1(A)) does not inhibit its catalytic activity for selective oxidation. Although TiO_2 anatase itself is not active, TS-1(A), which contains TiO_2 anatase, shows higher activity for phenol hydroxylation compared to the other TS-1 catalysts. To study this phenomena, TNBT was hydrolyzed to TiO_2 anatase in the presence of TS-1(C) and pure-silica ZSM-5. Table 2.3 shows the catalytic activity of these materials for phenol hydroxylation. The conversion for phenol hydroxylation was increased by the impregnation of TiO_2 on TS-1(C). However, TiO_2 impregnated pure-silica ZSM-5 does not show any activity. When TiO_2 anatase was physically mixed with TS-1(C), the activity of this physical mixture is the same as pure TS-1(C). These results suggest that

TiO_2 works synergistically with the titanium in the framework of TS-1 for phenol hydroxylation.

In contrast to the high activity of TS-1(C), its amorphous precursor, TiO_2-SiO_2 shows no catalytic activity for alkane, alkene and phenol hydroxylations using aqueous H_2O_2 as oxidant (see Table 2.2). However, TiO_2-SiO_2 is catalytically active for epoxidation using a non-aqueous alkyl hydroperoxide as oxidant. Moreover, it has also been reported that silica supported titanium is used commercially for epoxidation of alkenes using a non-aqueous alkyl hydroperoxide as oxidant *(1)*. It seems that the mechanism for epoxidation is different than for the other reactions shown here. Although the state of Ti in TiO_2-SiO_2 coprecipitate may be the same as the one in TS-1(C) (IR absorption at 960 cm^{-1}), the environmental conditions are different. This may suggest that the presence of titanium in a hydrophobic environment (e.g., inside the ZSM-5 micropores) is necessary for epoxidation of alkenes using aqueous H_2O_2 as oxidant. For alkane and phenol hydroxylations, clearly the Ti environment is unique amongst the materials investigated in this study.

Effect of sodium and aluminum on TS-1

The catalytic activities of aluminum and/or sodium containing TS-1 are depicted in Table 2.4. The data show that the addition of aluminum during the synthesis of TS-1 yields a material (Al-TS-1(D)) that has a lower activity for *n*-octane oxidation and a smaller IR peak ratio. The existence of the acid sites due to the incorporation of aluminum into the framework of

TS-1 may accelerate the decomposition of H_2O_2 to water and oxygen during the reaction. However, reducing the number of acid sites by exchanging with sodium ions only increases the conversion by 1% (Na/Al-TS-1(D)). Therefore, the addition of aluminum into the synthesis mixture most likely reduces the amount of titanium present in the sample.

The addition of sodium during the synthesis of TS-1 completely eliminates the activity for *n*-octane oxidation and also the IR band at 960 cm^{-1} (this IR band is present in the amorphous precursor, TiO_2-SiO_2 coprecipitate). It has been shown *(11)* that the presence of sodium in the synthesis gel prevents the incorporation of titanium into the zeolite framework. However, the addition of sodium after the zeolite crystallizes does not have any significant effect on the catalytic activity, as shown by the catalytic data in Table 2.4.

Conclusions

Several preparation methods have been used to synthesize TS-1. TS-1 is catalytically active for the oxidation of alkanes, alkenes and phenol using aqueous H_2O_2 as oxidant at temperatures below 100 °C. Although some of the physicochemical properties of these materials are similar, significant differences are found amongst the catalysts prepared in different ways. Framework titanium in TS-1 appears to be necessary for alkane and phenol hydroxylation. For epoxidation, the presence of titanium in a hydrophobic environment is necessary for catalytic activity if aqueous H_2O_2

is used as oxidant. Titanium species in the TiO_2-SiO_2 coprecipitate are not catalytically active for the oxidation of alkanes, alkenes and phenol using aqueous H_2O_2 as oxidant.

The addition of aluminum during the synthesis of TS-1 reduces its activity for *n*-octane oxidation. The presence of sodium in the synthesis gel of TS-1 completely eliminates the catalytic activity for alkane oxidation. However, the presence of sodium in preformed TS-1 does not have a significant effect on its catalytic activity.

Figure 2.1. Infrared spectra of titanium containing materials and pure-silica ZSM-5

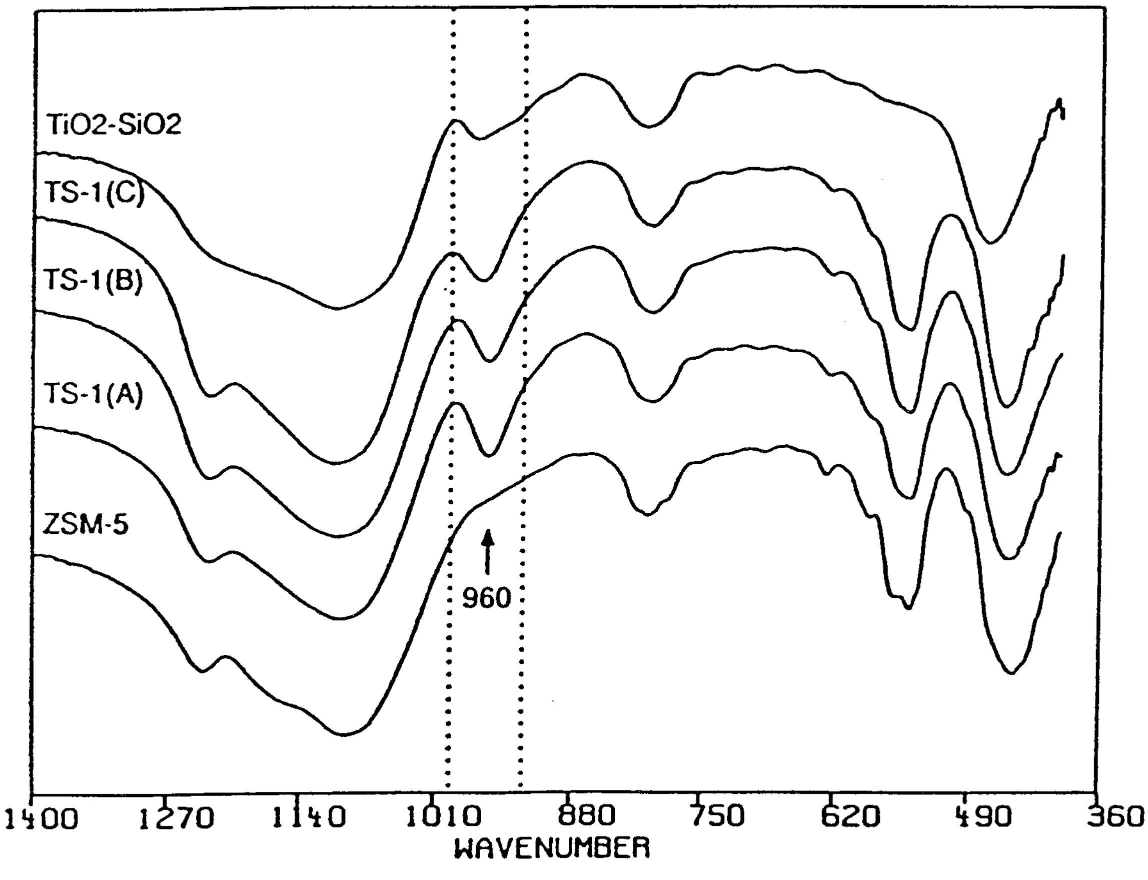

Figure 2.2. Raman spectra of titanium containing materials. (Band marked by * is at 960 cm^{-1})

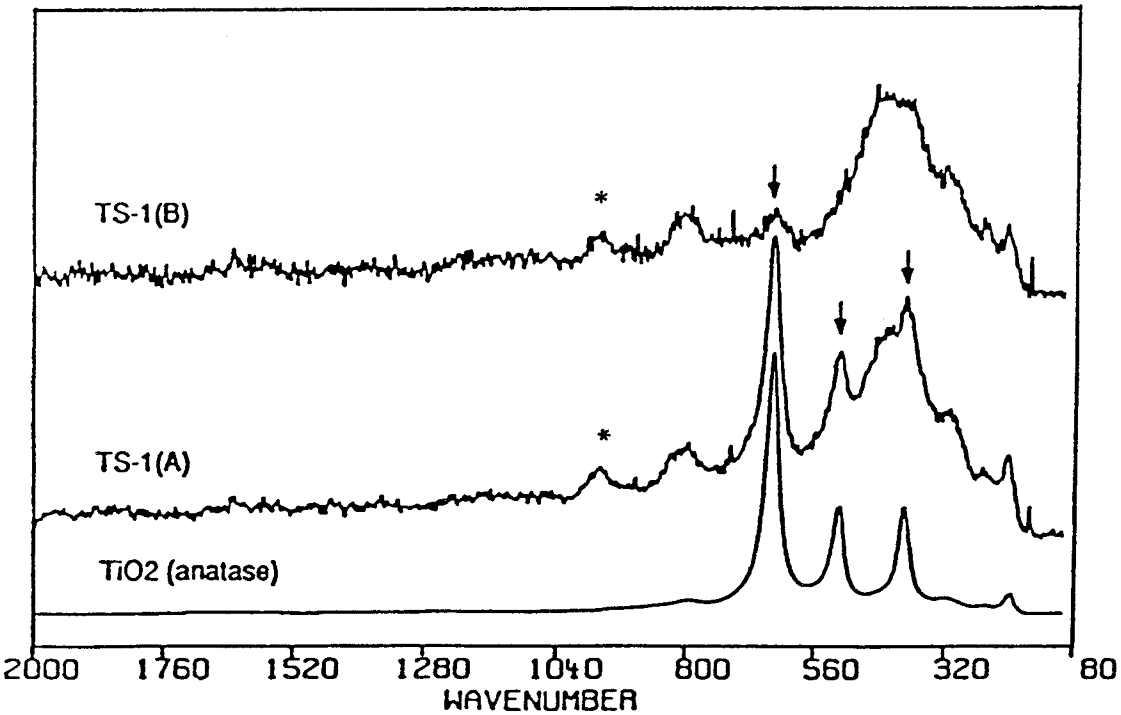

Figure 2.3. DR-UV spectra of TS-1 (A)

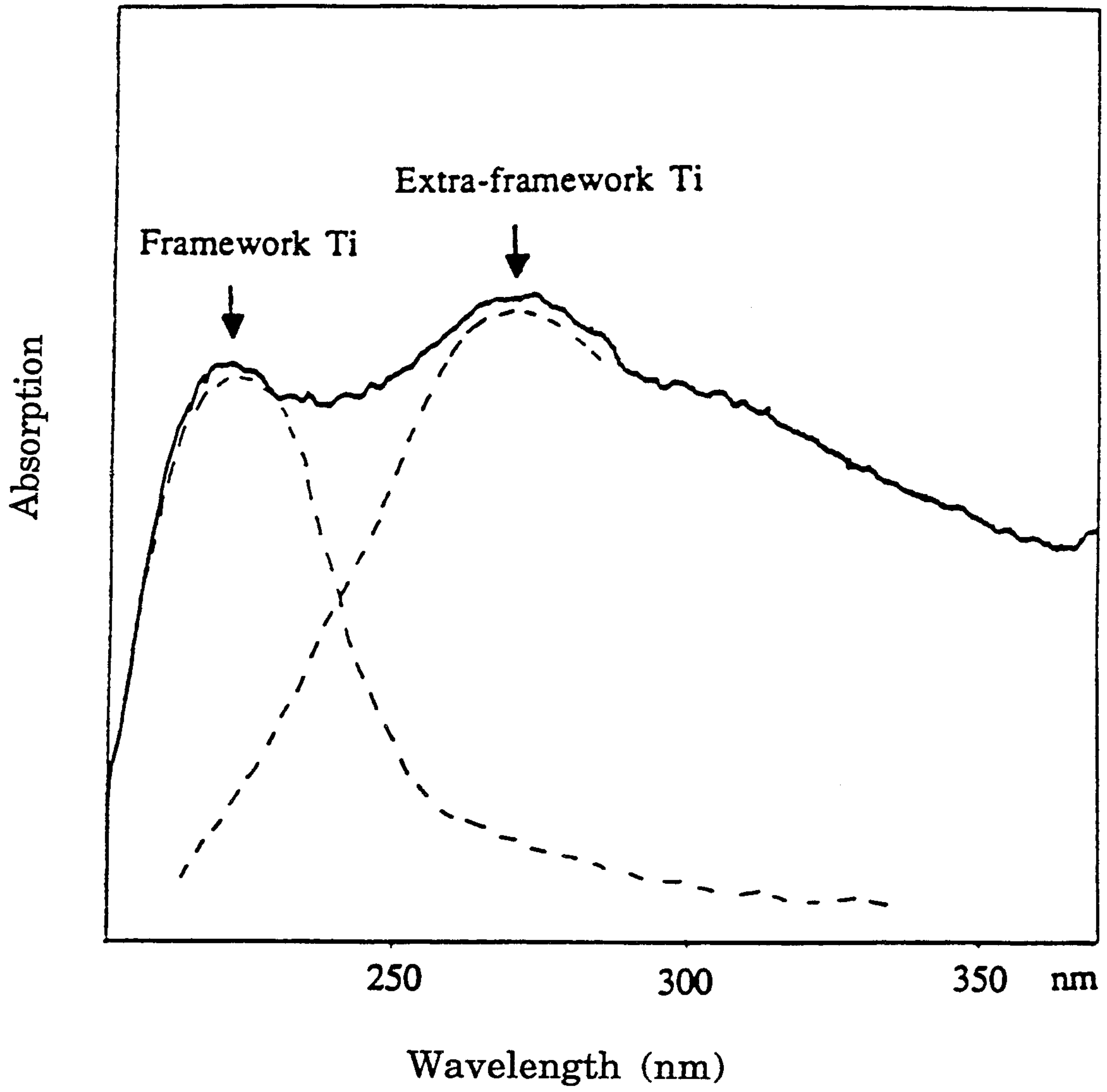

Table 2.1. Sample preparations

Sample	Composition			Crystallization	
	Si/Al	Si/Na	Si/Ti	Temp. (°C)	Time (d)
TS-1(A)[a]	-	-	30	175	10
TS-1(B)[a]	-	-	30	175	4
TS-1(C)[b]	-	-	56	150	10
Al-TS-1(D)[b]	50	-	56	175	7
Al-TS-1(E)[b]	200	-	56	175	7
Na-TS-1[b]	-	10	56	175	7
Na-Al-TS-1[b]	50	10	56	175	7

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[a] Synthesized from a solution containing TEOS, TNBT, TPAOH and water.

[b] Synthesized from a mixture containing TiO_2-SiO_2 (Grace), TPAOH, water and $NaNO_3$ and/or $Al(NO_3)_3$.

Table 2.2. Catalytic hydroxylation of *n*-octane, 1-hexene and phenol with aqueous H_2O_2

Catalyst	Si/Ti[a]	Conversion[b] (%)			IR peak ratio[f]
		n-octane[c]	1-hexene[d]	phenol[e]	
TS-1(A)	30	19	4.3	8	1.11
TS-1(B)	30	15	4.0	3	0.91
TS-1(C)	56	12	4.7	4	1.05
TiO_2-SiO_2	56	<1 (0)[g]	0 (3.1)[g]	0	0.47
TiO_2	0	<1	0	0	0
ZSM-5	-	<1	0	0	0

[a] For TS-1, the values reported are Si/Ti in the solution.

[b] Conversion is based on the substrates.

[c] Reaction conditions: 100 mg catalyst, 30 mmol of *n*-octane, 24 mmol of H_2O_2 (30% in H_2O), 6 ml acetone, 100 °C, stirred at 500 RPM for 3 hr.

[d] Reaction conditions: 100 mg catalyst, 40 mmol of 1-hexene, 29 mmol of H_2O_2 (30% in H_2O), 6 ml acetone, 80 °C, stirred at 500 RPM for 1.5 hr.

[e] Reaction conditions: 100 mg catalyst, 25 mmol of phenol, 5 mmol of H_2O_2 (30% in H_2O, injected at a rate of 1 ml/hr), 5 ml acetone, at reflux temp., stirred for 2 hr.

[f] Ratio of peaks areas of the band at 960 cm^{-1} to the one at 800 cm^{-1}.

[g] *tert*-Butyl hydroperoxide (3 M in 2,2,4 trimetylpentane) is used as oxidant.

Table 2.3. Influence of TiO_2 on the activity of TS-1(C) and pure-silica ZSM-5 for phenol hydroxylation

Catalyst	Phenol Conversion (%)[a]
TS-1(C)	4
TS-1(C) + TiO_2[b]	7
TS-1(C) + TiO_2[c]	4
ZSM-5 + TiO_2[b]	0

[a] Reaction conditions: 200 mg catalyst, 25 mmol of phenol, 5 mmol of H_2O_2 (30% in H_2O, injected at a rate of 1 ml/hr), 5 ml acetone, reflux temp., stirred for 2 hr.

[b] TiO_2 (50%wt) was impregnated by hydrolyzing Ti-butoxide in the presence of uncalcined TS-1(C)/pure-silica ZSM-5, then calcined at 550 °C.

[c] TiO_2 (50%wt) was added as a physical mixture.

Table 2.4. ***n*-Octane oxidation on aluminum and/or sodium containing TS-1**

Catalyst	*n*-Octane Conversion (mol %)	IR peak ratio[a]
Al-TS-1(D)	7	0.36
Al-TS-1(E)	12	0.96
Na-TS-1	0	0
Na-Al-TS-1	0	0
Na/TS-1(C)[b]	11	1.05
Na/Al-TS-1(D)[c]	8	0.36

[a] Ratio of peaks areas of the band at 960 cm^{-1} to the one at 800 cm^{-1}.

[b] TS-1(C) impregnated with $NaNO_3$ (10 %wt).

[c] Al-TS-1(D) exchanged with 1 M solution of $NaNO_3$.

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CHAPTER THREE

Mechanism Studies on the Catalytic Oxidation of Alkanes and Alkenes by Titanium Silicates

[Khouw, C. B., Dartt, C. B., Labinger, J. A. and Davis, M. E., *J. Catal.* **149**, 195 (1994)]

Abstract:

Titanium containing, aluminum-free ZSM-5 (TS-1) and amorphous TiO_2-SiO_2 coprecipitate are investigated as catalysts for the selective oxidation of alkanes and alkenes using a variety of oxidants at temperatures below 100 °C. Comparisons between the activities of TS-1 and the TiO_2-SiO_2 coprecipitate for alkane oxidation and alkene epoxidation using nonaqueous H_2O_2 indicate that the absence of water is crucial for the catalytic activity of silica-supported titanium. Due to the hydrophobicity of TS-1, the concentration of water surrounding the titanium is maintained at low value, and thus TS-1 can be used as an oxidation catalyst with aqueous H_2O_2 as oxidant. Alkyl hydroperoxides are active as oxidants for alkene epoxidation on the TiO_2-SiO_2 coprecipitate but not for alkane oxidation reactions on both TS-1 and the TiO_2-SiO_2 coprecipitate. A plausible explanation for the above results is provided. The presence of stereo-scrambling without any "radical clock" rearrangement during alkane oxidation on TS-1 indicates that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur. A proposal for the mechanism of alkane oxidation on TS-1 is given and compared to a mechanism suggested for alkene epoxidation on TS-1 and the TiO_2-SiO_2 coprecipitate.

Introduction

Titanium substituted ZSM-5 (TS-1) is able to catalyze a wide spectrum of selective oxidation reactions that include aromatic hydroxylations, alkane oxidations and alkene epoxidations *(1-8)*. These conversions are performed using dilute aqueous hydrogen peroxide (40% aqueous H_2O_2 or less) as an oxidant and produce water as the by-product. Additionally, the reactions are operated at relatively low temperatures (< 100 °C) and pressures (~1 atm). Due to the outstanding catalytic activity and selectivity of TS-1, this catalyst has been used commercially in Italy for the production of catechol and hydroquinone from phenol *(1)*.

Numerous studies investigating the nature of the titanium environment in TS-1 have been recently reported. Based on the unit cell expansion, the titanium atoms in TS-1 are believed to be incorporated in the zeolite framework *(9,10)*. Additionally, Boccuti *et al.* *(11)* claim by UV-VIS spectroscopy that the titanium sites in TS-1 are tetrahedrally coordinated (TiO_4) contrary to the previously proposed titanyl structure (Ti=O) *(1)*. Furthermore, Pei *et al.* *(12)* show by EXAFS experiments that the titanium sites in TS-1 are tetrahedrally coordinated. Further EXAFS studies on the nature of titanium in Ti-Al-ß suggest that the coordination number of titanium varies depending upon whether the samples are as-made, calcined, hydrated or dehydrated *(13)* and this is likely to be the case for TS-1 as well. The XPS data of TS-1 show an identical binding energy to that of Ti(IV) in TiO_2-SiO_2 glasses suggesting that the oxidation state of titanium in TS-1 is +4 *(14,15)*.

It has been reported that the oxidation of alkanes on TS-1 occurs only at secondary and tertiary carbons without any activation at primary C-H bonds *(7,16)*. It has also been shown that TS-1 can differentiate linear from branched and cyclic alkanes *(16)*. The selectivity has been attributed to the transport restrictions that inhibit branched/cyclic molecules from passing through the pores and this implies that the catalytic reaction occurs inside the zeolite pores. Although no extensive mechanistic study has been performed for alkane oxidation on TS-1, it has been postulated that the oxidation proceeds through a homolytic mechanism that gives rise to radical intermediates *(7)*. Nevertheless, better knowledge of the mechanism of alkane oxidation on TS-1 is needed in order to understand the limitations of this catalyst, e.g., no terminal activation, and the conditions necessary for a titanium atom to be an active catalyst for alkane oxidation, e.g., why is amorphous TiO_2-SiO_2 not active for alkane activation ?

In this work, we investigate TS-1 and amorphous TiO_2-SiO_2 as catalysts for the selective oxidation of *n*-octane using aqueous H_2O_2 and organic hydroperoxides as the oxidants at temperatures below 100 °C. For comparison, similar experiments have been conducted on the epoxidation of 1-hexene. The mechanism of alkane activation on TS-1 is further investigated by determining the stereoselectivity of this catalyst for *cis*- and *trans*-1,3-dimethylcyclopentane oxidations and by studying the "radical clock" rearrangement of ethyl cyclopropane and iso-propyl cyclopropane during the oxidation reaction. A proposal for the mechanism of alkane hydroxylation is given and compared to a mechanism suggested for olefin epoxidation.

Experimental

Samples

TS-1 was synthesized following the preparation method reported in the patent literature *(9)*. Tetraethylorthotitanate (TEOT) (Johnson Matthey), tetraethylorthosilicate (TEOS) (Aldrich), tetrapropylammonium hydroxide (TPAOH) (1 M, Johnson Matthey) and distilled deionized water were mixed, forming a clear solution with the following composition:

$$\text{TEOS} : \text{TEOT} : \text{TPAOH} : H_2O = 1 : 0.03 : 0.4 : 20$$

This solution was heated in Teflon-lined autoclaves at 175 °C for 10 days. The product was recovered by filtration. Prior to catalytic tests, the material was calcined in air at 550 °C for 8 hours to remove the organic species occluded in the pores of TS-1. The Si/Ti ratio of this sample is 70.

Sodium exchanged TS-1 (Na/TS-1) was prepared by mixing 1 g TS-1 (calcined) with 100 ml of 1.0 M NaOH solution at 25 °C for 24 hours.

TiO_2-SiO_2 coprecipitate (type III, no. 2) was obtained from W. R. Grace. Before catalytic tests, it was dried in air at 200 °C for 24 hours. The Si/Ti ratio of this sample is 56.

TiO_2 anatase (~5 mm) was obtained from Aldrich and the nanophase TiO_2 anatase (~6 nm) was synthesized by the method reported in Ref. 17.

The titanium peroxo-derivative was prepared by mixing 1 g TS-1 with 5 ml aqueous H_2O_2 for 1 minute. The sample was then filtered and dried for 4 hours at room temperature.

Analysis

An X-ray powder diffraction (XRD) pattern of TS-1 was collected on a Scintag XDS-2000 diffractometer equipped with a liquid-nitrogen-cooled Germanium solid-state detector using Cu-K_α radiation. The Fourier transform infrared (FTIR) spectrum was obtained on a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) using the KBr pellet technique (~2.5 wt% TS-1). The Raman spectrum of TS-1 was recorded on the Nicolet Raman accessory for the FTIR system described above (CaF_2 beamsplitter and a liquid-nitrogen-cooled germanium detector). The diffuse reflectance UV (DR-UV) spectrum of TS-1 was obtained on a spectrometer system constructed from an EG&G PAR diode array (1024 element Si) detector and a high-radiance Oriel deuterium lamp. The spectrum was ratioed to a reference spectrum obtained from powdered MgO. Adsorption capacities of various organic molecules were determined with a McBain-Bakr balance. The nitrogen adsorption isotherm were collected at 77 K on an Omnisorp 100 analyzer. Temperature program desorption experiment was performed in a flow type, fixed-bed reactor connected to a Dycor M200M Quadrupole Gas Analyzer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Catalytic Reactions

Epoxidation of 1-hexene using aqueous and anhydrous H_2O_2. The epoxidation of 1-hexene with aqueous H_2O_2 as oxidant was carried out using 20 mg TS-1, 5 mmol 1-hexene, 2 mmol H_2O_2 (30% in H_2O, stabilized) (Mallinkrodt) and 3 ml methyl ethyl ketone (MEK) (Mallinkrodt) as the solvent. The reaction was conducted at 50 °C for 2 hours with vigorous stirring in a 10 ml glass reactor immersed in a constant temperature bath. For the TiO_2-SiO_2 coprecipitate, 0.2 g of catalyst was used and the reaction was carried out at 50 °C for 4 hours. The epoxidation of 1-hexene was performed using anhydrous H_2O_2 and the procedure was the same as listed above except 2 mmol of H_2O_2 was provided from an anhydrous H_2O_2 solution (7.8% in MEK, prepared by adding anhydrous $MgSO_4$ to 30 % aqueous H_2O_2 in MEK solution). The amount of solvent was reduced so that the total amount of the solution was the same as with the reaction using aqueous H_2O_2. Anhydrous $MgSO_4$ (25 mg) was added to the solution as a water adsorbent.

Epoxidation of 1-hexene using alkyl hydroperoxides. A procedure similar to that listed above for the epoxidation with anhydrous H_2O_2 was used for the epoxidation at nonaqueous conditions with 2 mmol of alkyl hydroperoxide used as the oxidant rather than aqueous H_2O_2. The oxidants were *tert*-butyl hydroperoxide (TBHP) (5.5 M in 2,2,4-trimethylpentane) (Aldrich) and *n*-butyl hydroperoxide (NBHP) (synthesized by the method reported in Ref. 18). Anhydrous $MgSO_4$ (25 mg) was introduced into the solution as a water adsorbent. The reaction was conducted for 4 hours at 50 °C with vigorous stirring in a 10 ml glass reactor.

Oxidation of alkanes using aqueous and anhydrous H_2O_2. The oxidations of *n*-octane (Aldrich), ethyl cyclopropane, iso-propylcyclopropane (Wiley Organics), *cis*-1,3-dimethylcyclopentane (Pfaltz and Bauer) and *trans*-1,3-dimethyl-cyclopentane (Wiley Organics) were performed in a 10 ml glass reactor immersed in a constant temperature oil bath. The reaction mixture would typically contain 20 mg TS-1, 0.5 ml alkane, 2.9 mmol H_2O_2 (30% in H_2O, stabilized) and 0.5 ml MEK as the solvent. The reactions were conducted at 80 °C for 24 hours with vigorous stirring except for *n*-octane, where the reaction was carried out for 4 hours. With the TiO_2-SiO_2 co-precipitate, 50 mg of catalyst were used and the reaction was performed at 80 °C for 4 hours. The procedure for the oxidation of *n*-octane using anhydrous H_2O_2 was the same as the outline above for epoxidation except that 2.9 mmol of H_2O_2 (7.8% in MEK) were used. As with the epoxidation reaction, the amount of solvent was reduced so that the total amount of solution was the same as when using aqueous H_2O_2. Finally, 25 mg of anhydrous $MgSO_4$ were added into the solution as a water adsorbent.

Oxidation of n-octane using alkyl hydroperoxides. The procedure was similar to that used for the oxidation of *n*-octane with nonaqueous H_2O_2 except that 2.9 mmol alkyl hydroperoxide were employed as the oxidant.

Oxidation of aromatics. The oxidation of benzene, toluene, ethyl benzene, *para*-xylene and 4-methyl ethylbenzene (Aldrich) were also conducted in a 10 ml glass reactor immersed in a constant temperature oil bath. The reaction mixture would typically contain 20 mg catalyst, 0.5 ml aromatics, 2.9 mmol H_2O_2 (30% in H_2O, stabilized) and 0.5 ml MEK as the solvent. The reactions were run for 6 hours at 80 °C with vigorous agitation.

Solvolysis of cis-2,3-epoxybutane. A typical procedure for the solvolysis of *cis*-2,3-epoxybutane in methanol involved contacting 20 mg catalyst with 0.1 ml *cis*-2,3-epoxybutane, 0.05 ml H_2O_2 (30% in H_2O, stabilized) or 0.1 ml TBHP (5.5 M in 2,2,4-trimethylpentane) and 5 ml methanol as solvent in a 10 ml glass reactor at 30 °C for 4 hours. Both TS-1 and the TiO_2-SiO_2 co-precipitate were used as catalysts.

In all cases mesitylene was used as an internal standard for gas chromatography analysis. Prior to analysis, the product mixtures were diluted with acetone in order to obtain a single, homogeneous phase. The products were analyzed on a HP 5890 Series II Gas Chromatography equipped with a 25 m HP-FFAP (polar) capillary column. For the detection of *cis-* and *trans-*1,3-dimethylcyclopentane reaction products, a 50 m long ß-cyclodextrin capillary column was used. Hydrogen peroxide conversions were measured by titration with 0.1 N $Ce(SO_4)_2$ using ferroin as indicator. Hydrogen peroxide efficiency was calculated by dividing the amount of H_2O_2 converted to form the alcohols and ketones (1 mol of H_2O_2/mol of alcohol formed and 2 mol of H_2O_2/mol of ketone formed) by the amount of H_2O_2 consumed during the reaction.

Results and discussion

To ascertain whether the TS-1 sample prepared here has the same physicochemical and catalytic properties as reported previously *(19,20)*, the sample was extensively characterized. XRD data show that the material is highly crystalline and does not contain other crystalline phases. Both the IR and the Raman spectra of this sample exhibit an absorption band at 960 cm^{-1} that is characteristic of TS-1 *(20,21)*. The Raman spectrum (4,000-200 cm^{-1}) also reveals that no TiO_2 anatase is present in the sample. In addition to Raman spectroscopy, ultraviolet diffuse reflectance (DR-UV) spectroscopy has been used to probe the existence of framework and non-framework titanium *(11,20,22,23)*. It has been reported that DR-UV spectroscopy is one order of magnitude more sensitive than the Raman spectroscopy for detecting non-framework titanium. The DR-UV spectrum for the TS-1 sample is shown in Figure 3.1. The band at 220 nm has been assigned to isolated framework titanium in tetrahedral coordination *(11)*. A very small band appears between 300 nm and 350 nm that suggests the presence of non-framework titanium species (bands at approximately 312 nm have been assigned to anatase *(24)*). From the results of DR-UV and Raman spectroscopy, the amount of the non-framework titanium is very small and must be very close to the limiting concentration that can be detected using DR-UV spectroscopy (has been reported to be ~0.03 wt % for anatase *(22)*). Nitrogen adsorption data are very similar to that obtained with pure-silica ZSM-5, both in the relative pressure for adsorption and the final capacity. These data indicate that the amount of extra-framework titanium species presence in the sample is very small. *n*-Octane oxidation and 1-hexene epoxidation were performed on this catalyst at 80 °C and 50 °C, respectively. The epoxidation of 1-hexene gives only 1,2-epoxy hexane while the oxidation of *n*-octane yields a mixture of 2-, 3-, 4- octanols and octanones without any terminal alcohol being detected, as has been reported previously *(7,8,16,20)*. The conversions of 1-hexene and *n*-octane were 7% and 15%, respectively, while the hydrogen peroxide efficiencies were 64% and 32%, respectively. Since the conversions and the hydrogen peroxide efficiencies are dependent upon all the reaction conditions, e.g., temperature, solvent type *(16)*, no direct literature comparison could be made to these data. Because of this, *n*-octane was reacted at the exact condition used by Clerici *(16)*. Here, we obtained *n*-octane conversion of 18% with a hydrogen peroxide efficiency of 55% as compared to Clerici's conversion of 21% with a hydrogen peroxide efficiency of 63%. Thus, the combined physical characterizations and preliminary catalytic tests show that the TS-1 sample prepared here is of high quality.

It has been shown that anhydrous TBHP can not be used as oxidant for alkane activation with TS-1 *(16)*. To verify that it is not due to the inability of TBHP to enter TS-1 pores, the adsorption capacity of TS-1 for several molecules similar in size to TBHP was measured (we did not wish to use the data for the adsorption of TBHP directly in case there is some type of chemisorption occurring). The results are tabulated in Table 3.1. All the molecules tested adsorb into TS-1. Therefore, TBHP should be able to adsorb into the pores of TS-1. Thus, the lack of activity must not be due to the ability of TBHP to enter the interior of the TS-1 crystals. The hypothesis is supported by the lack of activity of TS-1 when NBHP, for which there is no doubt that it can enter TS-1 pores, is used as the oxidant for *n*-octane oxidation. This result is also in agreement with the fact that TS-1 catalyzes the reaction between *tert*-butyl alcohol and H_2O_2 to form *tert*-butyl hydroperoxide *(25)*.

In Scheme 3.1, we propose a plausible reason why alkylhydroperoxides are not active as oxidants. When aqueous hydrogen peroxide is in contact with TS-1, Clerici *(16)* has postulated that a Ti-peroxo complex is formed. Physicochemical characterizations (XRD, IR, UV, TGA and TPD) and catalytic tests for acidity imply the presence of a titanium peroxo derivative as shown in Scheme 3.1a *(26)*. It is known that titanium (IV) interacts readily with an organic hydroperoxide forming a Ti-alkylperoxo complex *(27)*. Thus, the titanium in TS-1 will most likely interact with organic hydroperoxides unless the position of the active titanium in TS-1 does not allow for the formation of a Ti-alkylperoxo complex due to steric effects. We believe this is unlikely especially when using NBHP. Hence, we postulate that when organic hydroperoxide is used as the oxidant for reactions with TS-1, a Ti-alkylperoxo complex as shown in Scheme 3.1b is formed. Since the complex is located in the intracrystalline void space of TS-1 the alkyl group of the complex could block the reactants from approaching the active titanium sites. Consequently, no activity is possible for either the alkane hydroxylation or olefin epoxidation reactions.

In an attempt to verify the above postulate, both the olefin epoxidation and alkane oxidation reactions were conducted on dry TiO_2-SiO_2 co-precipitate using an alkyl hydroperoxide as the oxidant. The IR spectrum of the TiO_2-SiO_2 coprecipitate shows a band at ~960 cm^{-1} like that observed on TS-1. Moreover, this material can be used as a precursor for the synthesis of TS-1 *(28)*. Hence, some of the titanium on the TiO_2-SiO_2 coprecipitate is most likely in a similar coordination state to the titanium on TS-1. Since this material is not microporous, the reaction will occur at the surface of the catalyst. Steric restrictions arising from the alkyl group on the Ti-alkylperoxo complex are less likely to occur than inside the TS-1 pores. Table 3.2 shows the results from the olefin epoxidation using the TiO_2-SiO_2 coprecipitate catalyst. Although the TiO_2-SiO_2 coprecipitate used here is not optimized for the epoxidation reaction (as compared to the commercial Shell catalyst *(29)*), it shows some activity for 1-hexene epoxidation with either TBHP or NBHP as the oxidant. Thus, TBHP and NBHP must interact with the titanium in the TiO_2-SiO_2 coprecipitate most likely giving an alkyl peroxide. On the other hand, no catalytic activity is observed for alkane activation.

It has been claimed that the Ti-hydroperoxo complex (Scheme 3.1a) has a higher acidity than the pure TS-1 *(16)*. As reported earlier, the presence of acidity by this complex was evaluated by studying the acid-catalyzed solvolysis of *cis*-2,3-epoxybutane to 2-methoxy-3-butanol in methanol. To minimize the amount of H_2O_2 consumed by side reactions with the accompanying formation of organic by-products, we performed this reaction at 30 °C in methanol. Figure 3.2 compares the reactivity of TS-1 for the solvolysis of *cis*-2,3-epoxybutane in the presence and absence of H_2O_2 or TBHP. Similar to that reported previously *(16)*, the effectiveness of TS-1 for the solvolysis of *cis*-2,3-epoxybutane is greatly improved by the presence of H_2O_2. The increase in activity is attributed to the presence a stable five-membered cyclic structure (Scheme 3.1a) which enhances the acidity. Conversely, the presence of TBHP does not have any significant effect on the hydrolysis reaction suggesting that if the Ti-alkylperoxo complex (Scheme 3.1b) is formed, it is less acidic than the Ti-hydroperoxo complex (Scheme 3.1a). These results also imply that the presence of the acidity is not related to the silanol group that is speculated to appear upon the formation of the Ti-hydroperoxo or Ti-alkylperoxo complex. (The presence of this silanol group and its effect on the catalytic behavior of TS-1 is discussed below.) Similar experiments were performed on the TiO_2-SiO_2 coprecipitate (Figure 3.3). As with TS-1, the activity of the TiO_2-SiO_2 coprecipitate for the solvolysis of *cis*-2,3-epoxybutane is greatly enhanced by the presence of H_2O_2 but not by TBHP suggesting that the lack of acidity on the Ti-alkylperoxo complex is not related to steric restrictions inside the TS-1 pores. Comparison between the activity of the two catalysts indicates that TS-1 is much more reactive than TiO_2-SiO_2 coprecipitate for the solvolysis reaction. This may be attributed to a smaller number of titanium sites involved in the reaction on the TiO_2-SiO_2 coprecipitate when compared to TS-1. Based on the difference in acidity between the Ti-alkylperoxo complex and Ti-hydroperoxo complex, it is likely that the acidity of the Ti-hydroperoxo complex is important for the abstraction of hydrogen that occurs in alkane activation. Hence, organic hydroperoxides are active as oxidants for olefin epoxidation on silica supported titanium *(29)* but not for alkane oxidation presumably because no hydrogen abstraction is necessary for epoxidation.

To understand the effect of water on the catalytic activity of TS-1 and the TiO_2-SiO_2 coprecipitate, anhydrous hydrogen peroxide in MEK (less than 1% water) was used as the oxidant for alkane oxidation and alkene epoxidation. For all cases, anhydrous $MgSO_4$ was added into the reaction medium to adsorb the water formed from H_2O_2 decomposition (from catalytic reaction or thermal decomposition). With TS-1, similar catalytic activities are observed for both alkane oxidation and alkene epoxidation whether aqueous H_2O_2 or anhydrous H_2O_2 is used as the oxidant (see Table 3.3). However, with the TiO_2-SiO_2 co-precipitate, activity is observed (with the same product distribution as the one on TS-1) only when anhydrous H_2O_2 is used as the oxidant (Table 3.3). Since the TiO_2-SiO_2 coprecipitate is hydrophilic (contains 50 wt% H_2O when it is exposed to humid air), its surface will preferentially adsorb water instead of the organics. The importance of the absence of H_2O for the epoxidation of olefins is well known for the Shell catalyst in the formation of propylene oxide *(29)* and for the Sharpless asymmetric epoxidation *(30)*. Since TS-1 is hydrophobic, the titanium active sites are effectively screened from bulk water and thus allow for the use of aqueous H_2O_2 as an oxidant. Moreover, this hypothesis is in perfect agreement with the recent paper by Tatsumi *et al.* showing that only alkenes with a hydrophilic group, e.g., unsaturated alcohols, can be adsorbed and oxidized on the TiO_2-SiO_2 coprecipitate using aqueous H_2O_2 as the oxidant due to the hydrophylicity of this material *(31)*.

The results for the decomposition of H_2O_2 on the TiO_2-SiO_2 co-precipiate, pure-silica ZSM-5, calcined TS-1 and uncalcined TS-1 are listed in Table 3.4. In the absence of titanium, less than 4% of the H_2O_2 is decomposed after 12 hours of reaction at 40 °C. The presence of titanium (as in TiO_2-SiO_2 coprecipiate and TS-1) accelerates the decomposition of H_2O_2 in agreement with previously reported results *(20).* This is especially true for the nanophase anatase. Anatase has been reported to catalyze the decomposition of H_2O_2 to water and oxygen *(20)* and both the samples used here do so as well; conversion increases for the higher surface area anatase (nanophase) as expected. As the temperature is increased to 80 °C, the decomposition of H_2O_2 increases for all the catalysts tested especially for TS-1. A temperature-programmed-desorption experiment on TS-1 contacted with H_2O_2 shows that oxygen is formed at approximately 50 °C (measured by mass spectroscopy). This result suggests that TS-1 becomes an active catalyst for the decomposition of H_2O_2 above ~50 °C. This threshold temperature may also be related to the temperature at which TS-1 becomes active for alkane oxidation (unlike epoxidation, TS-1 is not active for alkane oxidation at room temperature). The presence of an oxidizable substrate, e.g., *n*-octane, increases the conversion of H_2O_2 since in this case two competing reactions occur, the decomposition of H_2O_2 and the oxyfunctionalization of the substrate. However, when aromatics, e.g., toluene, *para*-xylene, are presence as the oxidizable substrate, the H_2O_2 conversion decreases. It is likely that the aromatic molecules are blocking the H_2O_2 molecules from reacting inside the TS-1 pores since the H_2O_2 conversion for TS-1 when aromatics are presence in the reaction mixture is similar to that of the uncalcined TS-1.

In order to understand further the mechanism of alkane activation on TS-1, the regioselectivity pattern of oxidizing a series of substrates was investigated. It has been reported that only monooxyfunctionalization of alkanes are observed *(7,16,20)*. Moreover hydroxylation of alkanes on TS-1 occurs preferentially at the tertiary and secondary positions without noticeable amounts of terminal oxygenated products. Table 3.5 shows the catalytic activity of TS-1 for the oxidation of various aromatic compounds. These data are in agreement with those reported previously *(16,32)*. The results show that for toluene and *para*-xylene, no activation occurs at the methyl group although this methyl group (benzylic carbon) has the weakest C-H bond. The lack of activity at the terminal position must therefore be inherent in the reaction mechanism of TS-1 and not solely due to the differences among the activation energies. For ethylbenzene, activation occurs both at the benzylic carbon and the benzene ring. Reaction using both *n*-octane and benzene in the same mixture shows that both substrates are functionalized, i.e., no significant for either benzene or *n*-octane is observed (Table 3.6). The activity for both *para*-xylene and 4-methylethylbenzene is lower than that of the other molecules investigated and can be attributed to the lower diffusivity of *para*-xylene and 4-methylethylbenzene in TS-1 (Table 3.5).

Comparison of the selectivities obtained for oxyfunctionalization with TS-1 to other oxidation catalysts reveals that the regioselectivity pattern of TS-1 is similar to that of vanadium (V) peroxo complexes (e.g., $[VO(O_2)(Pic)_2]^-A^+L$ $\{A^+ = H^+, PPh_4^+;\ L = H_2O$, hexamethylphosphoric triamide; Pic = pyridine-2-carboxylate$\}$) *(33)*. Both catalysts do not activate terminal C-H bonds. However, for the latter system, stereoscrambling occurs for both alkane oxidation and alkene epoxidation. The mechanism for both reactions is believed to proceed through radical intermediates and the active species is tentatively attributed to a V^{IV}-$OO^{\bullet}$ radical which adds to double bonds and aromatic nuclei or abstracts hydrogen atoms from alkanes to give carbon radical intermediates. Thus, we speculate that the mechanism of TS-1 for alkane oxidation is similar to that of vanadium (V) peroxo complexes catalyst but not for alkene epoxidation since no stereoscrambling is observed for alkene epoxidation on TS-1 *(34,35)*.

The color change of TS-1 from white to yellow upon contact with aqueous hydrogen peroxide suggests the formation of titanium peroxo derivatives which is supported by the results from UV-VIS spectroscopy *(36)*. To test whether this peroxo-derivative is the active species, the following experiment was performed. TS-1 was contacted with aqueous hydrogen peroxide and the color changed to yellow. After drying at room temperature for approximately 4 hours, the TS-1 sample, which was still yellow, was contacted with MEK and *n*-octane at 80 °C without any oxidant present in the solution. During the reaction, the color gradually faded and eventually disappeared after two hours of reaction. Analysis of the products indicates that alcohols and ketones were formed in the reaction. This result shows that a titanium peroxo derivative is active as the oxidant for alkane oxidation suggesting that either it is the active species or the precursor to the active species, in agreement with the generally accepted concepts *(1,7,32,37,38)*.

As mentioned earlier, the reaction for olefin epoxidation proceeds without any stereoscrambling, e.g., *cis*-epoxide is formed only from *cis*-olefin

(34,35). Additionally, it has been postulated that oxidation of alkanes and epoxidation of olefins on TS-1 proceed through different pathways *(20)*. Table 3.7 reports the results revealing the stereoselectivity of TS-1 in an alkane activation. It is shown that reacting *cis*-1,3-dimethylcyclopentane yields both *cis*- and *trans*-1,3-dimethylcyclopentanol. The same products are obtained when *trans*-1,3-dimethylcyclopentane is used as the reactant. The stereoscrambling suggests that alkane oxidation on TS-1 proceeds through a radical mechanism, in agreement with the previously postulated mechanism *(7)*.

The unimolecular rearrangements of radical intermediates have been widely used as a tool to study the mechanisms of reactions that proceed through radical intermediates *(39)*. This method is widely known as the "radical clock" technique. In this technique, the production of rearranged products indicates that a radical intermediate with a longer lifetime than the time required for radical rearrangement is formed in the reaction pathway. Usually, molecules with especially fast radical rearrangements are used so that competing reactions will not intercept the first-formed radical before rearrangement. Here, two hydrocarbon substrates, ethylcyclopropane and iso-propylcyclopropane (with a reactive secondary and tertiary carbon, respectively), were employed as probes in the oxidation catalyzed by TS-1. At 80 °C, the ring opening reaction for these two molecules has a rate constant (k_r) of 3.2×10^8 and 3.7×10^8 s^{-1}, respectively (calculated from the data in Ref. 40). For each case, if a free radical is formed in the reaction pathway, it could either rebound to form the unrearranged product or ring-open to afford the rearranged products as depicted in Scheme 3.2 for ethylcyclopropane depending on the lifetime of the radical intermediates.

Table 3.8 shows the results from the "radical clock" experiments. Analysis of the products reveals that ethylcyclopropane is converted only to 1-cyclopropylethanol and 1-cyclopropylethanone without any rearrangement products being detected. Additionally, iso-propylcyclopropane is converted to 1-cyclopropylisopropanol and another product (which most likely is from the cracking of the alcohol and not from the further reaction of the rearrangement product), however no species due to rearrangement are detected. Moreover, other possible products such as olefins, epoxides and oligomers that may be formed from further reactions of the rearrangement products are not detected either. These observations combined with the results from the stereoselectivity of TS-1 toward *cis*- and *trans*-1,3-dimethylcyclopentane oxidation suggests that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur. A similar observation has been reported for the stereoselectivity pattern of the methane monooxygenase enzyme for alkane activation in which stereoscrambling occurs but no "radical clock" rearrangement is detected *(41,42)*.

It has been shown that sodium has a significant effect on the catalytic activity of TS-1 *(19)*. Further study on the effect of sodium on the catalytic activity of TS-1 indicates that TS-1 exchanged with sodium hydroxide (Na/TS-1) is inactive for both alkane oxidation and alkene epoxidation (Table 3.9). Unlike TS-1, Na/TS-1 does not change color upon contact with aqueous H_2O_2 suggesting that a titanium hydroperoxo complex similar to that as the one on TS-1 is not present. The IR spectrum of the Na/TS-1 shows that the band at 960 cm^{-1} is shifted and converted into a shoulder at ~985 cm^{-1} as shown in Figure 3.4. The IR band at 960 cm^{-1} was originally assigned to the stretching vibration of $Si\text{-}O^{\delta-}...Ti^{\delta+}$ *(11)*. However, more recently, Camblor *et al.* *(13)* have reported that this band is better assigned to the stretching vibration of the $Si\text{-}O^-$ groups where H^+, tetraethylammonium$^+$ and/or Na^+ can act as the countercations. This assignment is in agreement with the fact that the IR band of the calcined sample is different than that of the uncalcined one and also consistent with the shifting of the IR band for Na/TS-1. Moreover, it also suggests that sodium exchange on TS-1 occurs at the silanol group as illustrated in Scheme 3.3. The absence of catalytic activity on Na/TS-1 suggest that the presence of a silanol group in the neighborhood of titanium is necessary for both alkane oxidation and alkene epoxidation activity.

Clerici and Ingallina *(43)* have postulated that epoxidation on TS-1 proceeds through a heterolytic peracid-like mechanism and that the active species is a five-membered cyclic structure which is formed by a titanium hydroperoxo (Ti-OOH) and a protic molecule ROH (Scheme 3.1a). The proposed mechanism for the alkene epoxidation is depicted in Scheme 3.4. On the basis of steric arguments, Clerici and Ingallina argue that the oxygen atom closer to the hydrogen atom (Scheme 3.4a) is transferred directly from the titanium hydroperoxo complex into the epoxide. However, there is really no strong evidence to rule out oxygen transfer from the oxygen atom closer to the titanium (Scheme 3.4b). Thus, the questions of which oxygen atom is transferred to the olefin remains unresolved at this time. As reported earlier the presence of solvents (ROH, $R_1R_2C=O$) have a significant effect on the catalytic activity of TS-1 for alkene epoxidation *(43)*. However in the absence of solvents, TS-1 still shows activity for alkene epoxidation (~5 % conversion versus 7% conversion of 1-hexene in MEK), indicating that organic solvent is not necessary for activity (it only enhances the catalytic activity).

The mechanism for alkane oxidation remains far less clear. Assuming the same titanium hydroperoxo complex is involved, two possible mechanisms are illustrated in Scheme 3.5a & 3.5b. The first (Scheme 3.5a) involves an alkyl(hydroperoxo)-titanium(IV) intermediate, which rearranges to an (alkoxo)(hydroxo)titanium(IV) species. Such a route has precedence in the organometallic literature (although the properties of the metal centers involved there are probably quite different from that here). Activation of C–H bonds at high-valent, early transition metals such as Sc(III) are well known *(44)*; also, the hafnium(IV) complexes $(h^5\text{-}C_5Me_5)_2Hf(R)(OOCMe_3)$ readily rearrange to $(h^5\text{-}C_5Me_5)_2Hf(OR)(OCMe_3)$) for a variety of alkyl groups R *(45)*. On the other hand, such a route would not explain either the stereochemical scrambling or the regioselectivity: retention of configuration and preference for terminal activation would be expected.

The second mechanism (Scheme 3.5b) proceeds via homolytic $H^\bullet$ abstraction by a coordinated peroxo group, which may have some superoxo-like character *(36)*. (Such a species is not accessible from ROOH, consistent with the lack of alkane activation by that reagent.) This step generates an alkyl radical, accompanied by reduction to Ti(III). Ti(III) centers have been generated in TS-1, by reduction with CO, under fairly mild conditions *(46)*. The subsequent O–O bond cleavage to form the C–O bond would be facilitated by formation of a relatively stable Ti=O bond. The alkyl radical must either have a very short lifetime or somehow be restricted within the zeolite to account for the fact that stereoscrambling but not radical clock rearrangement is observed.

This radical mechanism would also be consistent with low reactivity at terminal positions, but it does not fully account for the complete absence of terminal activation, especially at benzylic C–H bonds as in toluene; the explanation remains uncertain at this time.

Summary

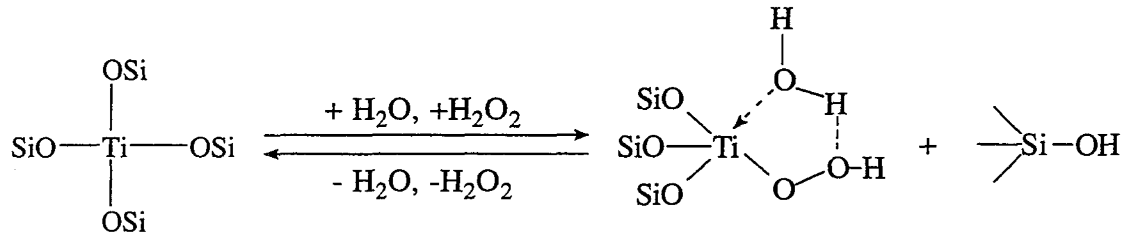
We have shown that the absence of water is crucial for the catalytic activity of silica supported titanium as has been known for quite some time *(29)*. Since TS-1 is hydrophobic, the concentration of water surrounding the titanium is maintained at a low value. Thus, TS-1 can be used as an oxidation catalyst with aqueous H_2O_2 as the oxidant. The titanium atoms on TS-1 are incorporated in the zeolite framework and hence they are all isolated. Isolated titanium minimizes H_2O_2 decomposition at low temperatures and enables all the titanium to be exposed to reaction environment. Our results show that if there is a low concentration of titanium in an amorphous TiO_2-SiO_2 coprecipitate, the state of the titanium is not much different than in TS-1. Recently, EXAFS data suggest this is true as well *(47)*. However, if the concentration of titanium is increased, phase separated TiO_2 is formed *(47)* and these types of titanium centers are not active for partial oxidation. Consequently, TS-1 is much more reactive than the TiO_2-SiO_2 coprecipitate for partial oxidation reactions even when non-aqueous H_2O_2 is used as the oxidant.

The lack of epoxidation activity on TS-1 when alkyl hydroperoxides are used as the oxidants is attributed to the bulkiness of the alkyl group on the Ti-alkylperoxo complex that blocks the reactants from approaching the active titanium. On the TiO_2-SiO_2 coprecipitate, no activity is observed for alkane oxidation when alkyl hydroperoxide is used as the oxidant. This may be due to the lack of hydrogen abstraction for the titanium alkylperoxo complex. Since no hydrogen abstraction occurs in epoxidation, non-aqueous alkyl hydroperoxide is active as an oxidant for alkene epoxidation on the TiO_2-SiO_2 coprecipitate.

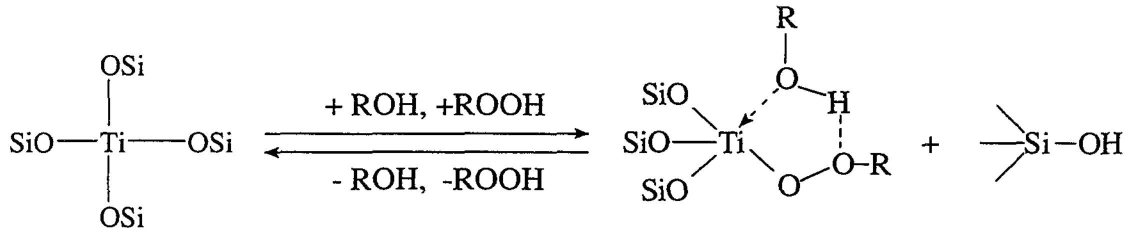
The stereoselectivity differences between alkane oxidation and alkene epoxidation on TS-1 suggests that these reactions proceed through different mechanisms. The presence of stereoscrambling without any "radical clock" rearrangement during alkane oxidation indicates that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur.

Scheme 3.1. Possible interaction between TS-1 and aqueous H_2O_2 or ROOH

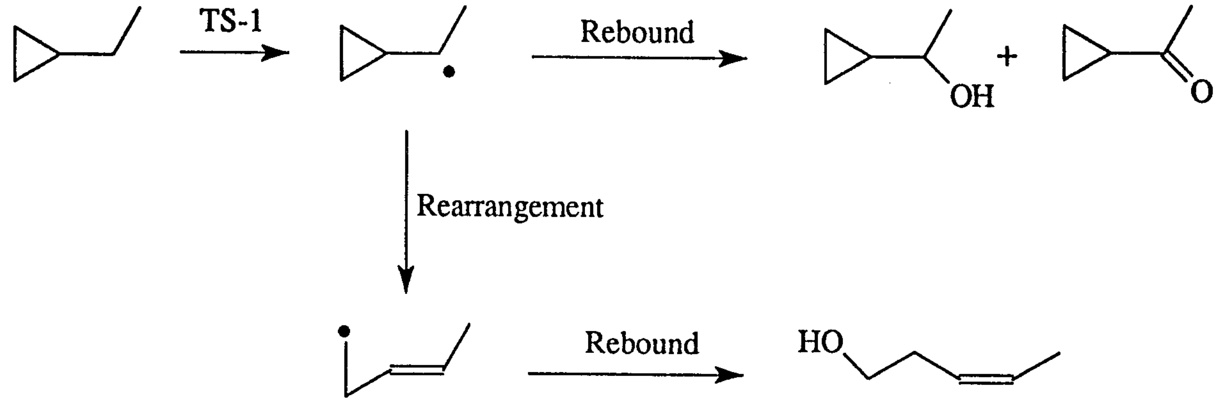
a. Aqueous H_2O_2 is used as oxidant (adapted from Ref. 16)



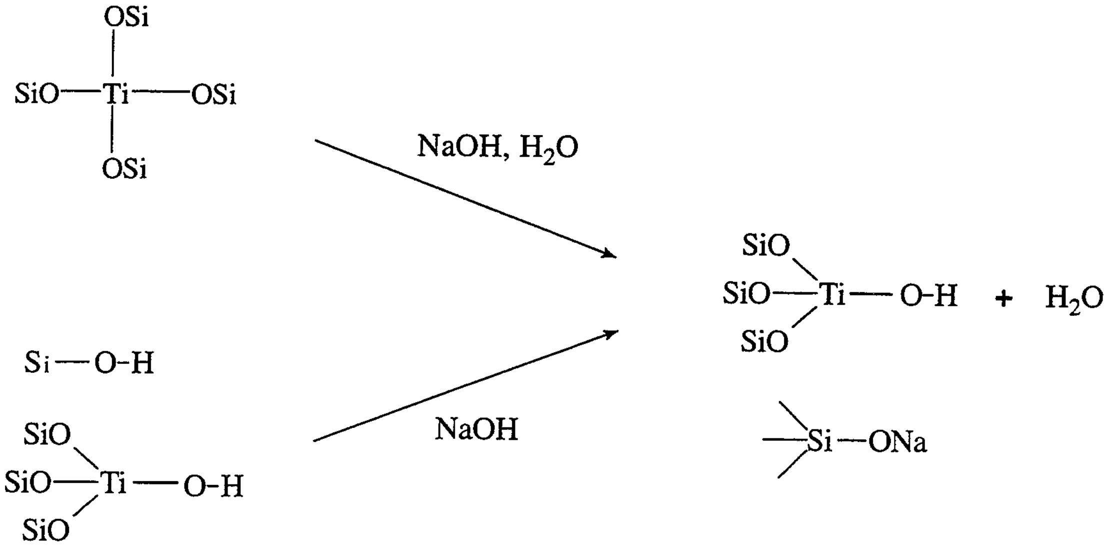
b. ROOH is used as oxidant



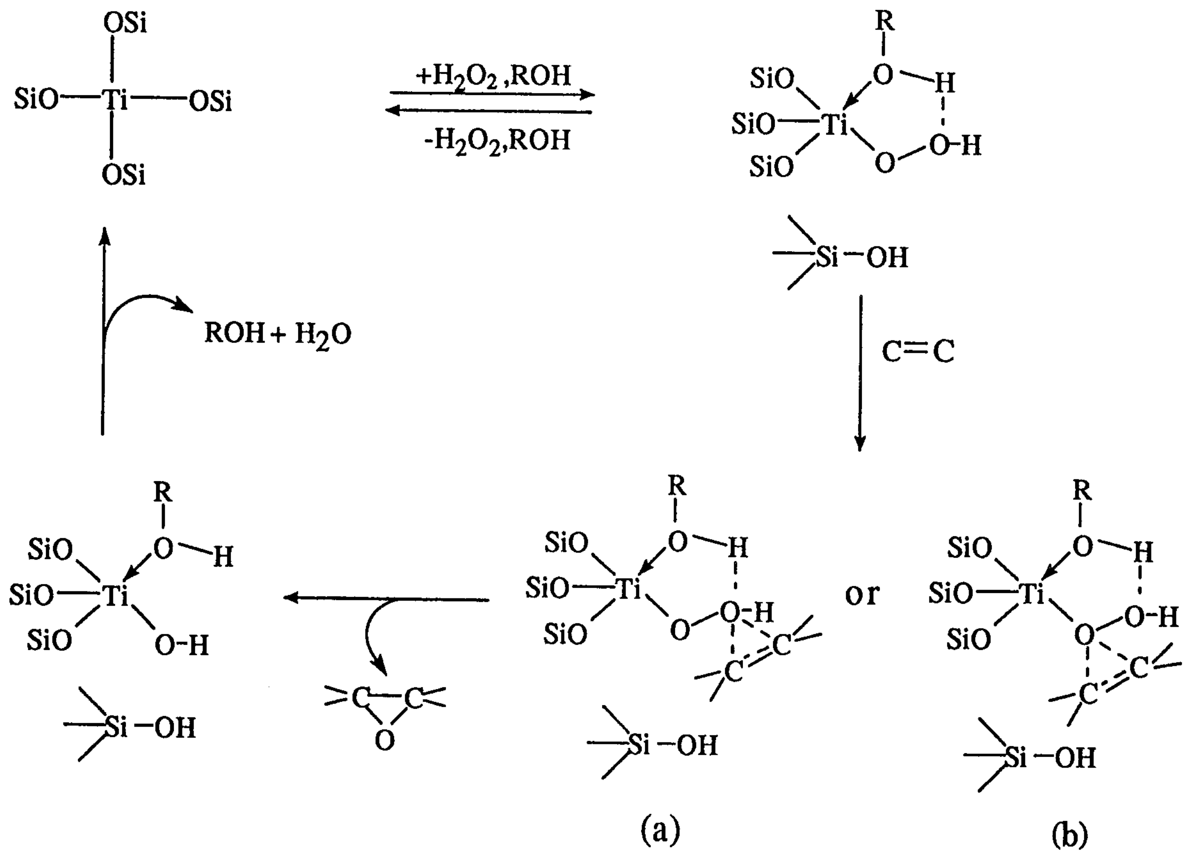
Scheme 3.2. "Radical clock" Technique



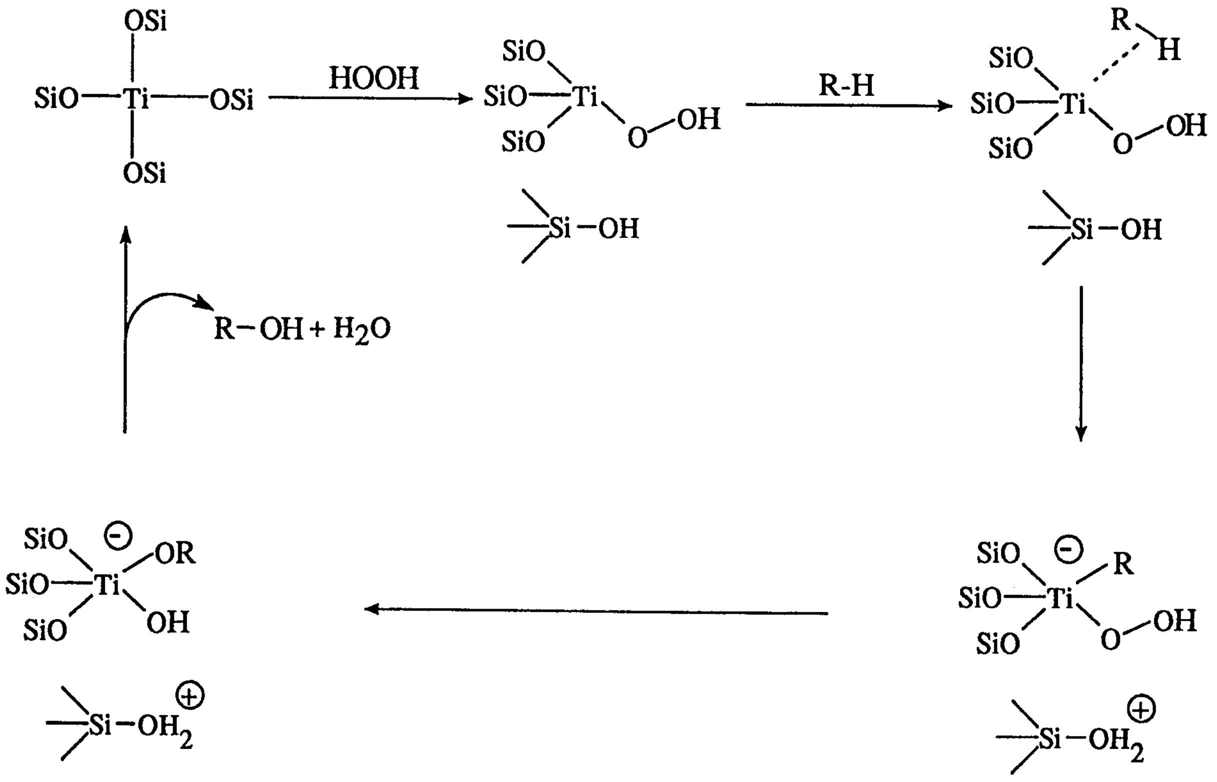
Scheme 3.3. TS-1 exchanged with NaOH



Scheme 3.4. Possible mechanism for alkene epoxidation on TS-1 (adapted from Ref. 43)



Scheme 3.5a. Possible mechanism for alkane activation on TS-1



Scheme 3.5b. Possible mechanism for alkane activation on TS-1

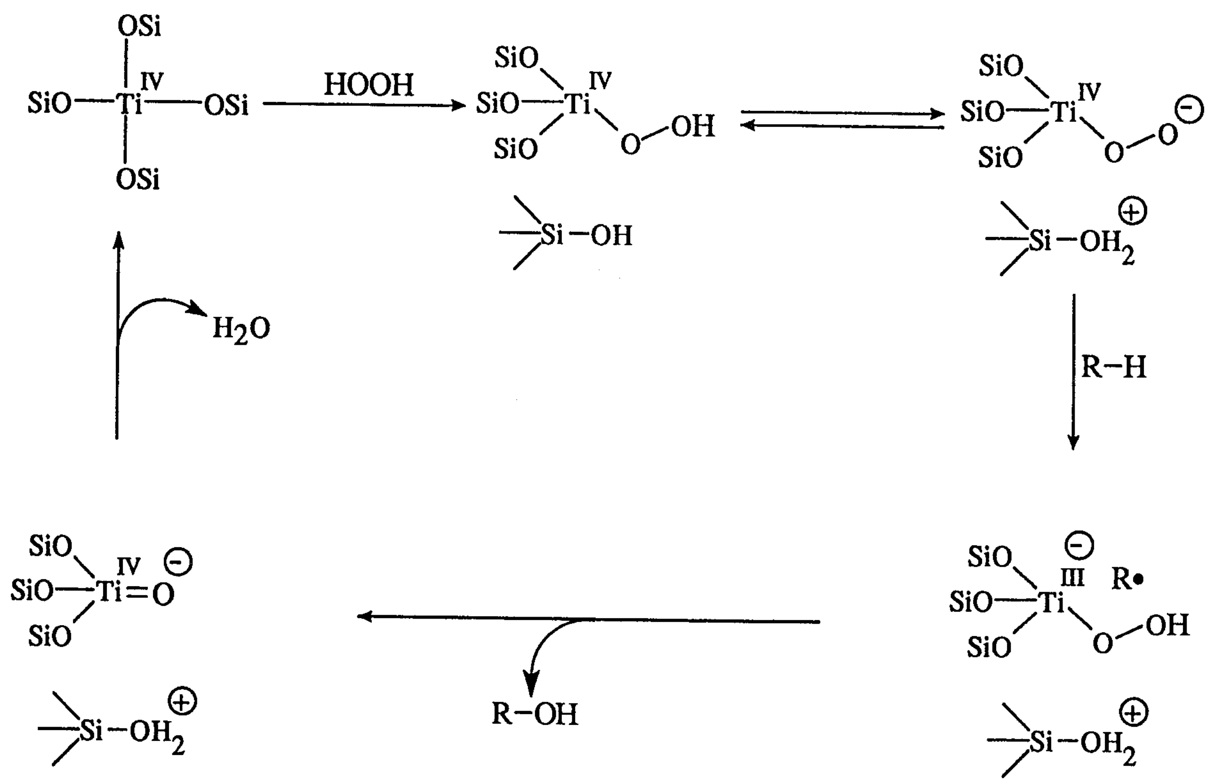


Figure 3.1. DR-UV spectrum of TS-1

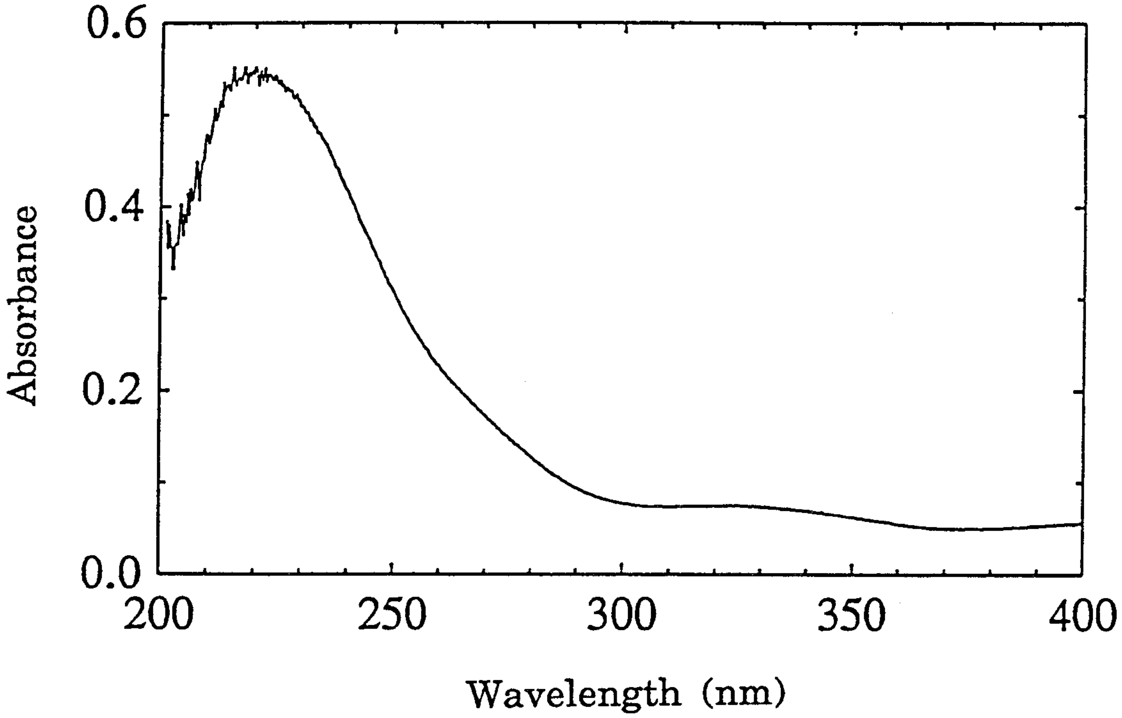


Figure 3.2. Solvolysis of *cis*-2,3-epoxybutane on TS-1

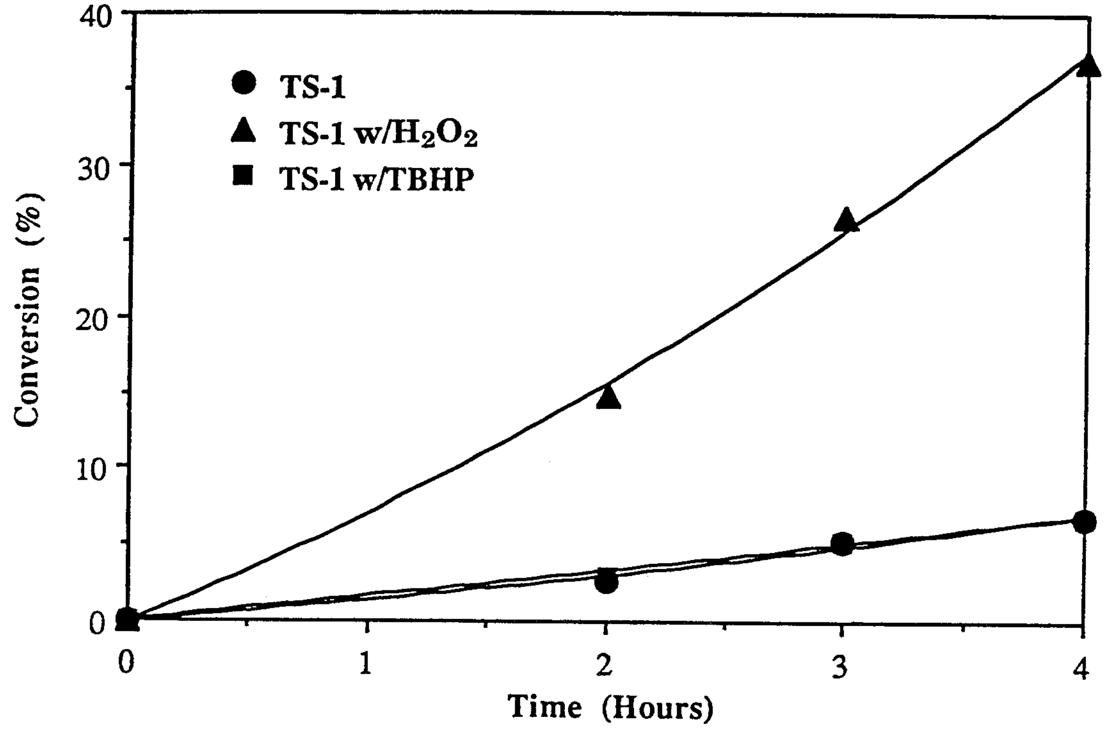


Figure 3.3. Solvolysis of *cis*-2,3-epoxybutane on TiO_2-SiO_2 coprecipitate

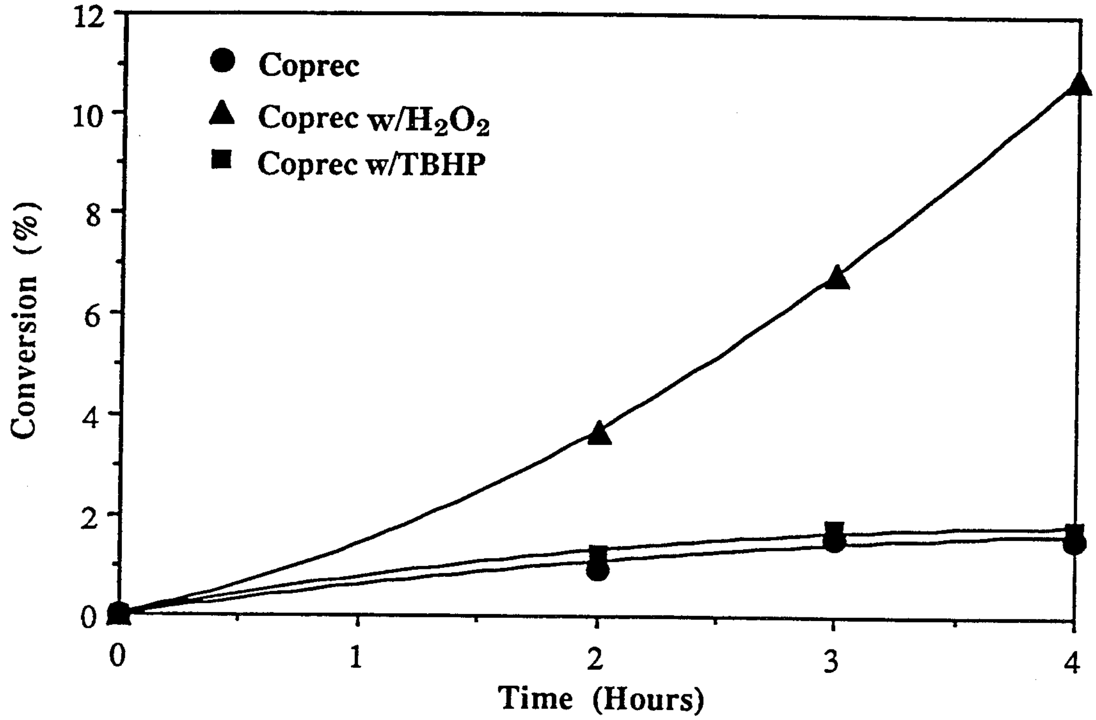


Figure 3.4. IR spectra of TS-1 and sodium exchange TS-1 (Na-TS-1)

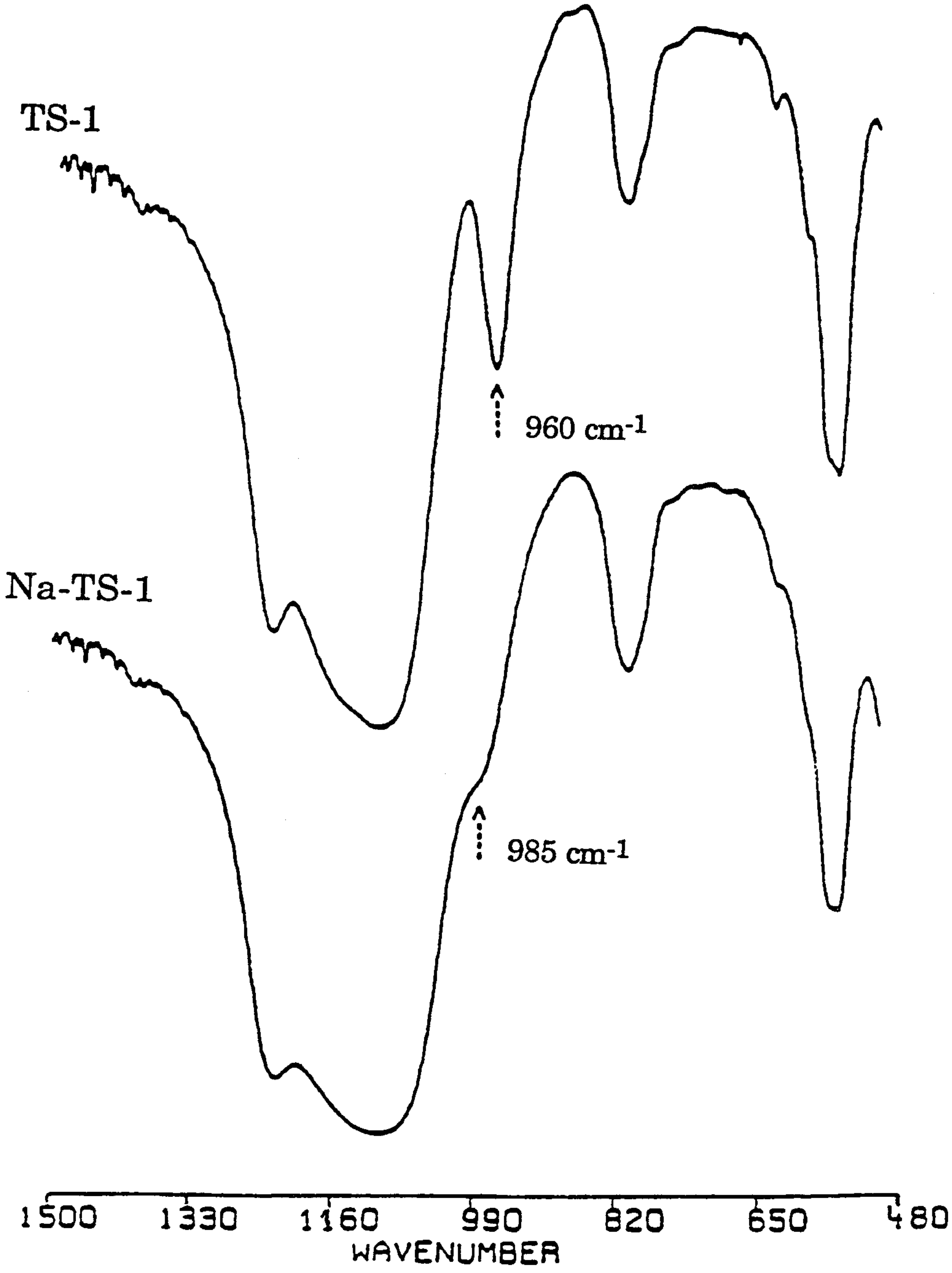
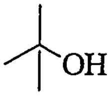
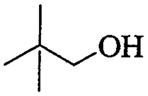
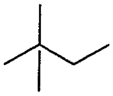


Table 3.1. Adsorption capacities of TS-1 for several organic molecules at room temperature

Molecules	Adsorption Capacity* (g/g zeolite)
	0.117
	0.057
	0.033

* $P/P_0 \approx 0.3$

Table 3.2. Epoxidation of 1-hexene on TiO_2-SiO_2 coprecipitate using alkyl hydroperoxides as the oxidants

Oxidant	Conversion (%)	Hydroperoxide eff. (%)
tert-Butyl hydroperoxide	0.7	3.6
n-Butyl hydroperoxide	1.3	5.1
tert-Butyl hydroperoxide (without catalyst)	0.1	0.6

Reaction condition: 200 mg dried TiO_2-SiO_2 coprecipitate, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol alkyl hydroperoxide, 3 ml MEK, 80 °C, for 4 hours.

Table 3.3. Epoxidation of 1-hexene and oxidation of *n*-octane with TS-1 and the TiO_2-SiO_2 coprecipitate using aqueous and anhydrous H_2O_2

Oxidant	TiO_2-SiO_2 coprecipitate		TS-1	
	Conv. (%)	H_2O_2 eff. (%)	Conv. (%)	H_2O_2 eff. (%)
***n*-octane oxidation**				
Anhydrous H_2O_2[a]	2.71	4.37	16	30
Aqueous H_2O_2[b]	0.14	0.24	15	32
1-hexene epoxidation				
Anhydrous H_2O_2[c]	1.86	8.58	8	68
Aqueous H_2O_2[d]	0.24	0.53	7	64

[a] Reaction condition: 50 mg dried TiO_2-SiO_2 coprecipitate or 20 mg TS-1, 25 mg $MgSO_4$, 3 mmol *n*-octane, 2.9 mmol H_2O_2 (7.8% in MEK) 80 °C, or 4 hours., stirred in a glass reactor.

[b] Reaction condition: 50 mg dried TiO_2-SiO_2 coprecipitate or 20 mg TS-1, 25 mg $MgSO_4$, 3 mmol *n*-octane, 2.9 mmol H_2O_2 in (30% in H_2O) and 1 ml MEK 80 °C, for 4 hours., stirred in a glass reactor.

[c] Reaction condition: 0.2 g dried TiO_2-SiO_2 coprecipitate or 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2, (7.8% in MEK), 2 ml MEK, 50 °C, for 4 hours., stirred in a glass reactor.

[d] Reaction condition: 0.2 g dried TiO_2-SiO_2 coprecipitate or 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2, (30% in H_2O), 3 ml MEK, 50 °C, for 4 hours., stirred in a glass reactor.

Table 3.4. H_2O_2 decomposition on TS-1, TiO_2-SiO_2 coprecipitate, anatase and pure-silica ZSM-5

Catalyst	H_2O_2 Conv. (%) (40 °C)	H_2O_2 Conv. (%) (80 °C)
Blank[a]	1.6	9.5
Pure-silica ZSM-5[a]	3.5	10.3
TiO_2-SiO_2 coprec.[a]	10.7	54.0
TS-1 (uncalcined)[a]	1.6	45.5
TS-1[a]	13.7	87.5
Anatase (~5 mm)	14.4	n.d
Anatase (~6 nm)	70.1	n.d
TS-1 + *n*-octane[b]	n.d	99.1
TS-1 + toluene[b]	n.d	49.2

[a] Reaction condition: 20 mg catalyst, 2.9 mmol H_2O_2 (30% in H_2O), 1.0 ml MEK stirred for 12 hours in a glass reactor.

[b] Reaction condition: 20 mg catalyst, 2.9 mmol H_2O_2 (30% in H_2O), 0.5 ml MEK and 0.5 ml *n*-octane/toluene stirred for 12 hours in a glass reactor.

n.d: not determined

Table 3.5. Oxidation of aromatics by TS-1

Substrates	Products	Conv. (%)	Selectivity (%)	H_2O_2 conv. (%)
Benzene	phenol	4.0	-	47
Ethylbenzene	acetophenone	5.8	56	69
	1-phenylethanol		4	
	ethylphenols		40	
Toluene	cresols	3.8	-	49
Para-xylene	2,5-dimethyl-phenol	2.5	-	59
4-methyl-ethylbenzene	1-ethanol-4-methylbenzene	2.5	29	58
	1-ethanone-4-methylbenzene		40	
	2-methyl-5-ethyl-phenol		31	

Reaction condition: 20 mg TS-1, 0.5 ml aromatic substrates, 2.9 mmol H_2O_2 (30% in water), 0.5 ml MEK as solvent, 80 °C for 12 hours in a glass reactor.

Table 3.6. Reactions of *n*-octane and benzene on TS-1

Substrate	Conversion[a] (%) Benzene	 *n*-Octane
Benzene[b]	3.7	-
n-Octane[c]	-	19.0
Benzene + *n*-octane[d]	1.5	15.6

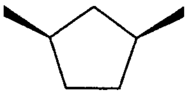
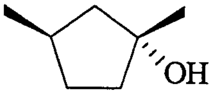
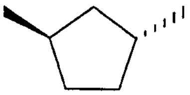
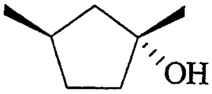
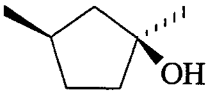
[a] Conversion is based on the substrates.

[b] Reaction condition: 20 mg catalyst, 0.5 ml benzene, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80 °C, stirred for 6 hours in a glass reactor.

[c] Reaction condition: 20 mg catalyst, 0.5 ml *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80 °C, stirred for 6 hours in a glass reactor.

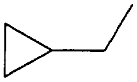
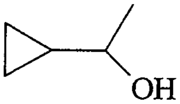
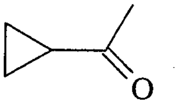
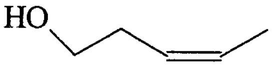
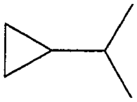
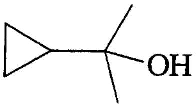
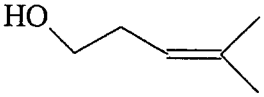
[d] Reaction condition: 20 mg catalyst, 0.5 ml benzene and 0.5 ml *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O), 1 ml MEK, 80 °C, stirred for 6 hours in a lass reactor.

Table 3.7. Stereoselectivity pattern of TS-1 for *cis-* and *trans-* 1,3-dimethylcyclopentane

Substrate	Conv. (%)	Products	Ratio (%)
	6		53
			47
	4		49
			51

Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80 °C, for 24 hours in a glass reactor.

Table 3.8. "Radical clock" study on TS-1

Reactant	Product	Selectivity (%)	Conversion (%)
		27	15.6
		73	
		0	
	Others	0	
		50	3.2
		0	
	Others	50	

Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80 °C for 24 hours in a glass reactor.

Table 3.9. Catalytic activity of sodium exchange TS-1 (Na/TS-1) for *n*-octane oxidation

Catalyst	Si/Ti	Si/Na	Conversion (%)
TS-1	70	797	15
Na/TS-1	70	21	~ 1

Reaction conditions: 20 mg catalyst, 0.5 ml substrate, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, stirred at 80 °C for 4 hours in a glass reactor.

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CHAPTER FOUR

Catalytic Activity of Titanium Silicates Synthesized in the Presence of Alkali Metal and Alkaline Earth Ions

[Khouw, C. B. and Davis, M. E., *J. Catal.* in press]

Abstract:

Titanium containing aluminum-free ZSM-5 (TS-1) synthesized in the presence and absence of alkali metal and alkaline earth ions are investigated as catalysts for the selective oxidation of alkanes and alkenes using aqueous H_2O_2 as oxidant at temperatures below 100 °C. Sodium-exchanged TS-1 is not active for alkane oxidations. Similarly, no catalytic activity is observed for TS-1 synthesized in the presence of high concentrations of alkali metal ions (Si/Na < 20). For both cases, the catalytic activity can be restored by washing the solid with acid solution prior to catalytic evaluation. Similar results are obtained for TS-1 synthesized in the presence of other alkali metal ions, e.g., Li, K. However, the presence of alkaline earth ions, e.g., Mg, in the synthesis gel does not have a significant effect on the catalytic activity of TS-1. Based on the catalytic data and the physicochemical properties of the samples, a plausible explanation for the above results is described. The acid treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali metal ions, e.g., TPAOH solutions. More importantly, this treatment opens the possibility of synthesizing other titanium containing silicate structures that require the presence of alkali metal ions in the synthesis gel for their formation.

Introduction

The hydrothermal synthesis of the titanium-containing derivative of high-silica ZSM-5 (TS-1) was first reported by Taramasso *et al.* *(1)* in 1983. Subsequent studies on TS-1 have shown that it is an active catalyst for numerous oxidation reactions including aromatic hydroxylations, alkane oxidations and alkene epoxidations using aqueous hydrogen peroxide (40 wt% aqueous H_2O_2 or less) as the oxidant *(1-9)*. All of these reactions are conducted at relatively low temperatures (<100 °C) and pressures (~1 atm). Due to the outstanding catalytic activity of this material, TS-1 is being used commercially in Italy for the production of catechol and hydroquinone *(6)*. Additionally, the TS-1 catalyzed conversion of cyclohexanone into cyclohexanone oxime is operating at pilot-plant scale *(10)*.

Several studies have been conducted to understand the nature of the titanium active site in TS-1. It has been postulated that the catalytic activity on TS-1 is related to the presence of isolated framework titanium species *(11)*. Boccuti *et al.* *(12)*, using UV-VIS spectroscopy, showed that the titanium sites are tetrahedrally coordinated in contrast to the previously proposed titanyl structure [Ti=O] *(6)*. Tuel *et al.* *(13)* provided further support for tetrahedral coordination by investigating the EPR spectra of Ti^{+3} (obtained by reducing the Ti^{+4} in TS-1 with CO). Additionally, Pei *et al.* *(14)* show by EXAFS experiments that the titanium sites in TS-1 are tetrahedrally coordinated. EXAFS analyses on the nature of titanium in Ti-Al-ß suggest that the coordination number of titanium varies depending upon whether the samples are as-made, calcined, hydrated or dehydrated *(15)*. Additionally, EXAFS studies carried out by Bonneviot *et al. (16)* 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. The XPS data of TS-1 show an identical binding energy to that of Ti(IV) in TiO_2-SiO_2 glasses suggesting that the oxidation state of the titanium in TS-1 is +4 *(17,18)*.

It has been reported that the presence of alkali metal, even in very small amounts, eliminates the catalytic activity of TS-1 *(19)*. This result severely limits the preparation procedures that can be used to synthesize TS-1 since the reagents must be essentially free of alkali metal cations. This is especially true for the preparation of tetrapropylammonium hydroxide (TPAOH) which is used as the structure-directing agent, since the available commercial products contain alkali metal ions *(20)*. Further study on this phenomenon revealed that the presence of alkali metal ions, e.g., Na^+, K^+, in the synthesis gel can completely eliminate the catalytic activity of TS-1, however the presence of alkali metal ion in the preformed TS-1 does not have any significant effect on the catalytic activity *(21)*. It has been postulated that alkali metal ions present in the synthesis gel prevent the insertion of titanium into the silicalite framework *(19)*. In this study, we report the effect of alkali metal ions on the synthesis of TS-1, the subsequent physicochemical properties and the catalytic activity and show that the catalytic activity of TS-1 samples synthesized in the presence of alkali metal ions can be restored by acid treatment.

Experimental

Samples

TS-1 was synthesized following the preparation method reported in the patent literature *(1)*. Tetraethylorthotitanate (TEOT) (Johnson Matthey), tetraethylorthosilicate (TEOS) (Aldrich), tetrapropylammonium hydroxide (TPAOH) (1 M, Johnson Matthey) solution and distillated deionized water were mixed, forming a clear solution with the following composition:

$$\text{TEOS} : \text{TEOT} : \text{TPAOH} : H_2O = 1 : 0.03 : 0.4 : 20$$

Alkali metal and alkaline earth ion containing TS-1 samples were prepared by adding $NaNO_3$ (Aldrich), KNO_3, (Aldrich), $LiNO_3$ (Aldrich) and $MgNO_3$ (Aldrich) into the clear solution described above. Table 4.1 shows the amount of salt added into the clear solution. The samples are designated as A-TS-1/x, where A is the type of the alkali metal or alkaline earth ions and x is the Si/A ratio in the gel. After the addition of the salt, the mixture becomes cloudy and the pH of the synthesis mixture decreases slightly, e.g., the pH for TS-1 and Na-TS-1/10 synthesis mixtures are 12.34 and 12.08, respectively. These solutions were then stirred for 2 hours, transferred into Teflon-lined autoclaves and statically heated at 175 °C for 7 days. The products were recovered by filtration. Prior to the catalytic reactions, all the materials were calcined in air at 550 °C for 8 hours.

Sodium exchanged TS-1 was prepared by stirring 1 g TS-1 (calcined) in 100 ml of 1 M NaOH or 1 M $NaNO_3$ solution at 25 °C for 24 hours.

The washed TS-1 samples were prepared by stirring the calcined samples in 1 M H_2SO_4 (Fisher) for 12 hours at room temperature or by stirring in 1 M NH_4NO_3 (Aldrich) solution for 12 hours at reflux temperature followed by calcination at 550 °C for 8 hours.

Analysis

X-ray diffraction (XRD) powder patterns were collected on a Scintag XDS-2000 diffractometer that is equipped with a liquid-nitrogen-cooled Germanium solid-state detector and uses Cu-K_α radiation. Silicon was used as an internal standard for the calculation of unit cell parameters. The XRD data were taken with a step size of 0.02° and a step time of 15 s. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) using the KBr pellet technique (~2.5 wt% sample). Raman spectra were recorded on the Nicolet Raman accessory for the FTIR system described above (CaF_2 beamsplitter and a liquid-nitrogen-cooled germanium detector). Diffuse reflectance UV (DR-UV) spectra were obtained on a spectrometer system constructed from an EG&G PAR diode array (1024 element Si) detector and a high-radiance Oriel deuterium lamp. The spectra were ratioed to a reference spectrum obtained from powdered MgO. The nitrogen adsorption isotherms were collected at 77 K on an Omnisorp 100 analyzer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Scanning electron micrographs were recorded on a CamScan Series 2-LV SEM.

Catalytic Reactions

The oxidation of *n*-octane (Aldrich) was performed in a 10 ml glass reactor. A typical reaction mixture would contain 20 mg catalyst, 3 mmol *n*-octane, 2.9 mmol H_2O_2 (30% in H_2O, stabilized) (Mallinkrodt) and 0.5 ml methyl ethyl ketone (MEK) (Mallinkrodt) as the solvent. The reactions were conducted at 80 °C for 4 or 24 hours with vigorous stirring. The epoxidation of 1-hexene (Johnson Matthey) was carried out using 20 mg catalyst, 5 mmol of 1-hexene, 2 mmol of H_2O_2 (30% in H_2O, stabilized) and 3 ml MEK as the solvent. The reaction was conducted at 50 °C for 2 hours with vigorous stirring in a 10 ml glass reactor immersed in a constant temperature oil bath.

Prior to analysis, the reaction mixtures were diluted with acetone in order to obtain a single, homogeneous phase. In all cases, mesitylene was used as an internal standard for gas chromatography analysis. The products were analyzed on a HP 5890 Series II GC equipped with a 25 m long HP-FFAP (polar) capillary column. Hydrogen peroxide conversions were measured by titration with 0.1 N $Ce(SO_4)_2$ using ferroin as the indicator. Hydrogen peroxide efficiency was calculated by dividing the amount of H_2O_2 converted to form alcohols and ketones (1 mol of H_2O_2/mol of alcohol formed and 2 mol of H_2O_2/mol of ketone formed) by the amount of H_2O_2 consumed during the reaction.

Results and Discussions

X-ray diffraction patterns reveal that all the materials synthesized here are TS-1 and do not contain additional crystalline phases. (The presence of any extraframework titanium in these materials is not observable by XRD.) The particle size of the materials used in this study ranges from 0.4 μm (TS-1) to 0.8 μm (Na-TS-1/5). The samples synthesized with alkali metal ions tend to be larger than in their absence. Figure 4.1 shows the scanning electron micrographs of the titanium silicates synthesized in the presence and absence of sodium. The addition of alkali metal ions in the synthesis gel appears to enhance the crystallization rate of TS-1, most likely in a manner described previously for the effect of alkali metal ion the crystallization rate of ZSM-12 *(22)*.

It has been reported that the presence of an IR band at ~960 cm^{-1} is a characteristic of titanium-containing molecular sieves *(11)*. Huybrechts *et al. (23)* have shown that after contacting TS-1 with H_2O_2, the magnitude of this band decreases and eventually disappears. However, by heating the H_2O_2 treated samples at 60 °C for one hour, the original IR spectrum of TS-1 reappears. Several years later, Clerici *et al. (24)* showed that a stable titanium peroxo complex in TS-1 can be synthesized by contacting TS-1 with H_2O_2 in basic medium e.g., NaOH, KOH. After this treatment, the IR band at ~960 cm^{-1} disappears. Figure 4.2 shows the IR spectra of TS-1 treated with H_2O_2 and/or base. Contrary to what has been reported earlier, the ~960 cm^{-1} IR band of TS-1 remains unchanged when contacted with H_2O_2. Nevertheless, when sodium hydroxide is present in the solution (independent of the presence of H_2O_2), the intensity of IR band at ~960 cm^{-1} decreases and the band is converted into a shoulder at 985 cm^{-1}. The IR band at ~960 cm^{-1} was originally assigned to the stretching vibration of $Si\text{-}O^{\delta-}\cdots Ti^{\delta+}$ *(12)*. However, more recently, Camblor *et al. (15)* reported that this band is better assigned to the stretching vibration of the $Si\text{-}O^-$ groups where H^+, tetraethylammonium$^+$ and/or Na^+ can act as the countercations. This assignment is in agreement with the fact that the IR bands of calcined and uncalcined samples are different and is also consistent with the shifting of the IR band position for Na-exchanged TS-1 (shown here). Moreover, this result suggests that sodium exchange on TS-1 occurs at the silanol group as illustrated in Scheme 4.1. This scheme is supported by the fact that a strong base is required in order for the exchanged to occur; the ~960 cm^{-1} IR band of TS-1 exchanged with $NaNO_3$ solution remains unchanged and elemental analysis on this material shows that the amount of sodium in the sample is very low.

Further study on the Na-exchanged TS-1 shows that the presence of an IR band at ~960 cm^{-1} can be regenerated by washing the sample with 1 M H_2SO_4 solution as shown in Figure 4.3. When this material is exchanged again with NaOH solution, the IR band at ~960 cm^{-1} is converted back into a shoulder. If this material is further washed with acid, the IR band at 960 cm^{-1} reappears again (Figure 4.3). Similarly, when the Na-exchanged TS-1 is washed with NH_4NO_3, the IR band at ~960 cm^{-1} reappears, although the magnitude is smaller than observed from the sample washed with H_2SO_4. When the NH_4^+ containing sample is calcined, the magnitude of the IR band at ~960 cm^{-1} increases in size similar to that of the unmodified TS-1 (Figure 4.4). As a reference, no IR band at ~960 cm^{-1} is observed for pure-silica ZSM-5 washed with 1 M H_2SO_4. Elemental analyses of these samples indicate that TS-1 exchanged with 1 M solution of NaOH contains a relatively high amount of sodium that can be washed away by treating the sample with a 1 M solution of H_2SO_4 (Table 4.2). Additionally, it is also shown that TS-1 exchanged with 1 M $NaNO_3$ solution contains only a trace amount of sodium indicating that the exchange only occurs at high pH on TS-1. These observations suggest that Na-exchanged TS-1 can be reversibly converted into its original form by washing it with 1 M H_2SO_4 or 1 M NH_4NO_3 (with recalcination) as illustrated in Scheme 4.2.

Table 4.3 shows the effect of sodium on the IR band at ~960 cm^{-1} and the catalytic activity of TS-1 for *n*-octane oxidation. TS-1 exchanged with 1 M solution of NaOH does not show any catalytic activity for *n*-octane oxidation. However, after washing with 1 M H_2SO_4, the catalytic activity of the sample is regenerated (the lack of the complete return of activity may be due to some loss of titanium; see Table 4.2). Similarly, some of the catalytic activity of Na-exchanged TS-1 is also restored by washing with NH_4NO_3 solution although the activity is lower than the one washed with sulfuric acid solution (even after the sample is heated). This is most likely related to the ion exchange equilibrium between the Na^+ and NH_4^+ ions; not all the sodium in the samples is exchanged by NH_4^+. The correlation between the IR band at ~960 cm^{-1} and the catalytic activity on these materials indicates that only the materials with an IR band at ~960 cm^{-1} are active for *n*-octane oxidation. These observations are in agreement with the previous hypothesis that the IR band at 960 cm^{-1} is a necessary condition for TS-1 to react alkanes *(25)*. Nevertheless, the magnitude of this band does not correlate well with the level of conversion.

It has been reported that the presence of alkali metal ions, e.g., Na, in the synthesis gel, even in a very small amount, completely eliminates the catalytic activity of TS-1 *(19)*. Our results on Na-exchanged TS-1 show that it is possible to restore the activity of this material by acid washing. Thus, we explored the possibility of whether acid treatment of TS-1 synthesized in the presence of sodium could restore its catalytic activity. Various amounts of sodium and other alkali metal/alkaline earth ions were introduced into the synthesis gel of TS-1 as indicated in Table 4.1. The elemental analyses of the sodium containing products are reported in Table 4.4. As expected, the amount of sodium in the unwashed product decreases as the amount of sodium in the gel is lowered. On the other hand, the amount of titanium in the unwashed products remains approximately constant at high concentration of sodium (Si/Na in the gel < 20), then decreases as the concentration of sodium in the gel is reduced. After the materials are washed with 1 M H_2SO_4, only trace amounts of sodium remain in the samples. The amount of titanium in the washed products also decreases from the amount in the as-synthesized form indicating that some of the titanium is removed by the acid treatment; this is especially true for materials synthesized at a high concentration of sodium in the synthesis gel (Si/Na in the gel < 20). It is likely that at high sodium concentration, the titanium inserts into the framework and also forms another compound with sodium; most of this additional compound can be washed away by acid, although some extraframework titanium still remains in the sample *(vide infra)*.

The IR spectra of the unwashed materials synthesized in the presence of sodium show a shoulder at 985 cm^{-1} instead of an IR band at ~960 cm^{-1}. However, after these materials are washed with acid, an IR band appears at ~960 cm^{-1} (Figure 4.5). Since this band is attributed to the stretching vibration of $Si\text{-}O^-$ *(12,15)* that is formed due to the incorporation of titanium into the framework, the magnitude of this IR band is also indirectly related to the amount of titanium incorporated into the framework. For the washed Na-TS-1 samples, the magnitude of this band increases as the amount of sodium in the gel decreases. These results indirectly imply that the amount of titanium incorporated into the framework increases as the amount of sodium in the gel decreases.

The Raman spectra of TS-1 and Na-TS-1/10, before and after acid washing, are shown in Figure 4.6. The spectra show that no anatase is present. (Anatase peaks occur at 386, 513 and 637 cm^{-1}.) In addition to Raman spectroscopy, ultraviolet diffuse reflectance (DR-UV) spectroscopy has been used to probe the existence of framework and non-framework titanium *(12,23,26,27)*. The DR-UV spectra for the washed Na-TS-1 samples are shown in Figure 4.7. The band at 220 nm has been assigned to isolated framework titanium in tetrahedral coordination *(12)*, a broad shoulder around 270 nm has been attributed to the extraframework titanium *(28)*, and the anatase band occurs at 312 nm *(29)*. All of the TS-1 samples synthesized in the presence of sodium show the framework titanium band at 220 nm along with the extraframework band of varying intensities which does not change with acid washing. The amount of extraframework titanium is presumably quite small and is not observed by Raman spectroscopy in the spectral region of greater than 200 cm^{-1}. Based on the DR-UV data, it is evident that only TS-1 synthesized in the absence of sodium is free of extraframework titanium (the spectrum contains only the band at 220 nm indicating all the titanium is in the framework) and the presence of sodium causes the formation of some extraframework titanium. Nitrogen adsorption data from the washed Na-TS-1 samples indicate that no pore blocking due to extraframework titanium and sodium occurs as shown in Figure 4.8 for washed Na-TS-1/10. However, the nitrogen adsorption capacity of the washed Na-TS-1 samples are lower than that obtained from "normal" TS-1. This is presumably due to the existence of extraframework materials, e.g., extraframework titanium in these samples that cannot be washed away by the acid treatment.

The catalytic activities of the unwashed materials for the oxidation of *n*-octane are tabulated in Table 4.5. No activity is observed when the Si/Na ratio in the gel < 20. However, as the concentration of sodium in the gel decreases, the activity increases. Our previous observations on the catalytic activity of Na-exchanged TS-1 suggest that the presence of a Si-ONa group in the neighborhood of the titanium sites inhibits the catalytic activity *(30)*. For TS-1 synthesized in the presence of sodium, we speculate that the sodium in the unwashed samples is in the form of a Si-ONa group that is most likely located in the neighborhood of the titanium sites. Thus, for Na-TS-1 with Na/Ti in the product > 1, all the titanium sites are accompanied by the Si-ONa group (similar to the case for Na-exchanged TS-1) so that no catalytic activity should be observed. On the other hand, for Na-TS-1 with Na/Ti < 1, not all the titanium sites are accompanied by the Si-ONa group and hence some catalytic activity should be detected. This hypothesis is in agreement with the experimental data (Tables 4.4 and 4.5) which indicate that the threshold for the activity occurs at Na/Ti ratio in the products ~ 1. The H_2O_2 conversions on these materials are close to 100 % indicating that sodium containing titanium silicates are very active toward H_2O_2 decomposition.

Table 4.5 summarizes the catalytic activity of the washed Na-TS-1 samples for alkane activation. All of the washed materials become active and the catalytic activity increases as the concentration of sodium in the synthesis gel decreases. The H_2O_2 conversions from the washed materials are lower than from the corresponding unwashed samples. It is possible that the lack of activity of the unwashed samples is simply because the unwashed materials are more active for H_2O_2 decomposition than for oxidizing the organic substrates.

Surprisingly, the most active material is Na-TS-1/100. Comparison of the IR spectra, elemental analyses and the catalytic data of this sample to those from "normal" TS-1 suggests that more titanium is incorporated into the framework of Na-TS-1/100 although some extraframework titanium may also be present in the sample. Table 4.6 shows the unit cell parameters calculated from the XRD analysis. Unit cell expansion measurements have been reported to be a very precise method for the evaluation of framework/extraframework Ti *(31)*. It is shown here that the unit cell volume of Na-TS-1/100 is slightly larger than that of TS-1 indicating that a small amount of sodium present in the synthesis gel appears to increase the amount of titanium that can be incorporated into the TS-1 framework. However, as the amount of sodium in the synthesis gel is increased, more extraframework titanium will be formed and less titanium will be incorporated into the framework. Consequently, the catalytic activity of the materials with increasing sodium content will eventually decline. Note that the differences in catalytic activity are not due to the crystal size effect since it has been shown previously that activities observed over the crystal size variation reported here are negligible *(32)*.

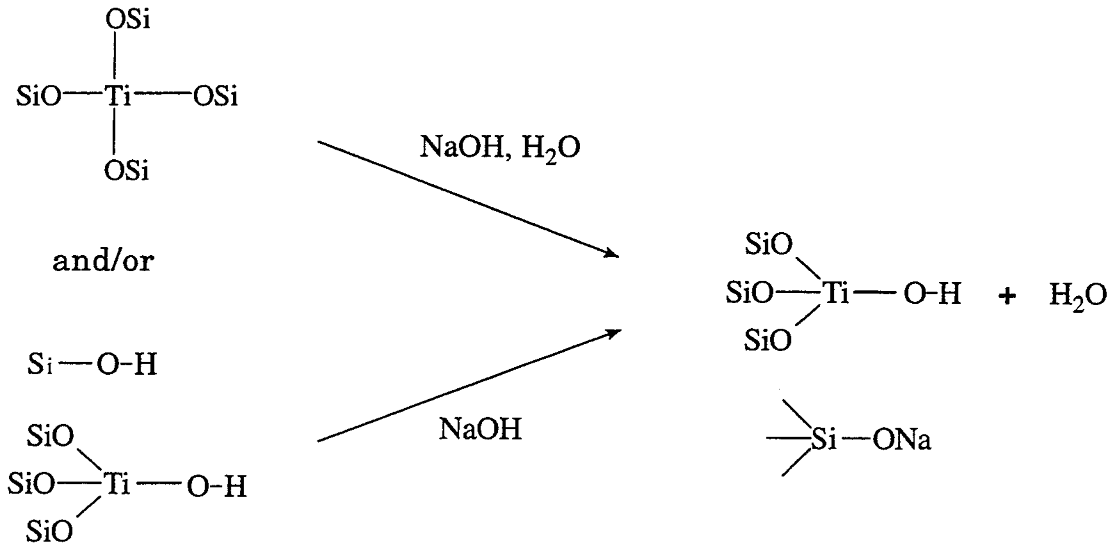
Similar to Na-TS-1, the IR spectra of TS-1 synthesized with lithium and potassium do not have a band at ~960 cm^{-1}, instead they show a shoulder at ~985 cm^{-1}. These materials are not active for alkane oxidation. On the other hand, TS-1 synthesized in the presence of magnesium does have an IR band at ~960 cm^{-1} and it is active for *n*-octane oxidation (~8% conversion). The addition of $MgNO_3$ into the synthesis gel results in the precipitation of a white powder. These observations suggest that Mg^{2+} is precipitated as $Mg(OH)_2$ at the basic, synthesis gel condition. Thus, magnesium does not play the same role as alkali metal cations in the synthesis of TS-1. The IR spectra of the TS-1 synthesized with Li, Na, K and Mg after being washed with acid are shown in Figure 4.9. All of these materials contain an IR band at ~960 cm^{-1} which increases in intensity in the following order: Li-TS-1 < Na-TS-1 < K-TS-1 < Mg-TS-1 (may also indirectly imply the incorporation of titanium into the zeolite framework increases in the same order). Figure 4.10 shows the DR-UV spectra of these materials. Similar to the spectrum of Na-TS-1, these samples display the framework titanium band at 220 nm along with the band for extraframework titanium. In agreement with the IR data, the DR-UV spectra also show that the amount of extraframework titanium decreases as the magnitude of the IR band at 960 cm^{-1} increases. The catalytic activity of these materials (Table 4.7) also increases following the same order as the increase in the IR band intensity at ~960 cm^{-1}. These observations suggest that more titanium is incorporated into the framework as the diameter of the alkali metal ion is increased. The presence of alkaline earth ions in the synthesis gel does not have any significant effect on the catalytic activity of TS-1. However, the material synthesized in the presence of alkaline earth ions contains more anatase than the other samples made with alkali metal ions as shown by the DR-UV broad shoulder at ~310 nm.

As a final test, the catalytic activities of the washed Na-TS-1 samples are examined for 1-hexene epoxidation using aqueous H_2O_2 as the oxidant. The results are listed in Table 4.8. All the samples are active and the activity increases as the concentration of sodium in the gel decreases. As for *n*-octane oxidation, Na-TS-1/100 is also the most active material in the series for 1-hexene epoxidation.

Conclusions

Sodium-exchanged TS-1 is not active for alkane oxidations using aqueous H_2O_2 as oxidant. However, the catalytic activity can be restored by washing the solid with acid solution. Similarly, the catalytic activity of TS-1 synthesized in the presence of sodium can be regenerated by washing with acid. This treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali metal ions, e.g., TPAOH solution. More importantly, this treatment opens the possibility of synthesizing other titanium containing silicate structures that require the presence of alkali metal ions in the synthesis gel for their formation. We have synthesized titanium containing SSZ-33 and ZSM-12 and are currently exploring the acid treatment on these materials in order to generate catalytic activity.

Scheme 4.1. TS-1 exchanged with NaOH



Scheme 4.2. Na-exchanged TS-1 washed with 1 M H_2SO_4 or 1 M NH_4NO_3

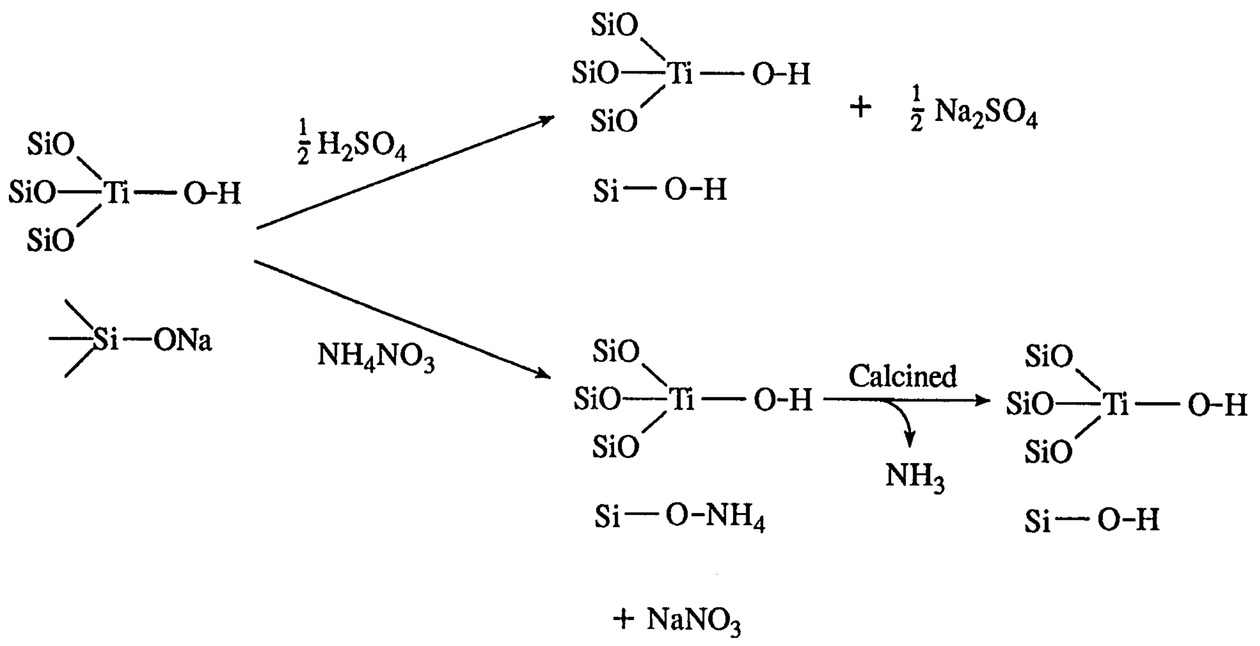
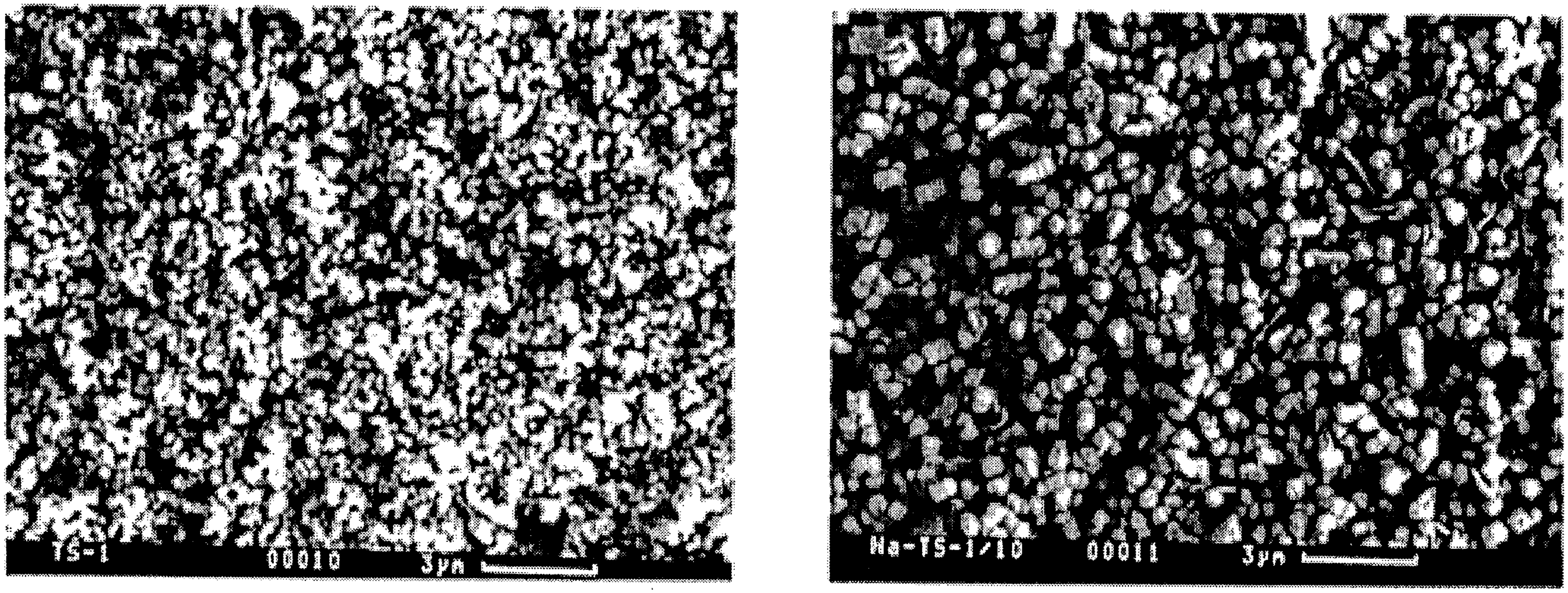


Figure 4.1. Scanning electron micrographs of TS-1 and Na-TS-1/10



TS-1

Na-TS-1/10

Figure 4.2. IR spectra of TS-1 treated with 1 M $NaNO_3$, H_2O_2 and/or 1 NaOH solution

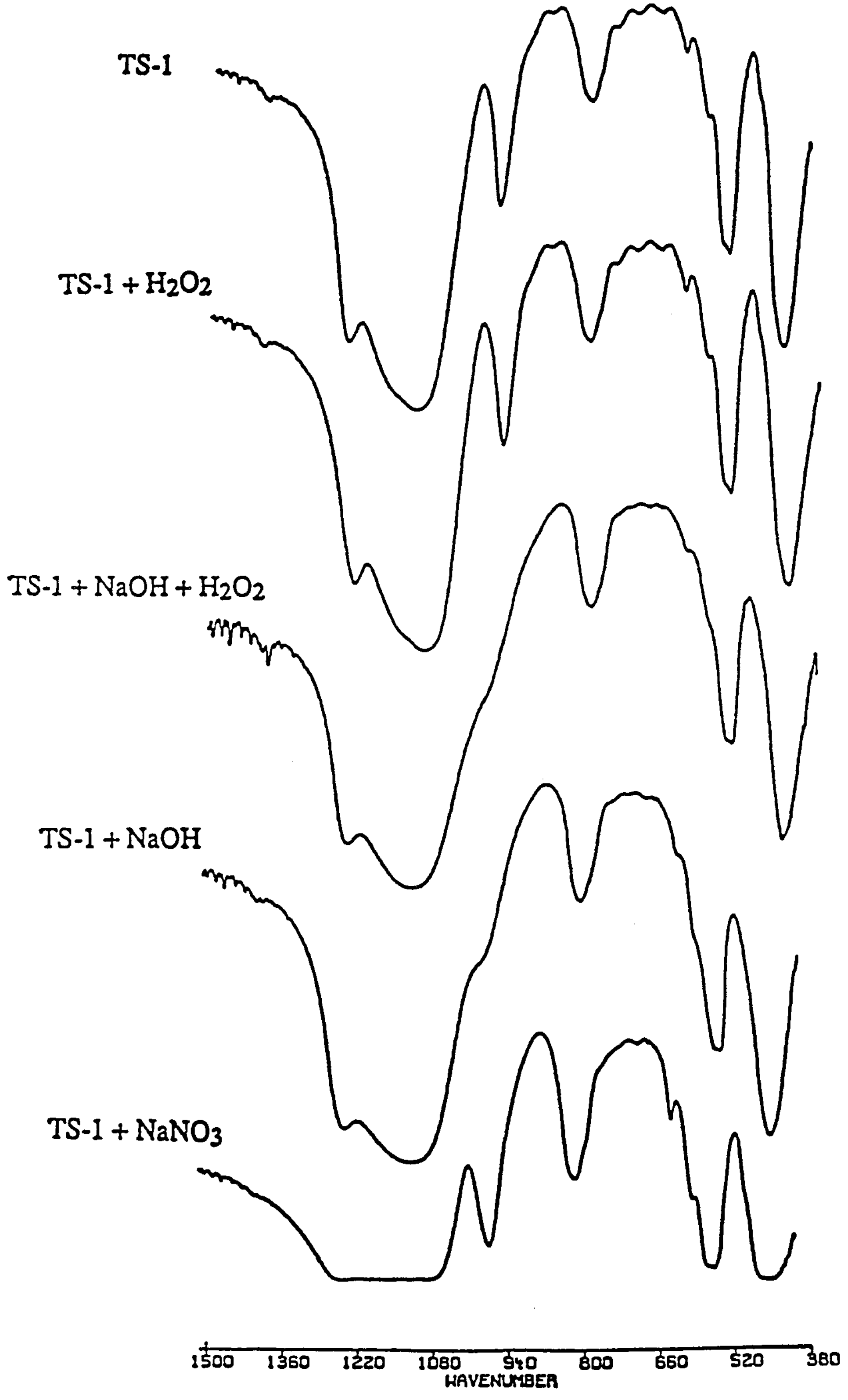


Figure 4.3. IR spectra of TS-1 treated with 1 M NaOH and/or H_2SO_4 solution

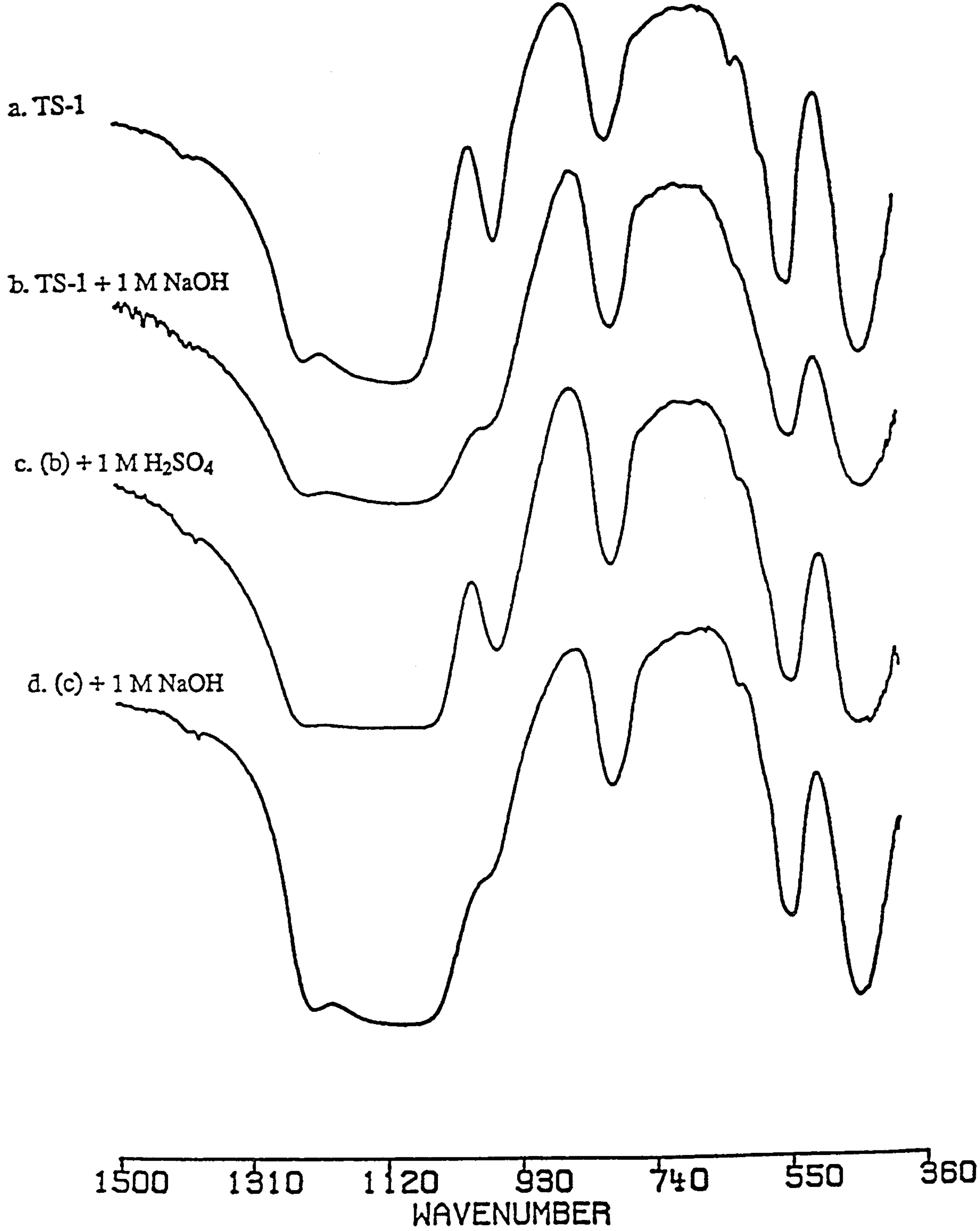


Figure 4.4. IR spectra of TS-1 treated with 1 M NH_4NO_3 and Si-ZSM-5 treated with 1 M H_2SO_4 solution

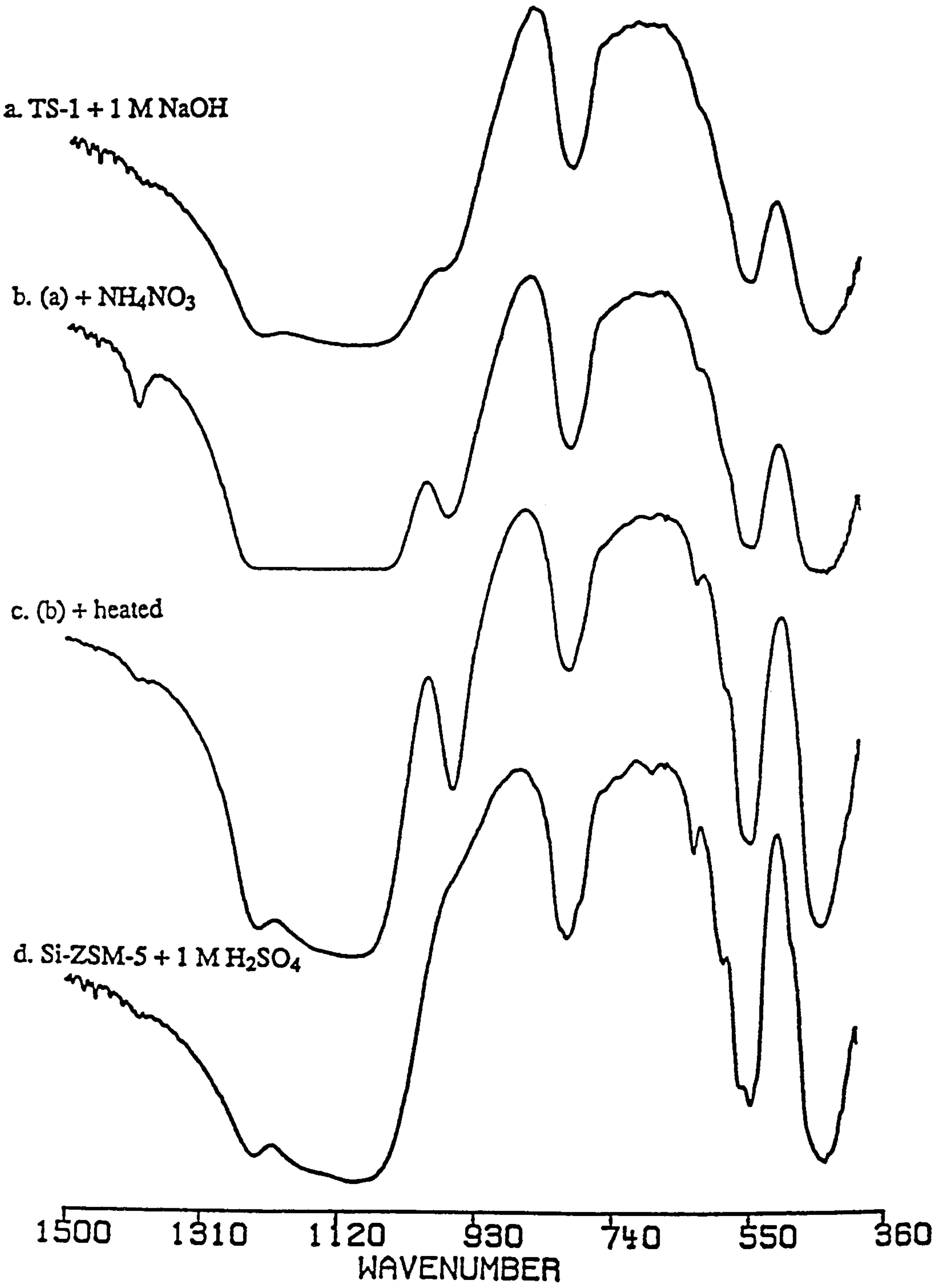


Figure 4.5. IR spectra of Na-TS-1 washed with 1 M H_2SO_4

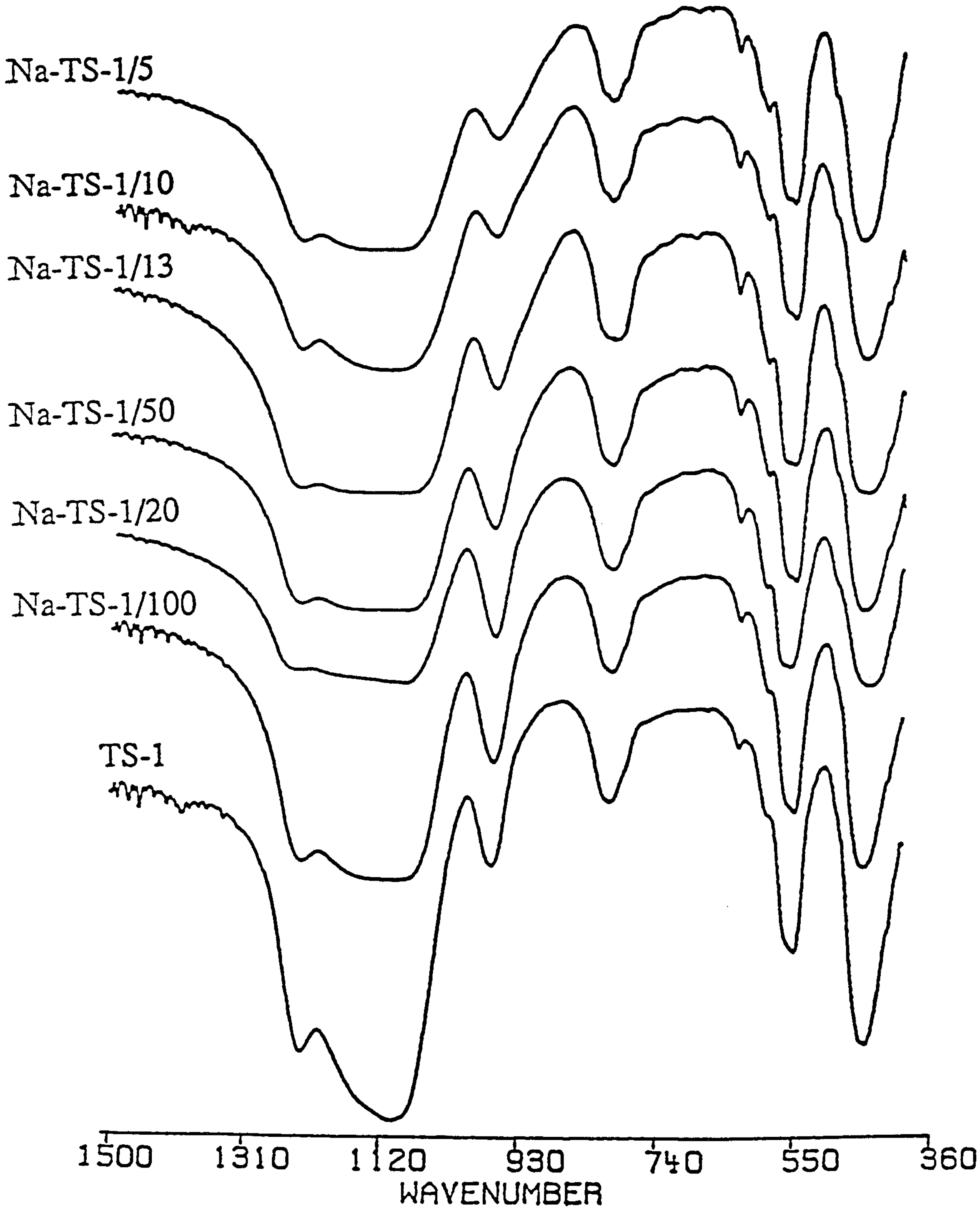


Figure 4.6. Raman spectra of TS-1 and Na-TS-1/10

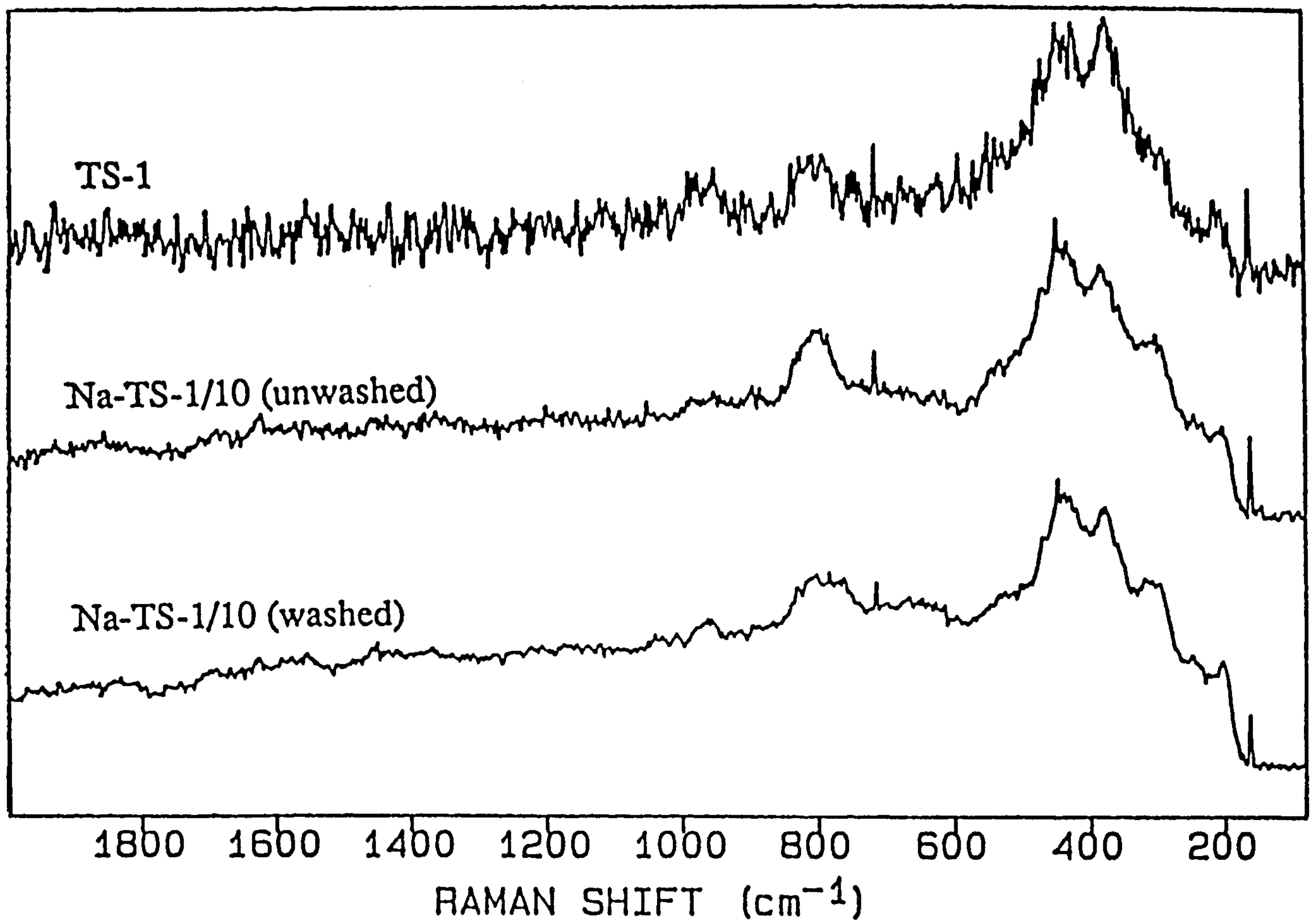


Figure 4.7. DR-UV spectra of Na-TS-1 washed with 1 M H_2SO_4

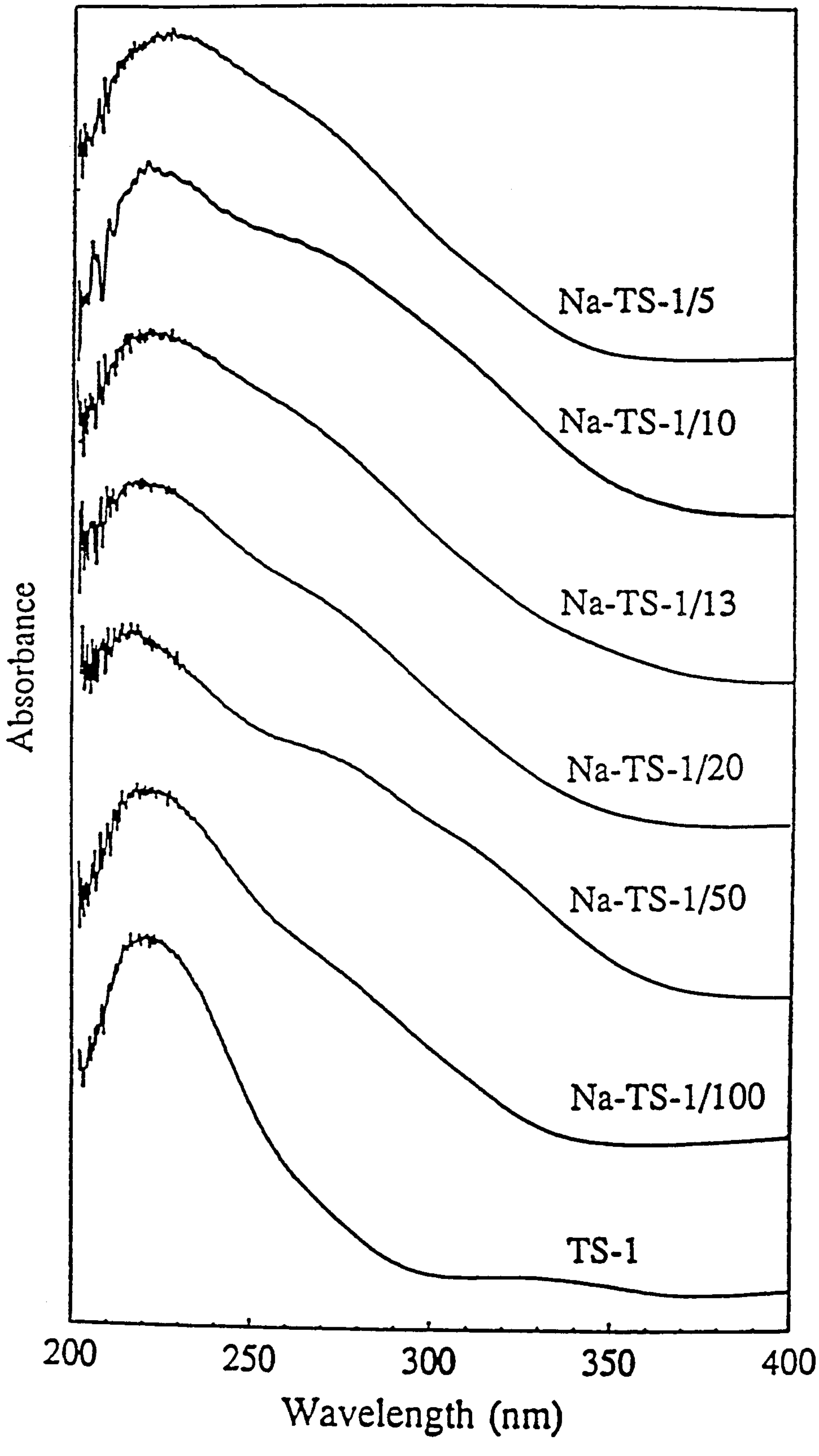


Figure 4.8. Nitrogen adsorption of TS-1 and Na-TS-1/10 washed with 1 M H_2SO_4 solution

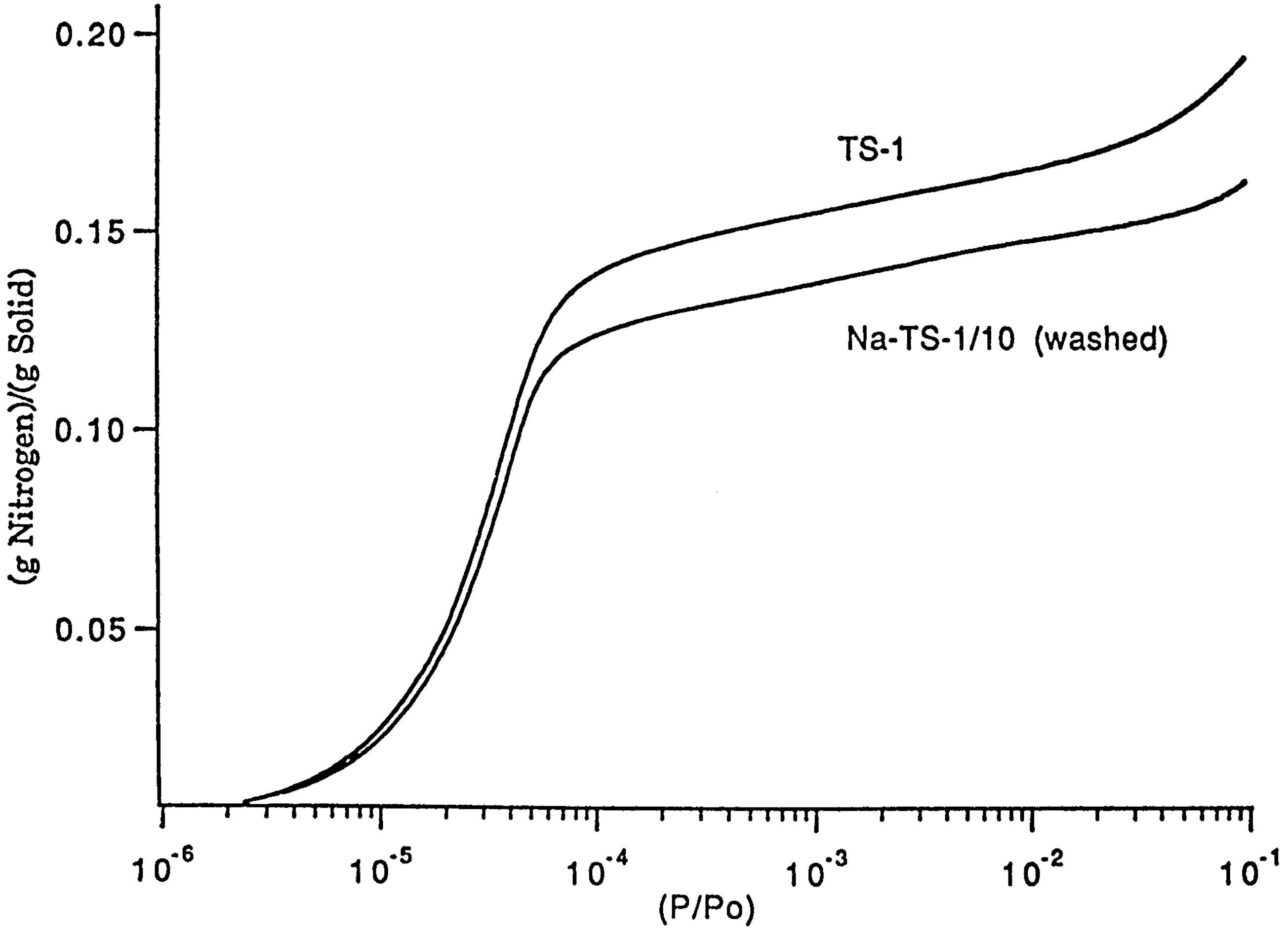


Figure 4.9. IR spectra of TS-1 synthesized in the presence of Li, Na, K and Mg and washed with 1 M H_2SO_4 solution

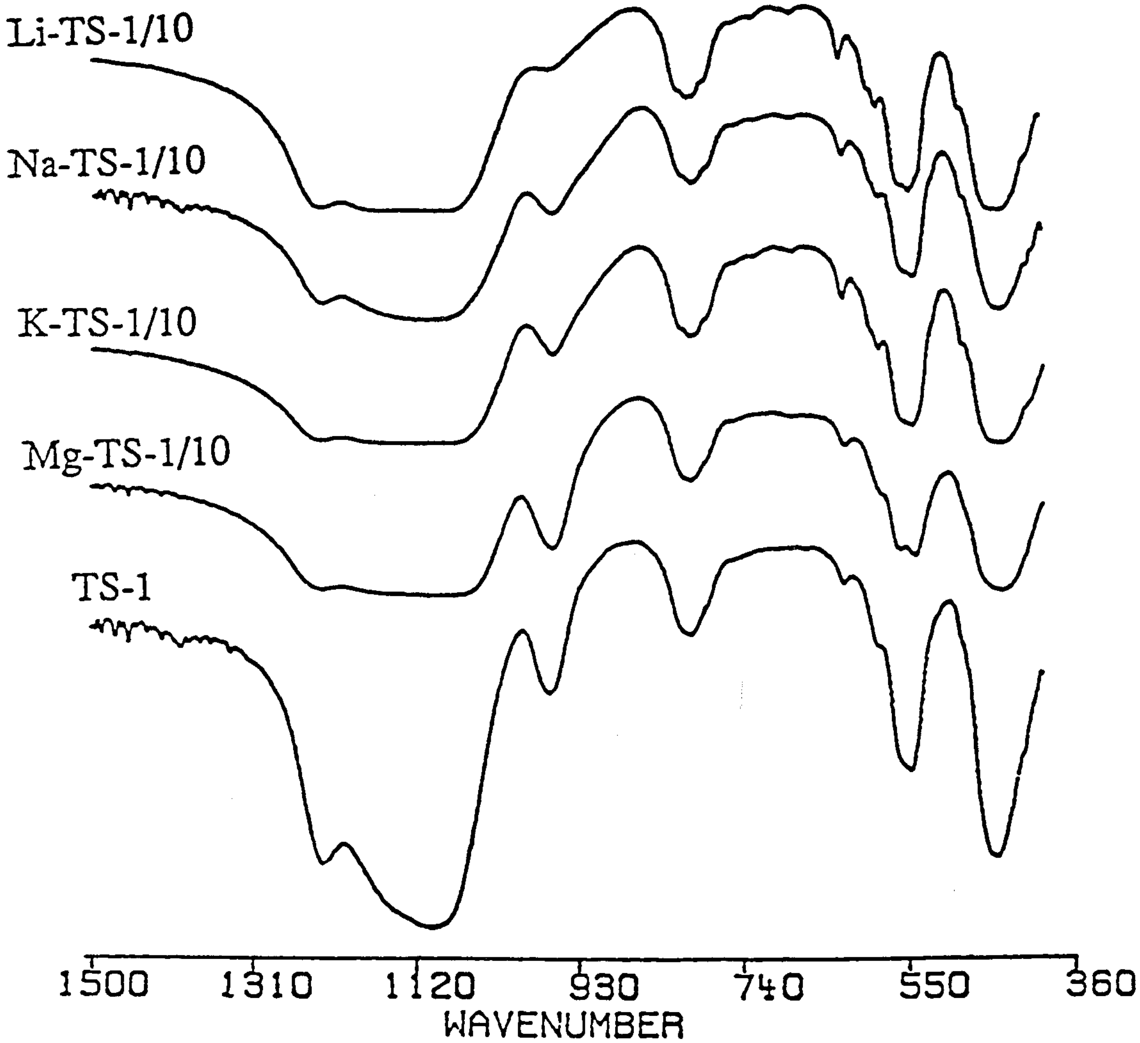


Figure 4.10. DR-UV spectra of TS-1 synthesized in the presence of Li, Na, K and Mg and washed with 1 M H_2SO_4 solution

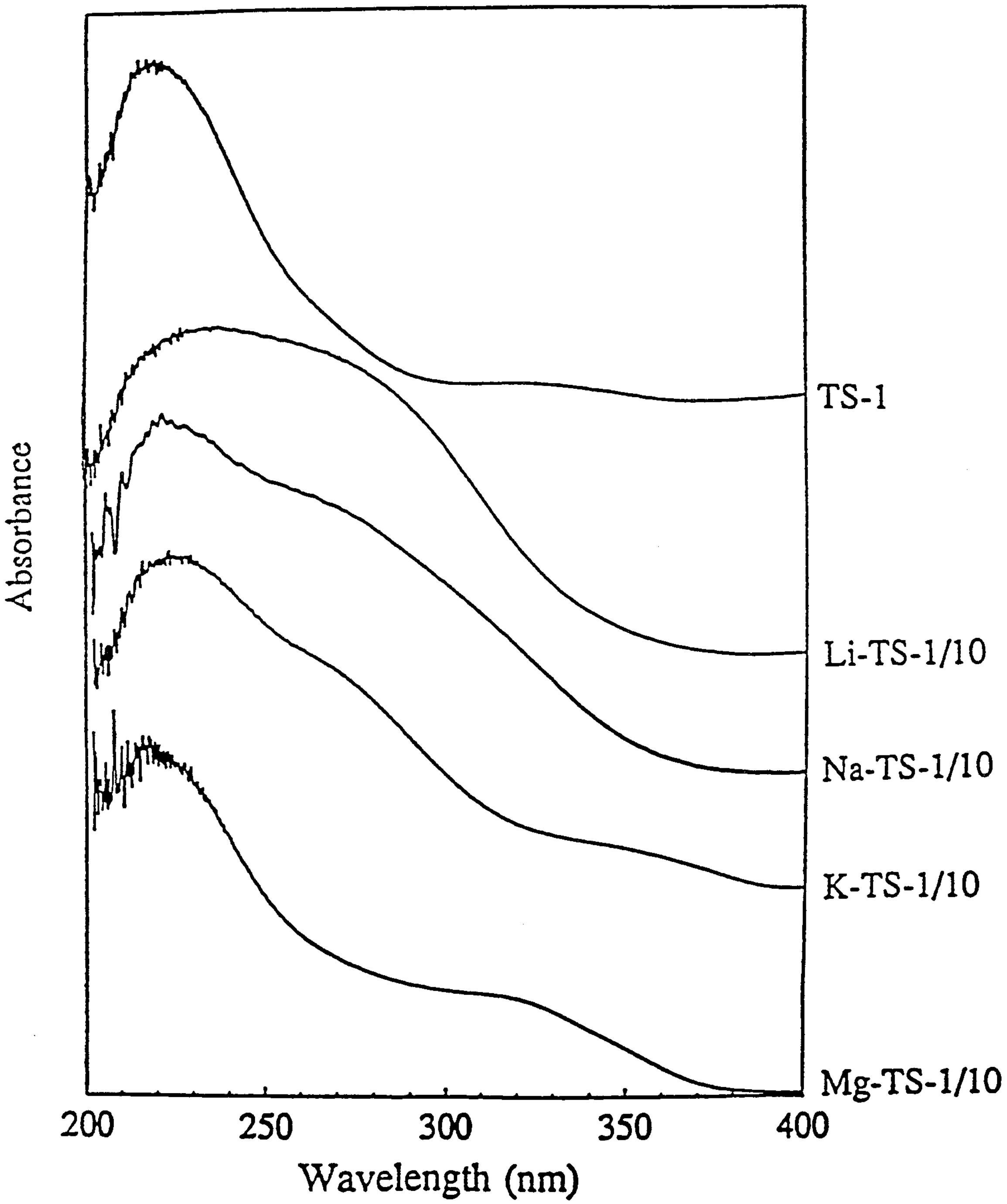


Table 4.1. Gel composition of alkali metal and alkaline earth containing TS-1

Catalyst	Na/Si	K/Si	Li/Si	Mg/Si
Na-TS-1/5	0.200	-	-	-
Na-TS-1/10	0.100	-	-	-
Na-TS-1/13	0.075	-	-	-
Na-TS-1/20	0.050	-	-	-
Na-TS-1/50	0.025	-	-	-
Na-TS-1/100	0.010	-	-	-
K-TS-1/10	-	0.10	-	-
Li-TS-1/10	-	-	0.10	-
Mg-TS-1/10	-	-	-	0.10

Table 4.2. Elemental analyses of TS-1 and TS-1 treated with sodium

Catalyst	Si/Ti	Si/Na
a. TS-1	70	797
b. TS-1 + $NaNO_3$	n.d	670
c. TS-1 + NaOH	70	21
d. (c) + H_2SO_4	81	> 1250

n.d: not determined

Table 4.3. The effect of sodium on the IR band at 960 cm^{-1} and on the oxidation of *n*-octane

	Catalyst	IR Band (cm^{-1})	Conv. (%)[a]
a.	TS-1	962	20.2
b.	TS-1 + $NaNO_3$	962	18.7
c.	TS-1 + NaOH	985[b]	~ 1
d.	(c) + H_2SO_4	962	14.2
e.	(d) + NaOH	985[b]	~ 1
f.	(c) + NH_4NO_3	970	4.8
g.	(f) heated	962	9.4

Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80 °C, stirred for 24 hours in a glass reactor.

[a] Conversion of *n*-octane.

[b] Shoulder

Table 4.4. Elemental analyses of TS-1 synthesized in the presence and absence of sodium

Catalyst	Unwashed		Washed w/H_2SO_4 (1.0M)	
	Si/Ti	Si/Na	Si/Ti	Si/Na
Na-TS-1/5	28	14	40	553
Na-TS-1/10	26	20	37	>1035
Na-TS-1/13	28	22	39	>924
Na-TS-1/20	36	45	43	>1271
Na-TS-1/50	41	101	42	>670
Na-TS-1/100	50	164	53	>901
TS-1	70	797	76	795

Table 4.5. Catalytic activity of Na-TS-1 for *n*-octane oxidation

		Unwashed Na-TS-1		Washed Na-TS-1 (w/ 1.0 M H_2SO_4)		
	Catalyst	Conv. (%)*	H_2O_2 conv.(%)	Conv.(%)*	H_2O_2 eff.(%)	H_2O_2 conv.(%)
a.	Na-TS-1/5	0	99.5	3.3	8.2	54.0
b.	Na-TS-1/10	0	99.5	7.3	19.8	53.6
c.	Na-TS-1/13	0	98.8	10.9	26.6	53.6
d.	Na-TS-1/20	0.5	98.2	13.7	36.7	61.7
e.	Na-TS-1/50	3.6	99.5	14.8	41.1	58.1
f.	Na-TS-1/100	14.5	99.5	28.0	55.3	91.9
g.	TS-1	16.2	86.5	18.4	41.5	75.2

Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80 °C, stirred for 4 hours in a glass reactor.

* Conversion of *n*-octane.

Table 4.6. Unit cell data for titanium molecular sieves[a]

Sample	a(Å)	b(Å)	c(Å)	Vol. (Å^3)
Silicalite-1[b]	19.885(4)	20.087(2)	13.374(2)	5341.7
TS-1[b]	19.912(6)	20.096(6)	13.397(7)	5361.2
Na-TS-1/10[c]	19.903(4)	20.084(4)	13.370(5)	5344.7
Na-TS-1/100[c]	19.937(6)	20.111(6)	13.396(7)	5371.5

[a] Orthorhombic symmetry used in all cases.

[b] After calcination.

[c] After calcination and acid treatment.

Table 4.7. Catalytic activity of TS-1 synthesized with various alkali/alkaline earth washed w/H_2SO_4 (1.0 M) for *n*-octane oxidation

	Catalyst	Si/Ti[a]	Si/Alk[b]	Conv.(%)[c]	H_2O_2 eff.(%)
a.	Li-TS-1/10	44	>567	0.9	7.4
b.	Na-TS-1/10	37	>1035	7.3	19.8
c.	K-TS-1/10	57	>644	9.0	41.9
d.	Mg-TS-1/10	29	56	12.9	24.1

Reaction conditions: 20 mg catalyst, 3 mmol of *n*-octane, 2.9 mmol of H_2O_2 (30% in H_2O), 0.5 ml MEK, 80 °C, stirred for 4 hours in a glass reactor.

[a] Si/Ti ratio in the products.

[b] Si/Alkali metal or alkaline earth ion ratio in the products.

[c] Conversion is based on *n*-octane.

Table 4.8. Catalytic activity of Na-TS-1 washed with H_2SO_4 (1.0 M) for 1-hexene epoxidation

	Catalyst	Conv.(%)*	H_2O_2 eff.(%)
a.	Na-TS-1/5	0.5	3.2
b.	Na-TS-1/10	2.6	29.9
c.	Na-TS-1/20	5.4	82.4
d	Na-TS-1/100	7.4	77.5
e.	TS-1	7.0	64.2

Reaction condition: 25 mg TS-1, 25 mg $MgSO_4$, 5 mmol 1-hexene, 2 mmol H_2O_2 (30% in H_2O), 3 ml MEK, 50 °C for 4 hours., stirred in a glass reactor.

* Conversion of 1-hexene

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CHAPTER FIVE

Synthesis of Various Titanium Containing Molecular Sieves Using Sodium Containing Synthesis Mixtures

Abstract:

We have shown earlier that the catalytic activity of TS-1 synthesized in the presence of alkali metal ions can be restored by washing the catalyst with acid solution. This synthesis method is explored further for the preparations of other titanium containing silicates (Na-Ti-ZSM-12, Na-Ti-SSZ-33 and Na-Ti-mordenite). Although some of the physicochemical properties of these materials are similar to those of TS-1, no catalytic activity is found from these materials. The presence of extraframework titanium appears to be the cause for the lack of activity on these materials.

Introduction

Recently, we have reported that it is possible to synthesize an active TS-1 catalyst in the presence of low concentrations of alkali metal or alkaline earth ions, e.g., Na/Ti < 1 *(1)*. The catalytic activity of these TS-1 samples can be obtained by treating the calcined solids with dilute sulfuric acid. We have also shown by diffuse reflectance UV (DR-UV) spectroscopy that extraframework titanium is present in these TS-1 samples and the amount depends on the concentration of the alkali metal or alkaline earth ions used in the synthesis mixture. Although, the presence of a large amount of extraframework titanium completely kills the catalytic activity, e.g., for TS-1 synthesized with Na/Ti > 1, a small concentration of extraframework material does not significantly affect the catalytic activity of the acid-treated TS-1 sample, e.g., TS-1 synthesized with Na/Ti < 1.

Although certain molecular sieves can be synthesized without alkali metal ions, e.g., ZSM-5, ZSM-48 and ZSM-12, most require the presence of alkali metal ions in the synthesis gel for the crystallization to occur. Moreover, it has also been reported that the presence of alkali metal ions enhances the crystallization rate of pure-silica ZSM-12 and it is most likely the case for other molecular sieves as well *(2)*. Hence, the acid treatment opens the possibility of creating catalytic activity for other titanium containing silicate structures that require the presence of a small amount of alkali metal ions in the synthesis mixture for their formation.

The substitution of titanium into the framework of large pore molecular sieves will be a breakthrough for the oxidation and epoxidation of large molecules, e.g., oxidation of biphenyl to 4,4'-biphenol. One of the potential candidates for this purpose is titanium substituted ZSM-12 which has a one-dimensional channel system with 12-membered ring pores. However, the addition of a small amount of titanium (titanium butoxide) into the synthesis mixture in the absence of alkali metal ions has been shown to completely stop the crystallization process *(3)*.

Here, we report the synthesis and the physicochemical properties of titanium containing ZSM-12 synthesized using sodium ions in the synthesis mixture. For comparison, other molecular sieves with 12-member ring pores like SSZ-33 and mordenite are also prepared using sodium ions in the synthesis mixture. Unlike ZSM-12, the presence of sodium ions in the synthesis mixture is crucial for the crystallization of both SSZ-33 and mordenite in the absence of titanium. Finally, we explore the acid treatment on these materials in order to generate catalytic activity.

Experimental

Samples

Na-Ti-Al-mordenite was synthesized following the preparation method reported by Kim *et al. (4)*. Titanium butoxide (TNBT) (Johnson Matthey) and hydrogen peroxide (Mallinckrodt) were mixed together to obtain titanium in the pertitanate form that is stable in basic solution *(5)*.

After stirring the solution for 2 hours, sodium hydroxide (Aldrich), aluminum isopropoxide and fumed silica (Hi-Sil 233) were sequentially added into the titanium solution. The final composition of the mixture is as follow:

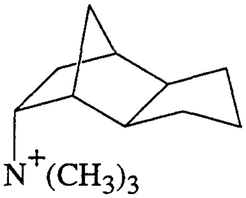
$$SiO_2 : Na_2O : Al_2O_3 : TiO_2 : H_2O = 1 : 0.13 : 0.03 : 0.013 : 17$$

This solution was stirred for 2 hours. Then, the mixture was statically heated at 175 °C for 10 days in a Teflon-lined autoclave. The solid obtained was filtered, washed and calcined at 550 °C.

Na-Ti-B-SSZ-33 was synthesized by modifying the preparation method reported by Zones *et al. (6)*. Tetraethylorthotitanate (TEOT) (Johnson Matthey), distillated deionized water and the structure directing agent (s.d.a), *endo*-N,N,N-trimethyl-8-trycyclo[5.2.1.$0^{2,6}$]-decaneammonium-hydroxide (supplied by S.I. Zones and Y. Nakagawa of Chevron Research and Technology Co., Richmond, CA) were mixed together. Hydrogen peroxide was added into this solution to obtain titanium in the pertitanate form. Then, sodium hydroxide, fumed silica (CabOSil M5), and sodium tetraborate ($Na_2B_4O_7$) (Aldrich) were sequentially added into the solution. The final mixture has the following composition:

$$SiO_2 : Na_2O : Na_2B_4O_7 : s.d.\ a : TiO_2 : H_2O = 1 : 0.1 : 0.01 : 0.4 : 60$$

s.d.a =

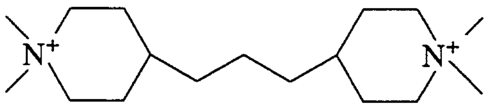


A small amount (1.5 wt%) of as-synthesized boron-SSZ-33 was also added to seed the crystallization. The mixture was transferred into a Teflon-lined autoclave and heated at 175 °C for 40 days with rotation. The solid obtained material was then filtered, washed and calcined at 625 °C .

Na-Ti-ZSM-12 was prepared by modification of the preparation method reported in the patent literature *(2,7)*. Propylene-*bis*(dimethylpiperidinium)dihydroxide (supplied by S.I. Zones and Y. Nakagawa) was used as the structure directing agent. TEOT, distillated deionized water and H_2O_2 were mixed together and stirred for 2 hours. Then, tetraethylorthosilicate (TEOS) (Aldrich) or Ludox AS-40 (DuPont) was introduced into the titanium mixture dropwise. After stirring the solution for 30 minutes, the structure directing agent and sodium nitrate (Aldrich) were sequentially added into the mixture to obtain the following composition:

$$SiO_2 : Na_2O : \text{s.d.a} : TiO_2 : H_2O = 1 : 0.06 : 0.18 : 0.03 : 80$$

s.d.a =



Similarly, 1.5 wt% as-synthesized pure-silica ZSM-12 were also added as seeds into the mixture. This solution was stirred for 2 hours before it was transferred into a Teflon-lined autoclave. It was then statically heated at 175 °C for 60 days followed by calcination at 625 °C in air. The sample synthesized with Ludox AS-40 is denoted as Na-Ti-ZSM-12L while the one prepared from TEOS is denoted as Na-Ti-ZSM-12T. The pure-silica form of

ZSM-12 is obtained from the same method using Ludox AS-40 as the silica source, except no titanium is added into the synthesis mixture. This material is designated as Na-ZSM-12.

The acid treatment was conducted by stirring the calcined samples in 1 M H_2SO_4 (Fisher) for 12 hours at room temperature followed by calcination of the collected solid at 550 °C for 8 hours. The untreated samples are denoted as (U) while the acid-washed samples are denoted as (W).

Analysis

X-ray diffraction (XRD) powder patterns were collected on a Scintag XDS-2000 diffractometer that is equipped with a liquid-nitrogen-cooled Germanium solid-state detector and uses Cu-K_α radiation. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) using the KBr pellet technique (~2.5 wt% sample). Raman spectra were recorded on the Nicolet Raman accessory for the FTIR system described above (CaF_2 beamsplitter and a liquid-nitrogen-cooled germanium detector). Diffuse reflectance UV (DR-UV) spectra were obtained on a spectrometer system constructed from an EG&G PAR diode array (1024 element Si) detector and a high-radiance Oriel deuterium lamp. The spectra were ratioed to a reference spectrum obtained from powdered MgO. Adsorption capacities of cyclohexane were determined with a McBain-Bakr balance at room temperature. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Catalytic Reactions

The oxidation of n-octane (Aldrich) was performed in a 10 ml glass reactor. A typical reaction mixture would contain 20 mg catalyst, 3 mmol n-octane, 2.9 mmol H_2O_2 (30% in H_2O, stabilized) (Mallinkrodt) and 0.5 ml methyl ethyl ketone (MEK) (Mallinckrodt) as the solvent. The reactions were conducted at 80 °C for 4 hours with vigorous stirring. The epoxidation of 1-hexene (Johnson Matthey) was carried out using 20 mg catalyst, 5 mmol of 1-hexene, 2 mmol of H_2O_2 (30% in H_2O, stabilized) and 3 ml MEK as the solvent. The reaction was conducted at 50 °C for 2 hours with vigorous stirring in a 10 ml glass reactor immersed in a constant temperature oil bath.

Prior to analysis, the reaction mixtures were diluted with acetone in order to obtain a single, homogeneous phase. In all cases, mesitylene was used as an internal standard for gas chromatography analysis. The products were analyzed on a HP 5890 Series II GC equipped with a 25 m long HP-FFAP (polar) capillary column.

Results and Discussions

The X-ray powder diffraction (XRD) patterns for the materials synthesized here are shown in Figure 5.1. The XRD patterns reveal that no additional crystalline phases are present in both Na-Ti-Mordenite and Na-Ti-SSZ-33. However, for Na-Ti-ZSM-12, phases other than ZSM-12 are present in the sample as shown by an extra peak at 2θ ~ 22°. Moreover, this phase is the predominate material in the solid for Na-Ti-ZSM-12T sample synthesized using TEOS as the silica source. It has also been shown that this peak progressively disappears as ZSM-12 is obtained *(3)*. Hence, this observation imply that Na-Ti-ZSM-12L synthesized from Ludox AS-40 as the silica source crystallizes faster than the one synthesized from TEOS, in agreement with the results from pure-silica ZSM-12 *(3)*.

It has been reported that the presence of an IR band at ~960 cm^{-1} is characteristic of titanium containing molecular sieves *(5)*. The IR spectra of Na-Ti-ZSM-12L before and after acid treatment are depicted in Figure 5.2a. Similar to TS-1 (the spectrum of TS-1 is depicted in Figure 5.2c), the spectrum of the unwashed sample of Na-Ti-ZSM-12L contains only a shoulder at ~960 cm^{-1} that is converted into a band at the same wavenumber after the sample is treated with sulfuric acid. For Na-Ti-mordenite, the unwashed sample already has a band at ~930 cm^{-1} that is shifted to 960 cm^{-1} after the material is treated with dilute sulfuric acid (Figure 5.2b). Similarly, the IR spectrum of the unwashed Na-Ti-SSZ-33 shows a small band at ~960 cm^{-1} that increases as the sample is treated with sulfuric acid (Figure 5.2c). For all these materials, the presence of an IR band at ~960 cm^{-1} in the acid-treated sample is similar to what was observed in Na-TS-1 *(1)*.

The elemental analyses of Na-Ti-ZSM-12L samples are tabulated in Table 5.1. Similar to TS-1, some of the sodium presence in the untreated Na-Ti-ZSM-12L can be washed away by contact with acid. As compared to the washed Na-TS-1, more sodium and titanium are present in the acid-treated Na-Ti-ZSM-12L sample. Based on the limited amount of titanium that can be incorporated in TS-1 *(8)*, it is most likely that some of the titanium present in Na-Ti-ZSM-12L resides as extraframework titanium *(vide-infra)*. To make sure that these extraframework titanium species do not cause any pore blocking, cyclohexane adsorption experiment was performed on both Na-Ti-ZSM-12L and pure-silica Na-ZSM-12. (Since ZSM-12 is a one-dimensional channel molecular sieve, its adsorption capacity is very susceptible to pore blocking.) Cyclohexane adsorption on Na-Ti-ZSM-12L gives a value of 0.06 g/g molecular sieve as compared to 0.08 g/g molecular sieve for pure-silica Na-ZSM-12, indicating that the extraframework material does not cause any significant pore blocking on Na-Ti-ZSM-12L. (The lower value found Na-Ti-ZSM-12L is most likely due to the presence of extraframework material presence in Na-Ti-ZSM-12L sample.)

Another method that has been used to probe the presence of extraframework titanium is Raman spectroscopy. Anatase has very strong Raman bands that are discernible at low concentration and these bands are observed at 386, 513 and 637 cm^{-1} in the region studied. No Raman bands due to anatase are present in the spectrum of Na-Ti-ZSM-12L (Figure 5.3). Instead, it has a small band at 960 cm^{-1} that has been taken as characteristic of titanium incorporation into the framework *(9)* (although it does not provide direct structural information of the titania species *(10)*). Additionally, this Raman band at 960 cm^{-1} is also present in the spectrum of both Na-Ti-SSZ-33 and Na-Ti-mordenite (Figure not shown). Hence, these observations provide further evidence for the incorporation of titanium into the framework of the materials studied here.

In addition to Raman spectroscopy, diffuse-reflectance ultraviolet (DR-UV) spectroscopy has been used to probe the existence of framework and non-framework titanium *(9,11-13)*. The DR-UV spectra of the acid-treated Na-Ti-ZSM-12L, Na-Ti-SSZ-33, Na-Ti-mordenite and TS-1 are shown in Figure 5.4. The band at 220 nm has been assigned to the isolated framework titanium species while the broad shoulder between 300 and 350 nm has been attributed to extraframework titanium *(12)*. All of the samples synthesized here show the presence of the framework titanium at 220 nm along with the extraframework band of varying intensities that does not change with acid treatment. From the DR-UV spectra, it is obvious that all the samples synthesized here contain some extraframework titanium. The amount of anatase is presumably quite small since it is not detected by Raman spectroscopy. (The detection limit of DR-UV spectroscopy is one order of magnitude more sensitive than the Raman spectroscopy for detecting non-framework titanium *(12)*). Based on the results from elemental analysis and Raman spectroscopy on Na-Ti-ZSM-12L, it is most likely that the majority of the extraframework titanium presence in the sample is not anatase, but another form of titanium that is not Raman active and gives a broad band between 250 and 300 nm on the DR-UV spectrum.

After the acid treatment, all the materials were tested for their ability to epoxidize 1-hexene and oxidize n-octane using aqueous H_2O_2 as the oxidant. Although some catalytic activity has been reported on Na-Ti-mordenite synthesized with the same method *(4)*, surprisingly none of the materials synthesized here are active. Spectroscopically, the only difference between these materials and TS-1 is the presence of a broad band between 250 and 300 nm on the DR-UV spectrum, especially for the spectrum of Na-Ti-ZSM-12L and Na-Ti-mordenite indicating the presence of extra-framework titanium. One possibility to explain the lack of inactivity of these materials is that the extraframework titanium may form a complex with the framework titanium. This complex would then contain adjacent titanium atoms and this configuration has been known to be active toward H_2O_2 decomposition to dioxygen *(9)*. We have tried to remove this extra-framework titanium by numerous methods, e.g., steaming, washing the samples with H_2O_2 as well as washing the samples with H_2O_2 in the presence of acid both at room temperature and at reflux temperature. However, all the approaches do not improve the catalytic performance of these catalysts. Similarly, almost every method available in our laboratory has been tested to characterize this extraframework titanium without satisfactory results. We have also performed Ti-NMR experiments on these samples, however the Ti-peaks are too broad for any meaningful results. Currently, we are collaborating with another laboratory to carry out EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy on these samples in order to characterize the extraframework titanium.

Recently, a new method for synthesizing Ti-SSZ-33 has been developed *(14)*. Instead of using a direct method, the boron atom on the calcined SSZ-33 sample is replaced by titanium from $TiCl_4$ vapor following the method reported by Rigutto *et al. (15)*. This material has been shown to be active for 1-hexene epoxidation with reasonable conversion (~5% conversion compared to 7% for TS-1). The DR-UV spectrum of this material show that less extraframework titanium is present on this sample as compared to the one synthesized by the direct method used here. Further investigation on the materials synthesized by both the direct and indirect methods using EXAFS spectroscopy may provide further insights into the structure of the extraframework titanium. This may lead to the understanding of the lack of activity on the materials synthesized here.

Conclusions

We have shown here that the presence of extraframework titanium is crucial for the catalytic activity of titanium silicates. Although the spectroscopic data of the materials synthesized here (Na-Ti-ZSM-12L, Na-Ti-SSZ-33 and Na-Ti-mordenite) suggest the incorporation of some titanium into the framework, no catalytic activity on these materials is observed. The lack of activity is most likely due to the presence of extraframework titanium. However, it has been reported earlier that the presence of anatase on TS-1 does not have a significant effect on the catalytic activity of this catalyst for alkane oxidation and alkene epoxidation *(16)*. Hence, further study on the type of extraframework titanium presence in titanium silicates, e.g., using EXAFS spectroscopy, may lead to the understanding of the lack of activity on these catalysts.

Figure 5.1. XRD pattern of Na-Ti-mordenite, Na-Ti-SSZ-33 and Na-Ti-ZSM-12

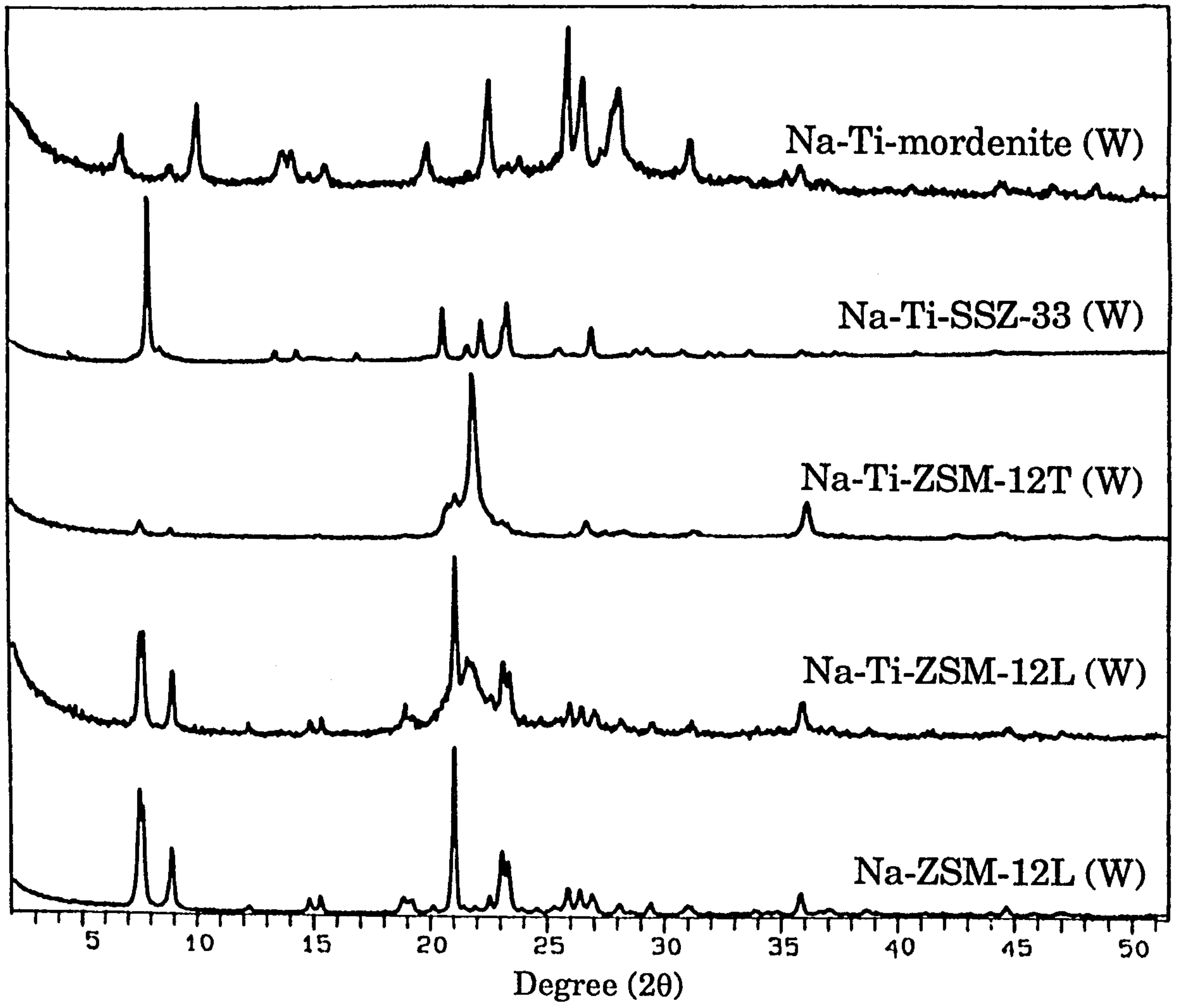


Figure 5.2a. IR spectra of Na-Ti-ZSM-12L

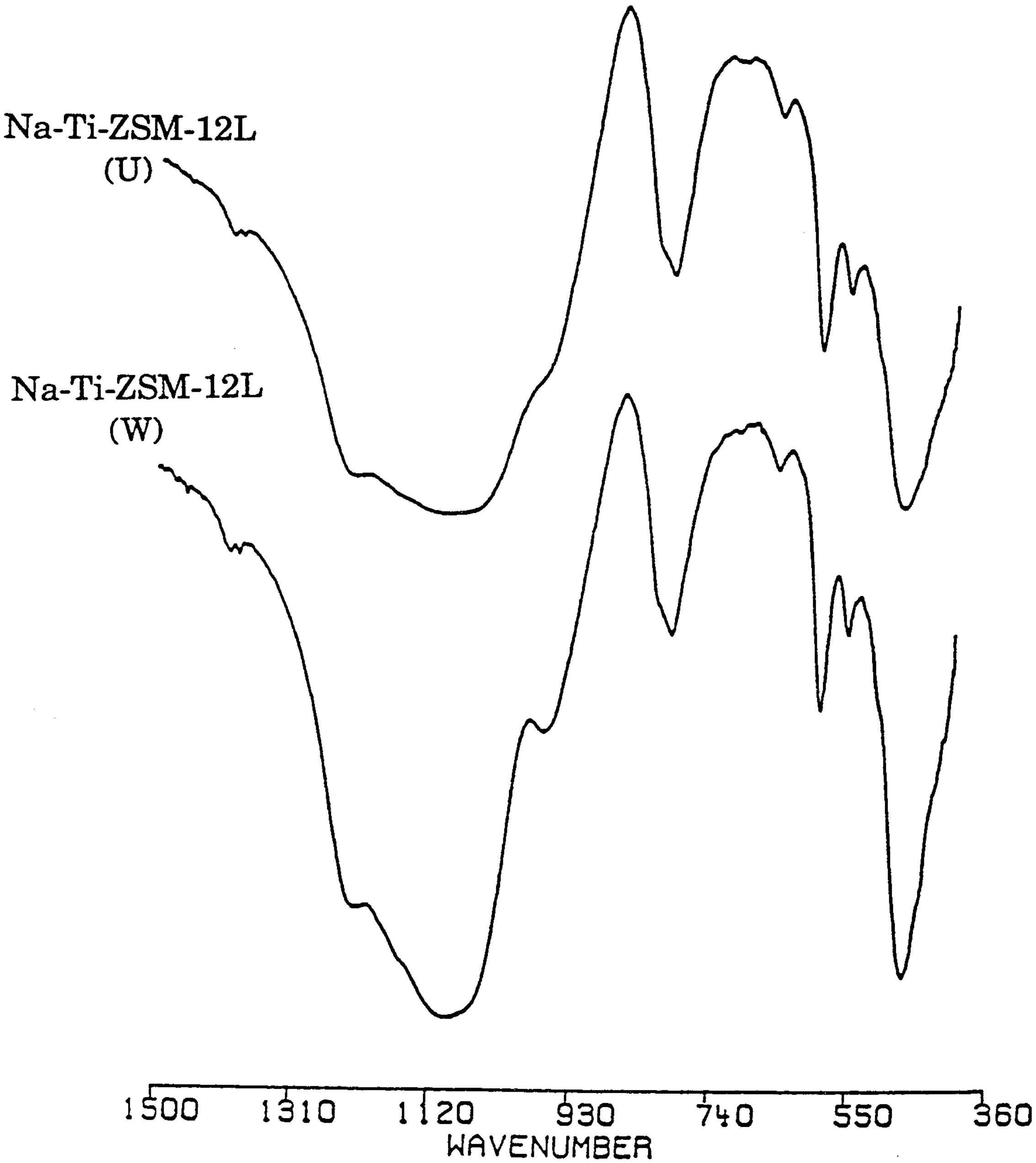


Figure 5.2b. IR spectra of Na-Ti-mordenite

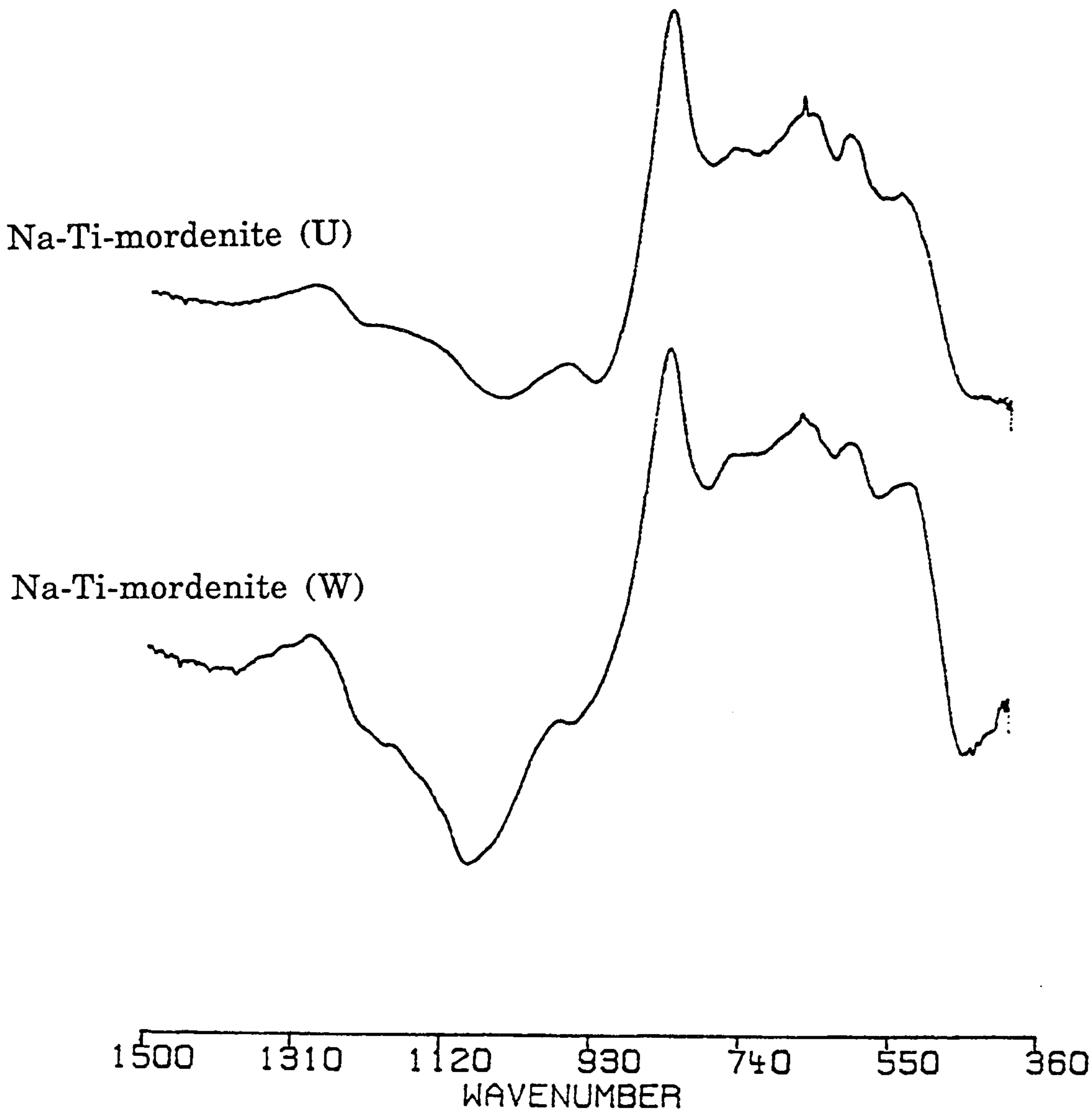


Figure 5.2c. IR spectra of Na-Ti-SSZ-33 and TS-1

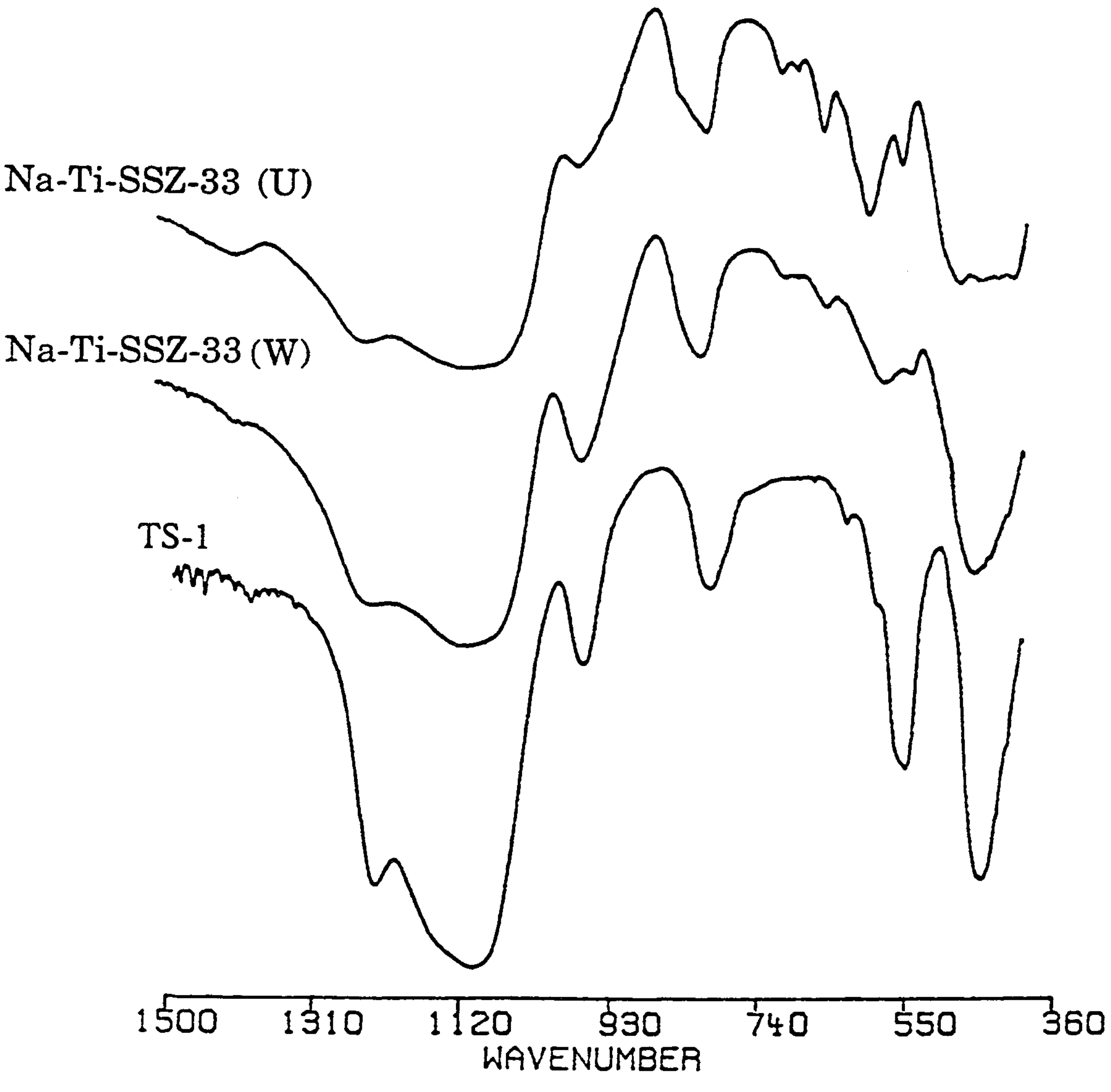


Figure 5.3. Raman Spectra of Na-Ti-ZSM-12L and TS-1

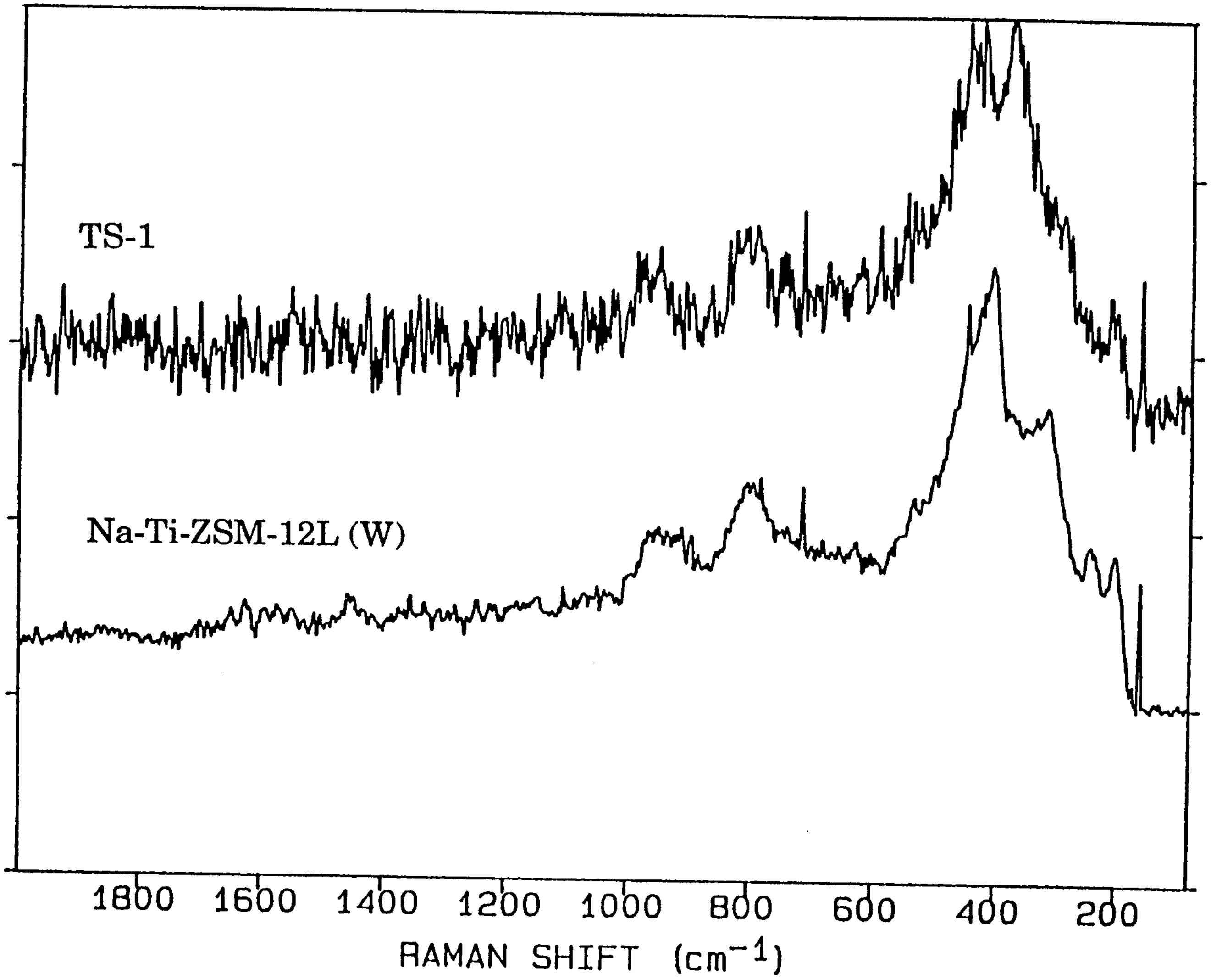


Figure 5.4. DR-UV spectra of Na-Ti-ZSM-12L, Na-Ti-SSZ-33 and Na-Ti-mordenite after washing with 1 M H_2SO_4

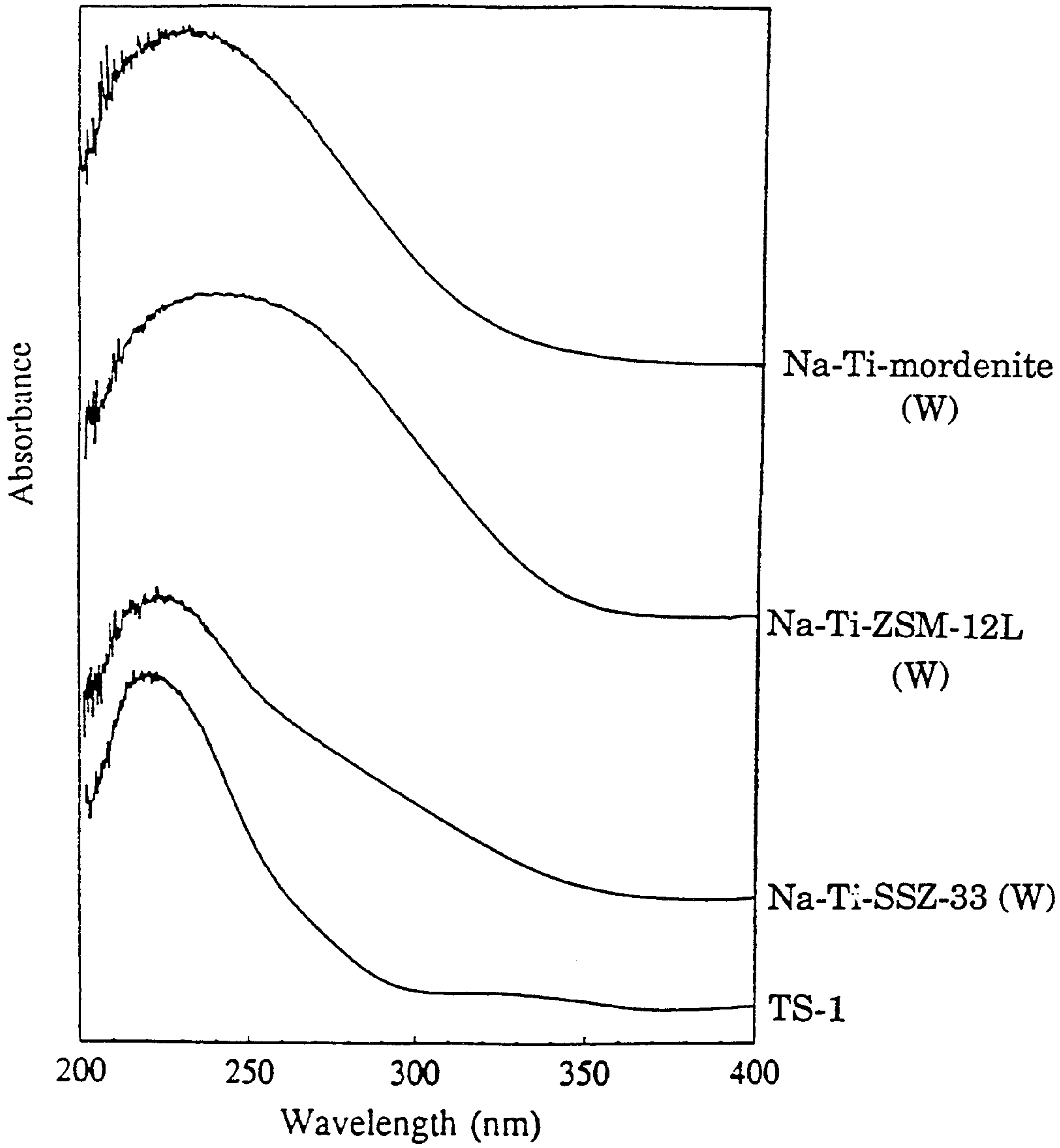


Table 5.1. Elemental analysis of Na-Ti-ZSM-12L and Na-TS-1 synthesized in the presence of sodium

Catalyst	Si/Ti	Si/Na
Na-Ti-ZSM-12L (U)	17.6	18.6
Na-Ti-ZSM-12L (W)	19.6	60.7
Na-TS-1 (U)	26.0	20
Na-TS-1 (W)	37.0	>1035

(U) : unwashed
(W) : treated with 1 M sulfuric acid

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CHAPTER SIX

Conclusions

In this work, we have synthesized TS-1 via several preparation methods that use both titanium ethyl orthosilicate and TiO_2-SiO_2 coprecipitate as the silica source. The catalytic activity of these samples is compared to other titanium containing materials such as anatase and amorphous TiO_2-SiO_2 coprecipitate for the oxidation of alkanes, alkenes and phenol using aqueous H_2O_2 as the oxidant. Although some of the physicochemical properties of these materials are similar, e.g., both TS-1 and amorphous TiO_2-SiO_2 coprecipitate show an IR band at 960 cm^{-1}, significant differences are found on the catalytic activities. TiO_2-SiO_2 coprecipitate is not catalytically active for the oxidation of alkanes, alkenes and phenol when aqueous H_2O_2 is used as the oxidant although it is active for alkenes epoxidation using *t*-butyl hydroperoxides. Framework titanium in TS-1 is necessary for the oxidation of alkanes, alkenes and phenol using aqueous H_2O_2 as the oxidant.

In contrast to the TiO_2-SiO_2 coprecipitate, TS-1 is hydrophobic. Hence, it allows the use of aqueous H_2O_2 as the oxidant since the concentration of water surrounding the titanium is always maintained at a low value. Our results show that if there is a low concentration of titanium in an amorphous TiO_2-SiO_2 coprecipitate, the state of the titanium is not much different from that in TS-1. Consequently, reactions which are catalyzed by TS-1, like alkane oxidation and alkene epoxidation, are also catalyzed by TiO_2-SiO_2 coprecipitate provided anhydrous H_2O_2 is used as the oxidant and the water formed during the reactions is constantly removed. However, if the concentration of titanium in this material is increased, phase separated TiO_2 is formed and this type of titanium is more active toward H_2O_2 decomposition to water and oxygen. Therefore, TiO_2-SiO_2 coprecipitate with a high concentration of titanium is not active for partial oxidation. Since TS-1 is a microporous material, it has a higher surface area than the amorphous TiO_2-SiO_2 coprecipitate. Therefore a greater number of isolated titanium is exposed to the reaction environment in TS-1 than in the TiO_2-SiO_2 coprecipitate. Hence, TS-1 is much more reactive than the TiO_2-SiO_2 coprecipitate for partial oxidation reactions even when anhydrous H_2O_2 is used as the oxidant.

The lack epoxidation activity on TS-1 when alkyl hydroperoxides are used as the oxidants is attributed to the bulkiness of the alkyl group on the Ti-alkylperoxo complex that blocks the reactants from approaching the active titanium. Since no pore blocking occurs on TiO_2-SiO_2 coprecipitate, this catalyst is active for alkene epoxidation using alkyl hydroperoxides as the oxidant. However, no activity is observed both on TS-1 and TiO_2-SiO_2 coprecipitate for alkane oxidation when alkyl hydroperoxide is used as the oxidant. Comparison between the Ti-alkylperoxo and the Ti-hydroperoxo complex both on TS-1 and the amorphous TiO_2-SiO_2 coprecipitate shows that Ti-hydroperoxo complex is more acidic than the Ti-alkylperoxo complex. This result also implies that Ti-hydroperoxo has some superoxo like character that is important for the hydrogen abstraction during alkane oxidation. Since such a species is not obtainable from a Ti-alkylperoxo complex, alkyl hydroperoxide is not an active oxidant for alkane oxidation. However, since no hydrogen abstraction occurs in epoxidation, anhydrous alkyl hydroperoxide is active as an oxidant for alkene epoxidation with the TiO_2-SiO_2 coprecipitate.

The difference between the stereoselectivity for alkane oxidation and alkene epoxidation on TS-1 suggests that these reactions proceed through different mechanisms. Unlike alkene epoxidation, alkane oxidation occurs with stereoscrambling, suggesting that the reaction proceeds by a homolytic mechanism involving radical species as intermediates. However, the presence of stereoscrambling without any "radical clock" rearrangement during alkane oxidation indicates that the radicals formed may have a very short life-time or their movements are restricted such that no rearrangement can occur. Nevertheless, the reason for the lack of terminal activation on TS-1 remains unknown at this time.

The presence of sodium in the synthesis gel of TS-1 completely eliminates the catalytic activity of this material for alkane oxidation and alkene epoxidation. However, our results show that the catalytic activity of TS-1 synthesized in the presence of alkali-metal ion can be restored by washing the catalyst with acid solution. This treatment may be useful in overcoming the problems of synthesizing TS-1 from reagents that contain alkali-metal ions, e.g., the TPAOH solution. More importantly, this treatment opens the possibility of synthesizing other titanium containing molecular sieves that require the presence of alkali metal ions in the synthesis mixture for their formation.

The spectroscopic data of other titanium containing materials, e.g., Na-Ti-ZSM-12, Na-Ti-SSZ-33 and Na-Ti-mordenite, synthesized using sodium ions in the synthesis mixture suggest the incorporation of some titanium into the framework. All the materials synthesized here show an

IR band at 960 cm^{-1} which is one of the necessary condition for catalytic activity. Surprisingly, no catalytic activity is observed on these materials. The presence of extraframework titanium other than anatase seems to be the reason for the lack of activity on these materials. Almost all techniques available in our laboratory have been used to characterize this extraframework titanium without any satisfactory results regarding the nature of this titanium. Further investigation on the extraframework titanium, e.g., using EXAFS spectroscopy, may lead to the understanding of the lack of activity on these materials.

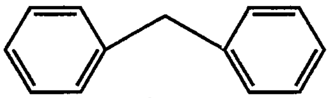
CHAPTER SEVEN

Future Directions

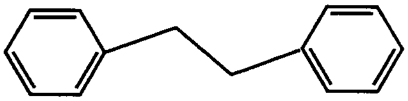
Although some of the important features of TS-1 have been rationalized in this work, they are still several issues that are not well resolved. For example, the reason for the lack of terminal activation on TS-1 remains unclear at this time. If we consider the activation energy of abstracting hydrogen, the energy requires for breaking a C-H bond on a benzylic carbon is much lower than on either a secondary or a tertiary carbon. Therefore, TS-1 should be able to activate benzylic carbons if the activation energy is the primary factor. However, this is not the case. Moreover, TS-1 is also not capable of oxidizing primary alcohols to the corresponding aldehydes. For example, no hexanal is observed when 1-hexanol is used as the reactant although this reaction requires a lower activation energy than alkane activation. It appears that the determining factor for TS-1 activation is not the energy required for hydrogen abstraction. One possible hypothesis for the observed activity pattern is that the active site on TS-1 requires at least two aliphatic or benzylic unsaturated carbons. This hypothesis agrees with the experimental results. For example, for toluene or *para*-xylene, there is only one benzylic carbon and no reaction is observed. For the case of ethane, no reaction is also observed. However in this case, the lack of reactivity may be due to the low concentration of ethane in the reaction mixture since ethane is introduced as gas into the reactor.

To prove this hypothesis, the reactivity of diphenylmethane [I] and bibenzyl [II] should be tested. If this hypothesis is true, then [I] will not be activated while [II] should react to form 1,2 diphenylethanol. The problem with this experiment is that these molecules may be too large to enter the

ZSM-5 pores. To overcome this problem, other titanium containing silica molecular sieves with larger pore size than TS-1 (e.g., Ti-Beta) may be used.



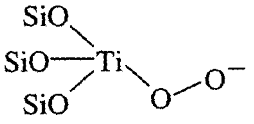
[I]



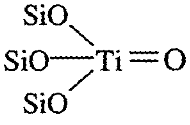
[II]

Our experimental results have shown that alkane oxidation proceeds with stereoscrambling, suggesting that radical species are involved as intermediates. Electron Paramagnetic Resonance (EPR) spectroscopy is a valuable tool for studying radical intermediates. However, direct detection and identification of short-lived free radicals by EPR is possible only if the radicals are produced in relatively high concentration in the EPR cavity by intense *in situ* irradiation or by rapid-mixing flow systems. Indirect techniques provide another alternative for the detection and identification of low concentration free radicals. This method involves trapping of the reactive free radical by an addition reaction to produce a more stable radical which is detectable by EPR and its hyperfine coupling parameters permit identification of the initial radical trapped. The indirect method appears to be a better alternative since the temperature required for TS-1 to be active is ~100 °C. This technique should enable not only the confirmation that the mechanism proceeds through radical intermediates but also the elucidation of the type of radicals formed during the reaction.

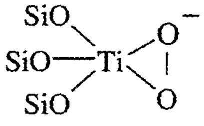
We have proposed that Ti species [III] and [IV] are involved in alkane oxidation. Similarly, Ti species [V] has been proposed to be formed on TS-1 with H_2O_2 in basic media and it is most likely formed on TS-1 exchanged with alkali-metal ions as well *(1)*. However, more experiments are necessary to confirm the presence of these complexes. EPR spectroscopy appears to be a good candidate for this purpose. Moreover, it has also been reported that upon activation of TS-1 with H_2O_2, EPR active species are formed *(2)*. In this case, the structure of the intermediate states of the titanium can be investigated by monitoring the g-values and the line shapes of the EPR spectrum during the activation process and during the reaction.



[III]



[IV]



[V]

EPR spectroscopy is also useful for studying the decomposition of H_2O_2 on TS-1 since it involves the formation of free radicals. By combining the results from H_2O_2 decomposition on TS-1 and sodium exchanged TS-1, the possible structures of the Ti species formed may be elucidated and a plausible explanation for the acceleration of H_2O_2 decomposition on sodium exchanged TS-1 may be deduced.

As previously mentioned, further work on understanding the type and effect of the extraframework titanium in the titanium silicates synthesized in the presence of alkali-metal ions will also be important to the understanding of the lack of activity on these materials. Investigations by EXAFS spectroscopy may provide further insight into the structure of this extraframework titanium.

References

1. Clerici, M. G., Ingallina, P., Millini, R., *in "Proceedings from the Ninth International Zeolite Conference"* (von Ballmoos, R., Higgins, J. B., Treacy, M.M.J., Eds.), p. 445. Butterworth-Heinemann, Boston, 1993.
2. Romano, U., Esposito, A., Maspero, F., Neri, C., Clerici, M.G., *Stud. Surf. Sci. Catal.* **55**, 33 (1990).