SYNTHESIS AND CHARACTERIZATION OF TITANIUM-CONTAINING MOLECULAR SIEVES

Thesis by

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ABSTRACT

The use of zeolites and molecular sieves as catalysts for important organic reactions is reviewed. One emerging area of particular interest is the use of titanium-containing molecular sieves as partial oxidation catalysts and is chosen for further study.

In order to elucidate the relationships between the physicochemical properties of titanium-containing molecular sieves and their ability to act as partial oxidation catalysts, titanium-containing pure-silica ZSM-5 (TS-1) materials are synthesized using different methods. The activities of the titanium-containing catalysts for the oxidation of alkanes, alkenes, and phenol at temperatures below 100 °C using aqueous hydrogen peroxide (H_2O_2) as the oxidant are 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 are described. The addition of sodium during the synthesis of TS-1 is detrimental to the catalytic activity while sodium incorporation into pre-formed TS-1 is not. The framework substitution of aluminum for silicon appears to decrease the amount of framework titanium.

The relationships between catalytic performance and physicochemical properties that are controlled through synthetic methods are further investigated using a series of titanium-containing molecular sieves. Titanium-containing pure-silica ZSM-5 (TS-1), pure-silica ZSM-48 (Ti-ZSM-48) and zeolite beta (Ti-Al-beta) are synthesized and characterized by X-ray powder diffraction (XRD), elemental analysis, physical adsorption of N_2, Fourier transform infrared (FT-IR), FT-Raman, and diffuse reflectance ultraviolet (DR-UV) spectroscopies. TS-1 is synthesized by five different methods. All materials are evaluated for their ability to oxidize 1-hexene and n-octane using aqueous H_2O_2 as the oxidant. The relationships between the physicochemical and catalytic properties of these titanium-containing zeolites are discussed. TS-1 samples synthesized at high pH are catalytically active and framework titanium is shown to be necessary for olefin epoxidation and alkane hydroxylation to occur. The existence of anatase in active TS-1 samples results in decreased hydrogen peroxide efficiencies in the epoxidation reaction. TS-1 produced at pH=7.4 and Ti-ZSM-48 each contain anatase and are not active. Ti-beta is found to contain framework titanium and be free of anatase. However, at the conditions used in this study these samples are not able to activate 1-hexene or n-octane.

In attempts to prepare large pore titanium-containing molecular sieves, post-synthetic incorporation of titanium in the borosilicate SSZ-33 and the direct synthesis of an aluminum-free titanium-containing zeolite Beta (Ti-Beta) are reported. These materials are characterized by XRD, FT-IR, FT-Raman, and DR-UV spectroscopies. The molecular sieves are shown to catalyze the epoxidation of various olefins using aqueous hydrogen peroxide as the oxidant. The physicochemical properties as found by the characterization methods are correlated to the catalytic data and the results compared to a high quality sample of TS-1. The modified SSZ-33 samples contain titanium primarily in the form of isolated tetrahedrally coordinated Ti atoms, although some extra-framework Ti is observed by Raman and DR-UV spectroscopies. Ti-Beta samples show no evidence of extra-framework titanium. For the epoxidation of cis-cyclooctene, the Ti-Beta catalysts give quantitative conversion to epoxide, and both the Ti-Beta and Ti-SSZ-33 catalysts are able to epoxidize substrates too large to be oxidized by TS-1.

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LIST OF PUBLICATIONS

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"Flux Growth of Millimeter-Sized Single Crystal Aluminate Sodalite."

Okubo, T.; Sun, J. T.; Dartt, C. B.; Davis, M. E. Proceedings from Symposium on Synthesis of Zeolites, Layered Compounds and Other Microporous Solids, 209th National Meeting of the American Chemical Society, Anaheim, CA. Spring 1995, in press.

CHAPTER ONE

Introduction and Objectives

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1.1 Introduction

Catalytic oxidation is important to both the bulk and fine chemical industries. For example, governmental regulations now require the addition of oxygenated compounds to gasoline in certain urban areas in order to reduce emissions. Also, smaller volume, higher value products such as pharmaceutical intermediates often require the stereoselective addition of oxygen to form alcohol and ketone functional groups. Traditionally, oxidation chemistries have been environmentally detrimental. Even though oxygenated products are often produced in much smaller volumes than most bulk petrochemical products, the ratio of the volume of by-products to the volume of desired products is generally large for traditional oxygenations. This trend is shown in Table 1.1. The by-products result primarily from the oxidant and poor selectivity to the desired product.

The choice of oxidant is an extremely important issue. Until recently, cost has been the main criterion used in the choice of the oxidant. Molecular oxygen is the obvious winner due to its low cost and simplicity. It is also the cleanest of all oxidants from an environmental standpoint. Table 1.2 lists several other oxygen donors. Classical stoichiometric oxidants such as dichromate, permanganate, and manganese dioxide have been favorites with synthetic organic chemists for over one hundred years. These oxidants are used without a catalyst, and are converted to their corresponding salts after reacting. Environmental legislation is now making the disposal of large amounts of hazardous salts difficult and costly. Alkyl hydroperoxides have been used extensively for catalytic oxidations over the past 40 years. The by-products from these oxygen donors are alcohols. If these alcohols can not be used in other downstream processing they must be disposed of, thus creating their own environmental waste problem. The most promising oxidant (other than dioxygen) is hydrogen peroxide (H_2O_2). The by-product from H_2O_2 is water. If H_2O_2 can be used as an aqueous solution, it does not pose the handling problems associated with concentrated peroxides. These two facts alone give H_2O_2 (aq) great advantages in terms of environmental costs.

One area of oxidation chemistry where catalysis using hydroperoxides has triumphed over an environmentally undesirable process is in the manufacture of epoxides. The conventional process consists of two steps. The first step produces a chlorohydrin by reacting the olefin with hypochlorous acid. In the second step, the chlorohydrin is reacted with calcium hydroxide to yield the epoxide. In addition to the desired epoxide, large amounts of calcium chloride are formed. In fact, 2 tons of salt are produced for every ton of epoxide in the case of propylene oxide (Hölderich, 1993). Between the disposal of the salt and the handling of concentrated calcium hydroxide, this technology is not environmentally friendly. However, this process is still employed by several companies for the epoxidation of propylene to propylene oxide. It should be stressed that propylene oxide is of major commercial interest. In 1992, 2.7 billion pounds of propylene oxide were synthesized in the U.S. making it the thirty-ninth largest volume chemical (Reisch, 1993). Propylene oxide is used in the manufacture of polymers and glycols. Epoxides, in general, are extremely valuable compounds because they are easily opened to produce 1,2 functionality in a stereospecific manner. Additionally, asymmetric epoxidation is commercially viable (Harrington, 1990) and ring opening of the chiral epoxide can produce two contiguous chiral centers, a real bonus in the production of fine chemicals.

In the mid 1960's a breakthrough in epoxidation catalysis quickly led to Oxirane's commercial process (a joint venture between ARCO and Halcon) for propylene oxide production (Kollar, 1967). Molybdenum compounds such as $Mo(CO)_6$ were found to convert into catalytically active species under reaction conditions. Other homogeneous metal complexes, e.g., $W(CO)_6$, $Ti(OBu)_4$, were found to be active as well. Most alkyl hydroperoxides are suitable oxidants for this reaction and two popular choices are TBHP, and 1-phenylethyl hydroperoxide. The co-product of the former can be converted to methyl-tert-butyl ether, a high-octane component for gasoline, while the co-product of the latter can be dehydrated to styrene. H_2O_2 cannot be used because it is not soluble in non-polar solvents. If a polar solvent is used, e.g., alcohol or H_2O, the solvent molecules strongly coordinate to the catalytic centers and render them inactive (Sheldon and Van Doorn, 1973). This is a common problem among oxometal and peroxometal catalysts. However, this process is certainly more environmentally friendly than the salt-producing chlorohydrin route.

A heterogeneous catalyst capable of performing the epoxidation reaction was discovered in the early 1970's by researchers at Shell (Wulff, 1975). The catalyst consists of titanium supported on amorphous silica. The exact nature of the titanium site is not fully understood, however, but it is believed that titanium (IV) centers are responsible for the activity. The same alkyl hydroperoxides that are used with the homogeneous molybdenum catalyst can be used with the heterogeneous titanium catalyst. However, the $Ti(IV)/SiO_2$ material affords the advantages that go along with all heterogeneous catalysts: ease of regeneration, high thermal stability, ease of separation, and ease of handling. Like the Mo catalyst, the Ti catalyst is very sensitive to water and care must be taken to exclude H_2O from the reaction mixture.

The two preceding epoxidation examples demonstrate how catalytic processing has replaced stoichiometric chemistries that produce large quantities of by-products. The use of alkyl hydroperoxides as oxidants with the right catalysts leads to efficient low temperature, liquid phase reactions. If the large volume of co-products from the hydroperoxide can be utilized in a profitable manner with some type of solvent recycling, then these processes are quite environmentally sound.

Because of the cost, safety, and environmental concerns associated with alkyl hydroperoxides, there remains a continuing search for new chemistries that alleviate at least some of these hazards. Hydrogen peroxide certainly has some distinct environmental advantages over alkyl hydroperoxides. First and foremost, the by-product is water. Also, H_2O_2 has a high weight percentage of active oxygen and is soluble in both aqueous and polar organic media. Because concentrated solutions are expensive and dangerous to handle, hydrogen peroxide is often sold as an aqueous solution, e.g., 30 wt %. At this concentration, the peroxide is stable if care is taken to remove contaminants such as organics and alkali-metal ions (Schumb et al., 1955). When handled correctly, H_2O_2 will lose less than 1% by weight of its oxygen content per year (Dear, 1993). H_2O_2 based technology is well suited to compete with other oxidants, except O_2, and offers a greater environmental acceptability.

1.2 Titanium-Silicalite-1

One of the biggest breakthroughs in catalytic partial oxidation with H_2O_2 was the synthesis of titanium-silicalite-1 (denoted TS-1) by Taramasso et al. in 1983. TS-1 is a zeolite-based catalyst capable of activating a broad spectrum of hydrocarbons with aqueous hydrogen peroxide (see Figure 1.1). The shape-selectivity, ease of separation and recovery, and the regenerability of the zeolite make this type of catalyst more attractive than traditional homogeneous ones.

Although the active site in TS-1 is still not fully understood, it has been postulated that the same type of titanium site is present in the Shell catalyst (titanium deposited on amorphous silica) (Notari, 1988). The zeolite structure is relatively hydrophobic and this may result in screening out bulk water from the internal voids of TS-1 (Khouw et al., 1994). This may be the reason why TS-1 is not affected by water in contrast to the Shell catalyst. Hence, aqueous H_2O_2 can be employed as the oxidant with TS-1. Because the titanium resides in the zeolite lattice, all the Ti atoms are accessible and exposed to the same reaction environment; this is difficult to achieve by depositing metal complexes on an amorphous support. As a result, TS-1 is extremely active and selective (Huybrechts et al., 1992). For example, the reaction of propylene and H_2O_2 results in a propylene oxide selectivity of 97% at 97% peroxide conversion (Clerici et al., 1991) in methanol at 50 °C. These results compare favorably to those obtained from the Shell catalyst using alkyl hydroperoxides. Presently, the cost of the H_2O_2 is preventing the TS-1 process from having an economic advantage for epoxidation. Changes in the value of the co-product from the alkyl hydroperoxide (or the cost of disposal) and the development of a new, cheaper catalytic route to aqueous H_2O_2 by DuPont (Glosser, 1988) may swing the balance in favor of TS-1 in the future.

Shape-selective oxidation can be observed with TS-1. For the epoxidation of C_4 olefins, conversion rates followed the order: cis-2-butene > 1-butene > isobutene > trans-2-butene (Clerici and Ingallina, 1993). It has also been shown that 2-hexene can be selectively epoxidized when mixtures of 2-hexene/cyclohexene are used (Tatsumi et al., 1991).

Within a short time after its synthesis, TS-1 was employed as a commercial catalyst for the production of catechol and hydroquinone from phenol and aqueous H_2O_2 (Romano et al., 1990). The TS-1 catalyzed process now operates at 10 tons per year. The classical route to hydroquinone is shown in Figure 1.2. For every kilogram of hydroquinone produced in the conventional process, more than 10 kg of salt are formed. The yields from the TS-1 catalyzed reaction compare favorably to other H_2O_2/phenol reactions such as the acid-catalyzed scheme, as well as the process employing Fenton's reagent: an iron salt and H_2O_2 (see Table 1.3). TS-1 produces the lowest ratio of catechol to hydroquinone. Since hydroquinone is the desired product, there is less by-product from the reaction and the reaction is environmentally friendlier. The amount of tars produced with TS-1 is nearly equal to the liquid-acid catalyzed process and half that of the Fenton chemistry (Notari, 1988).

An important example of where TS-1 may be used to develop new chemistry to replace an environmentally undesirable process is in the manufacture of Nylon 6. This is the second most widely used polyamide (to Nylon 6-6) in the United States (Parshall and Ittel, 1992). It is produced from the ring opening polymerization of ε-caprolactam. The classical route to ε-caprolactam is shown in Figure 1.3. Because of the low yield and rapid catalyst deactivation in the ammoxidation step, other processes were developed by which the ketone was reacted with ammonia and H_2O_2 in the liquid phase using an acid catalyst (phosphotungstic acid). This process also suffers from low yields and catalyst deactivation (Roffia et al., 1990). TS-1 overcomes these problems and gives excellent yields at moderate temperatures. At a reaction temperature of 60 °C, cyclohexanone conversions above 90% and selectivities above 99% for the oxime have been reported (Thangaraj et al., 1991). Very little hydrogen peroxide decomposition to dioxygen is observed in contrast to the liquid-acid-catalyzed reaction.

While many routes to the oxime exist, all commercial caprolactam production makes use of a Beckmann rearrangement to transform the oxime to the desired product. Traditional methods employ oleum, a very strong acid consisting of H_2SO_4 and SO_3, to facilitate the rearrangement. In order to recover the product, the mixture must be neutralized with ammonium hydroxide. This produces approximately five tons of ammonium sulfate per ton of lactam (Immel, 1984). Mobil has patented a gas-phase process using a medium-pore zeolite, ZSM-5, with low to moderate acidity (Bell and Haag, 1990). Very high conversions (>95%) and selectivities (>90%) to oxime were reported at 300 °C. Union Carbide has already tested the molecular sieves SAPO-11 and SAPO-41 as catalysts for the rearrangement at pilot plant scale (Cusumano, 1992). At 350 °C the oxime is converted to ε-caprolactam with 95% selectivity at 98% conversion (Hölderich, 1989).

By using a heterogeneous catalyst all of the environmental disadvantages have been eliminated.

The comment has been made that “oxidation continues to be the most promising of the major process reactions used industrially for the conversion of hydrocarbons to useful organic products” (Marek, 1954). This statement was made in 1954 and is still true today. As environmental regulations (and consumer concerns) mandate the removal of stoichiometric oxidants due to massive amounts of by-products, new catalytic technologies must fill the void to produce this important class of chemicals. The use of homogeneous, transitional-metal catalysts with alkyl hydroperoxides as oxidants has already started to do just that. However, the use of hydroperoxides carries with it economic and environmental concerns. Hydrogen peroxide has been labeled “Mr. Clean” (Sheldon, 1993) and appears well suited to become the oxidant of choice as the chemical industry turns toward “green” processes. It is important to remember that the ultimate goal is the use of molecular oxygen at moderate temperatures in the liquid phase where overoxidation to carbon dioxide and water is eliminated. This will bring commercial catalytic oxidation towards the sophistication observed from enzymes.

1.3 Objectives

The trend towards environmentally benign processes in the manufacture of chemicals, along with the high profits derived from the sale of specialty chemicals, have focused much attention on “new generation” catalysts. It is no longer sufficient to simply produce a product at the lowest cost; the number of processing steps and the amount of waste must be significantly curtailed. This waste can be in the form of the spent catalyst, contaminated solvent, and/or undesired by-product. Titanium-containing molecular sieves, most notably TS-1, have gained much attention because of their ability to alleviate many of these concerns. However, little is known about the physicochemical properties required for successful application as partial oxidation catalysts. Also, no larger pore molecular sieves currently can compete with the catalytic abilities of TS-1. Thus, the objectives of this work are: (i) the elucidation of the relationships between the physicochemical properties of titanium-containing molecular sieves and their ability to act as partial oxidation catalysts and (ii) to synthesize large-pore, titanium-containing molecular sieves capable of performing partial oxidation catalysis.

This thesis is organized as follows. Chapter Two reviews areas where zeolite catalysis have aided in the synthesis of fine chemicals. The traditional role of zeolites as solid-acid catalysts is not extensively discussed. However, the use of molecular sieves for base-catalyzed reactions, enantioselective reactions, as well as partial oxidation chemistries is surveyed. The last of these was chosen for further study here. This class of materials differs from catalysts for base catalysis and asymmetric reactions because the active site appears to be due to elements added during synthesis rather than added after crystallization. The fact that the catalysis was performed at moderate conditions in the liquid phase also make this a unique system for study.

In Chapter Three, TS-1 samples are investigated and the results compared to other titanium-containing materials in terms of their spectroscopic characterization and catalysis. Using knowledge gained from the data illustrated in Chapter Three, a more extensive study was performed on the relationships between synthesis conditions and physicochemical properties. The results are presented in Chapter Four. In addition to TS-1, Ti-ZSM-48, and Ti-Al-Beta are also synthesized and investigated as catalysts. Chapters Three and Four show that objective (i) was completed.

Finally, in Chapter Five, a different approach towards the production of a partial oxidation catalyst is undertaken. By modifying an existing molecular sieve with titanium tetrachloride, Ti atoms may be placed into lattice positions of the crystal structure. Using this method a large-pore molecular sieve (SSZ-33) has been prepared with partial oxidation properties. Other methods of post-synthetic titanium insertion are evaluated. This chapter also contains the first catalytic data from a novel, aluminum-free version of Ti-containing zeolite-Beta. Chapter Five shows that objective (ii) was obtained.

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Table 1.1 Wastes Produced by Various Industrial Sectors*.

Industry segment	kg of by-product/ kg of product	Product (tons)	Sum of product and byproduct
Oil Refinery	~ 0.1	10^6 - 10^8	10^6 - 10^8
Bulk Chemicals	1 - 5	10^4 - 10^6	10^4 - 10^6
Fine Chemicals	5 - >50	10^2 - 10^4	10^2 - $>10^5$
Pharmaceuticals	25 - >100	10 - 10^3	10^2 - $>10^5$

**Adapted from Sheldon, 1992.*

Table 1.2 Oxygen Donors* (Bu=Butyl, Ph=Phenyl).

Molecule	Wt % Active Oxygen	By-Product
MnO_2	18.4	MnO
PhIO	7.3	PhI
H_2O_2	47.0	H_2O
t-BuOOH	17.8	t-BuOH
NaOCl	21.6	NaCl
$K_2Cr_2O_7$	21.8	Cr_2O_3
$KMnO_4$	20.2	MnO_2

**Adapted from Sheldon, 1993.*

Table 1.3 Phenol Hydroxylation Using Hydrogen Peroxide*.

	Rhone Poulenc ($HClO_4$, H_3PO_4)	Brinchima (Fe^{2+}, Co^{2+})	Enichem TS-1
Phenol Conv., %	5	10	25
H_2O_2 Conv., %	70	50	70
Diol Selectivity, %	90	80	90
Ratio catechol/hydroquinone	1.4	2.3	1

**Adapted from Notari, 1988.*

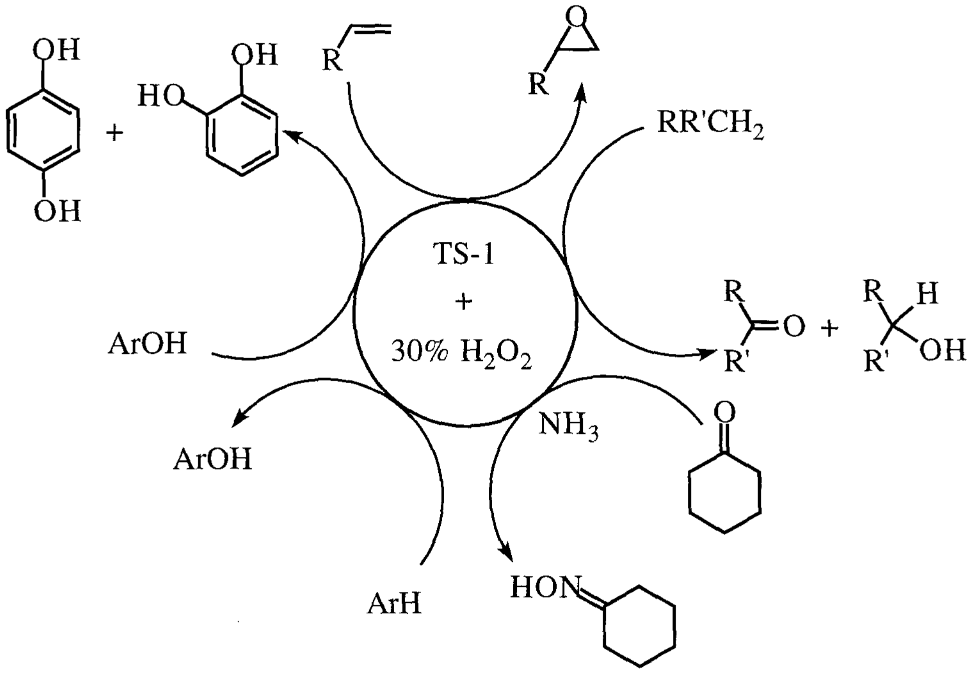
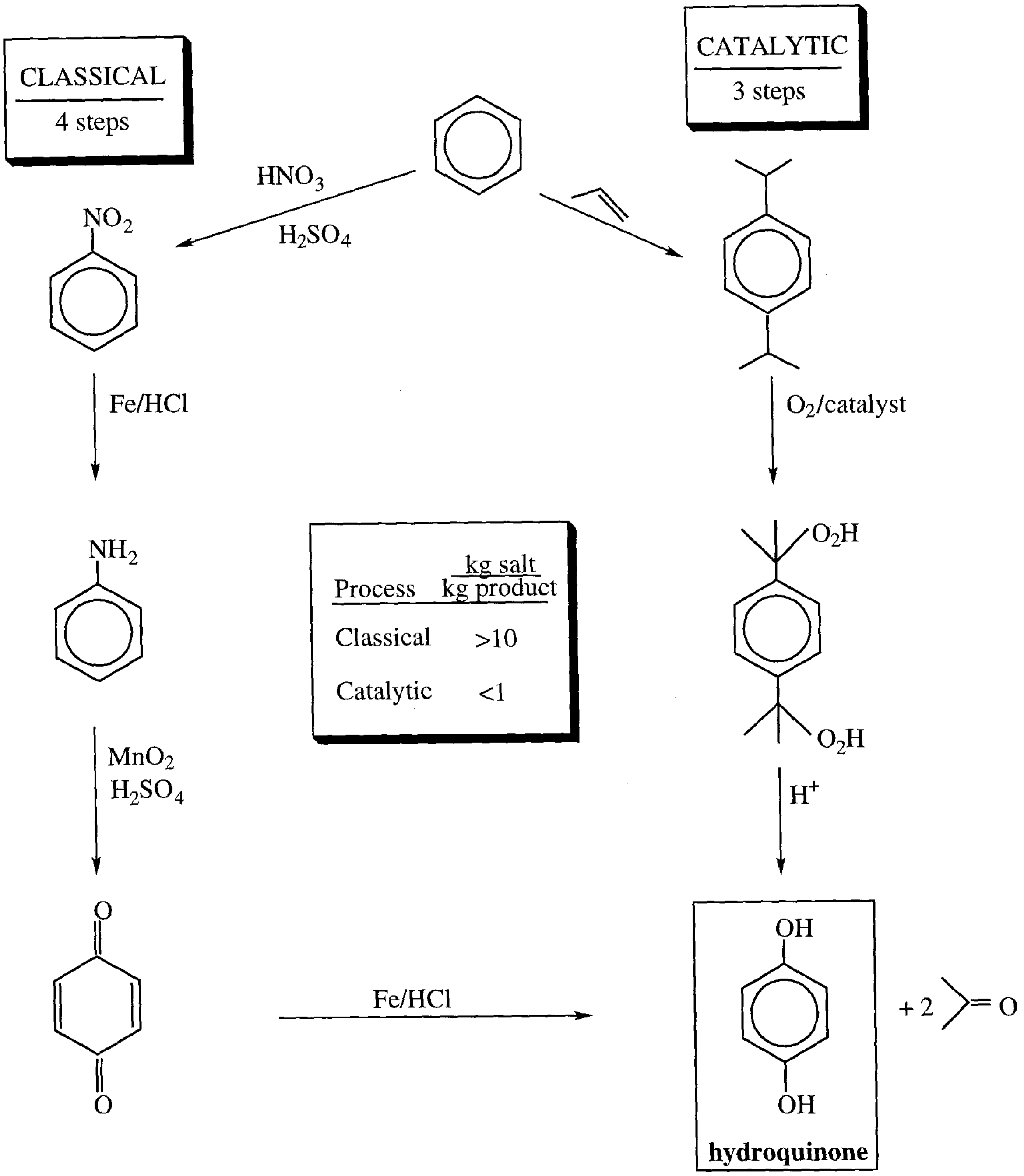


Figure 1.1 Oxidation reactions catalyzed by TS-1.



Process	kg salt / kg product
Classical	>10
Catalytic	<1

Figure 1.2 Two routes to hydroquinone. Adapted from Sheldon, 1990.

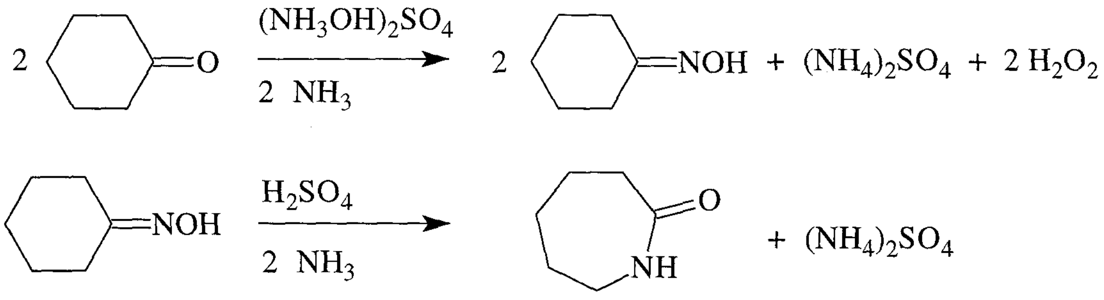


Figure 1.3 Conventional synthesis route to ε-caprolactam.

CHAPTER TWO

Applications of Zeolites to Fine Chemical Synthesis

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[C.B. Dartt and M.E. Davis, *Catalysis Today* **19**, 151 (1994)]

Applications of Zeolites to Fine Chemical Synthesis

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Abstract

The use of zeolites as catalysts for specific organic transformations is reviewed. The traditional role of zeolitic materials as acid catalysts is briefly discussed. Emphasis is focused on some of the more underdeveloped facets of zeolite catalysis that may prove to be valuable in the synthesis of fine chemical or fine chemical intermediates. Base catalysis with molecular sieves has been shown to be feasible, and examples of possible reactions are explored. Enantioselective catalysis is a very important tool in the manufacture of chiral drugs. Modification of non-chiral zeolites with chiral ligands, and the direct synthesis of a chiral zeolite structure are both described as possible catalysts for asymmetric reactions. The ability to control the acidity/basicity of molecular sieves also allows them to be used in ring transformation reactions where nitrogen or sulfur replace oxygen in small cyclic molecules. These compounds are very important in the manufacture of fine chemicals. The synthesis of a titanium-containing molecular sieve with partial oxidation properties has started an entirely new field of zeolite catalysis and some of the possible reaction schemes are reviewed.

2.1 Introduction

The use of zeolites as catalysts for organic reactions began in the early 1960's when it was discovered that they performed extremely well as cracking catalysts. The number of applications for the use of zeolites continued to grow in the petrochemical industry for more than a decade. The discovery of ZSM–5 in 1967 led to many important new processes such as dewaxing, methanol to gasoline and olefin oligomerization. Prior to the use of zeolites, these reactions all resulted in a spectrum of products and further refining was needed to reach the final product. The pioneering work of Venuto and Landis [1] showed that zeolites could be used to directly synthesize compounds that were essentially free from unwanted by–products and had uses outside the petroleum industry. As the number of zeolite structures increased and as the basic knowledge of zeolite acidity and shape–selectivity grew, it became evident that molecular sieves would play a large role in organic synthesis. The pores of zeolites are similar in size to small organic molecules and have shown the ability to recognize, discriminate and organize molecules with precisions that can be less than 1 Å [2,3]. The first report of shape–selective, acid catalysis using a zeolite catalyst was by Weisz et al. [4] who selectively dehydrated n–butanol in the presence of iso–butanol (difference in kinetic diameter less than 1Å). Another reason for the success of zeolites as commercial catalysts is the ability to control the catalytic properties by a variety of synthetic and post–synthetic methods. By choosing the appropriate organic template and synthesis conditions, the pore size and pore shape (dimensionality, intersections, cages) may be directly influenced. The acidity of the zeolite may also be controlled through various methods such as silicon/aluminum ratio, ion–exchange, and calcination conditions. Recent developments have shown that zeolites can even be converted into solid bases (vide infra). As heterogeneous catalysts, they possess the usual advantages over homogeneous systems: easy separation, easy handling, easy regeneration, etc. Zeolites may also be used as shape–selective supports for active components. Their high thermal stability permits them to be used at high temperatures that often result in higher yields and easier heat recovery. All of these characteristics, and especially the control of structure and acidity, make zeolites well suited as catalysts for organic reactions. A number of excellent review papers have dealt with the use of zeolites as acid–catalysts for a wide variety of organic syntheses [5–9]. The intent of this review is to examine some of the more underdeveloped facets of zeolite catalysis that may prove to be valuable in the synthesis of fine chemical or fine chemical intermediates. It must be realized that the size of these compounds is ultimately limited by the size of the zeolite pores. Thus, some of the reaction chemistries discussed in this paper may become even more valuable when extra–large pore zeolites are synthesized.

Since zeolites can impart high reaction selectivities it is most likely that they will find a place in the synthesis of fine chemicals. Additionally, zeolites can offer the possibility of environmentally attractive chemistries when substituting for other well-known catalysts, e.g., HF, H_2SO_4, etc. As government legislation and public opinion tend to mount in the area of environmental issues, zeolite catalysts appear to have a brighter future. However, one of the largest problems that needs to be addressed is how to bring researchers together from the fields of organic and biochemical synthesis and zeolite catalysis together.

2.2 Base Catalysis

2.2.1 Materials

Although zeolites were investigated as solid base catalysts many years ago [1], the use of zeolites as base catalysts is now an emerging field. Little is known about zeolites that act as solid bases in comparison to the body of knowledge on the traditional role of zeolites as acid catalysts. The major obstacle in synthesizing zeolite solid bases is the fact that they are inherently acidic. The motivation for using zeolitic solid bases is the same as using zeolites as solid acids: shape selectivity.

The acidic nature of zeolites is due to the negative charge of the framework. When all of the cations present inside the zeolite are exchanged with H^+, many Bronsted acid sites are formed. As is shown in Figure 2.1, tetrahedral atoms (Si and Al) are used as building blocks in the formation of zeolites. Each oxygen bridges two neighboring T-atoms and shares its –2 charge equally. This makes the SiO_4 unit electronically neutral due to the +4 charge of Si and the four –1 charges from the oxygen atoms. Using the same type of argument, the AlO_4 unit will be –1. Thus, a pure, defect–free SiO_2 framework will contain no charge, and a material containing Si and Al atoms will be negatively charged. Negatively charged Al tetrahedra are not observed next to one another since isolated charges are more stable. Lowenstein [10] was the first to rationalize the isolation of charges and this phenomenon has been called Lowenstein's rule. The combination of AlO_4 and PO_4 units leads to the 3–5 analogue of pure SiO_2 zeolites.

One could envision a material composed of alternating silicon and phosphorus atoms that could impose an overall positive charge. This would be an anion exchanger and could be considered a basic analogue of zeolites. However, these silicophosphate materials have never been synthesized and Pauling's bonding rules cast severe doubts to whether they will ever be formed. Pauling's bonding rules are violated when total bond strength on the oxygen atoms is greater than 2. Octahedral silicon bonded to tetrahedral phosphorus does not violate the Pauling bonding rules and indeed is found in some oxide glasses [11] and in some layered materials [12]. Tetrahedral silicon should not be able to bond with tetrahedral phosphorus making it unlikely that a molecular sieve will be found that contains a positive framework that could be used as a solid base catalyst.

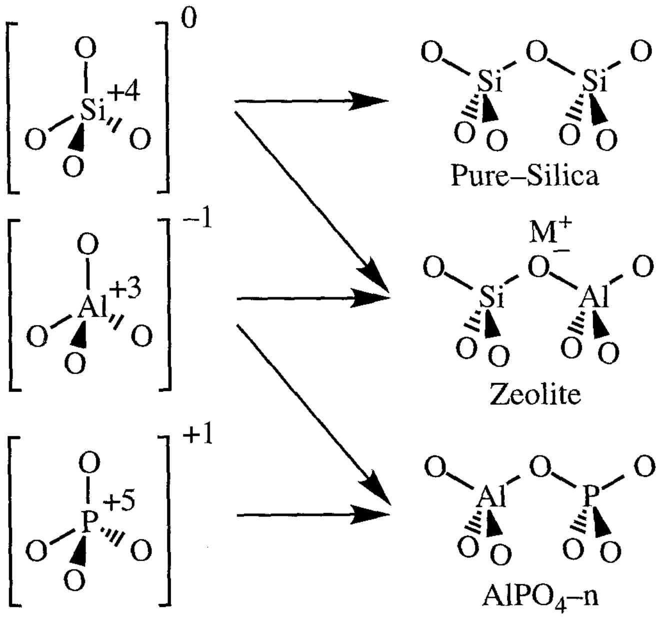


Figure 2.1 TO_2 units in zeolites and aluminophosphates (adapted from ref. [2]).

Due to the inherent acidity of zeolites, the emphasis of zeolite catalysis has been upon reactions catalyzed by weak or strong acids. This has begun to change due to a few discoveries involving post–synthetic treatments that are able not only to neutralize Bronsted acid centers, but also to give the zeolite basic character. Essentially three approaches have evolved.

The first of these involves ion exchanging the zeolite with large alkali metal cations such as Cs^+ and Rb^+. It was discovered quite some time ago [13] that faujasites exchanged in this manner are able to catalyze the side–chain alkylation of toluene with methanol or formaldehyde. Base catalysts lead to side–chain alkylation while acid catalysts brings about ring alkylation. This is due to the fact that in base catalyzed reactions an activated hydrogen atom is abstracted from the substrate to yield a carbanion. The finding that alkali metal exchanged zeolites performed side–chain alkylation gave an indication that zeolites could be modified to contain base characteristics. This discovery is tempered by the fact that the structure and location of the actual base sites are not clearly understood.

The strength of the base sites on exchanged zeolites is lower than that of basic metal oxides and the search for stronger basic zeolites has been an object of further study.

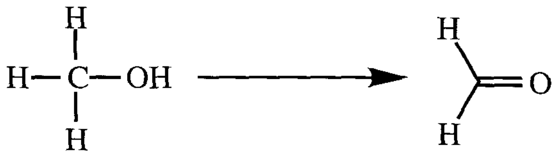
Another approach to the synthesis of basic zeolites is to use the zeolite as a "support" in the classical catalytic sense and impregnate the pores with clusters of atoms that can act as bases themselves. One of the earliest attempts involved placing clusters of sodium atoms in the pores of faujasites. According to Martens et al. [14], this is best accomplished by the thermal decomposition of sodium azide impregnated in dehydrated zeolites. This procedure leads to strong base sites inside the zeolite that are highly active for a variety of organic reactions as will be discussed below. The major problem with this type of catalyst is that it is highly air–sensitive. These materials are converted to sodium oxide when exposed to air, and in turn the activity is lost.

A promising approach in the development of a zeolitic base catalyst is the method pioneered by Hathaway and Davis [15]. As with the previous example, the zeolite acts as a support while the catalyst is deposited within the pores. Instead of sodium clusters, this preparation places nanophase cesium oxide within the pores of the zeolite. This is accomplished, for example, by impregnation of NaY with cesium acetate. The acetate can then be decomposed by calcination at 450 °C in air. This method produces strong base sites and has a few distinct advantages over the sodium azide method. The cesium oxide based catalyst has proven to be stable in air and is much easier to prepare. As will be discussed later, variations of this procedure have produced a catalyst that has quickly been investigated for use in the production of a fine chemical intermediate.

2.2.2 Reactions

Double–bond isomerizations can be catalyzed by both basic and acidic materials. Using acidic zeolites the reaction takes place via a carbenium ion and with a basic zeolite via a carbanion ion. Basic catalysts are often favored due to their higher selectivity. This selectivity arises from the fact that the base catalysts do not normally generate organic cations that can undergo skeletal isomerizations. Brownscombe [16] has patented a process for double bond isomerization of olefins that uses a zeolite impregnated with an alkali metal in excess of that required to provide a fully metal cation exchanged zeolite (similar to the method of Hathaway and Davis [15]). It was shown that with NaY impregnated with 20 equivalents of potassium per supercage the selectivity for the double bond isomerization of 1–octene to internal olefins was greater than 99% while NaY gave a selectivity less than 87%. No mention of the nature of the active sites is given, yet the excess metal is presumed to form oxide moieties that appear to be necessary for the observed increase in selectivity.

Basic zeolites show a high selectivity for the conversion of alcohols to their dehydrogenation products: aldehydes and ketones. Acid zeolites tend to favor the dehydration reactions to olefins and ethers. It has been found that methanol can be converted to formaldehyde (Scheme I) by oxidative dehydrogenation over Na–containing zeolites, even though this reaction is not thermodynamically favored [17]. The catalytic activity of these zeolites is largely related to the Na concentration, although the crystal structure and Si/Al ratio also play a secondary role. Even pure–silica zeolites that have been impregnated with sodium show good selectivities for this reaction. One reason why this reaction is important is due to the speculation that formaldehyde is a reactive intermediate in the side–chain alkylation of toluene with methanol when alkali metal exchanged zeolites are used at catalysts.

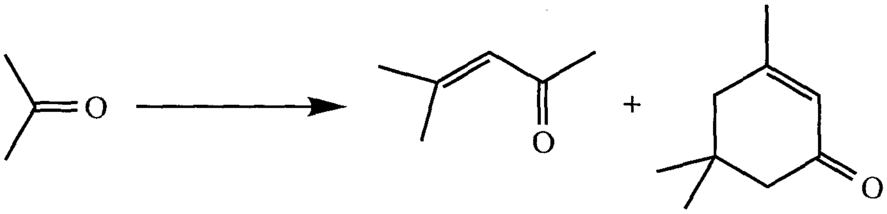


Scheme I

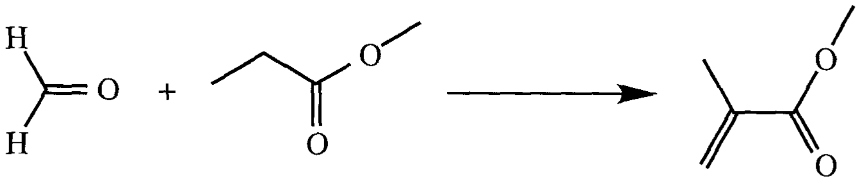
When higher molecular weight alcohols are reacted on basic zeolites, the amount of cation exchanged still influences the selectivity, but now the crystal structure becomes more important. NMR studies of K– and Cs– exchanged mordenite and ZSM–5 have shown that at 200 °C the type of zeolite and cation do not influence the level of acid catalyzed dehydration of isopropanol [18]. When the reaction is carried out at 300 °C the dehydrogenation reaction to acetone is increased on the Cs–exchanged zeolite. This is due to its increased basicity. The higher temperature indicates that there is a higher activation energy barrier for the base catalyzed reaction but once this barrier is overcome, the dehydrogenation product is favored.

As further evidence to prove that basic and acidic sites lead to dehydrogenation and dehydration products respectively, pre–reaction treatments that poison one type of site have been attempted. Poisoning of basic sites by pyridine has led to decreased dehydrogenation rates, and neutralization of acidic sites by phenol has led to decreased dehydration rates [19,20]. This indeed gives credence to the conventional wisdom that acid sites perform dehydration and basic sites perform dehydrogenation. Although this point holds true much of the time, one caveat must be noted. It is well known that Bronsted acid sites are able to catalyze the dehydration of alcohols to olefins by an elimination mechanism. The problem, however, is the possible misinterpretation that olefin activity is only a result of Bronsted acidity. It has been shown that alcohols can dissociatively adsorb over metal oxides to form alkoxide intermediates [21–23]. From this intermediate, dehydration or dehydrogenation may occur [24–28]. The pathway of the reacting alkoxide has been shown to depend on factors such as the structure [29] and electronic nature [25] of the oxide surface, as well as the structure [24,27,28] and partial pressure [25] of the reacting alcohol. This makes it difficult to discern olefin formation over Bronsted acid sites and that formed via alkoxide intermediates.

Basic zeolites have also been studied as catalysts for aldol condensation reactions. This class of reactions is extremely important in the manufacture of fine chemicals. Aldol condensation is an example of a reaction that may be catalyzed by either acids or bases, yet the product spectrum can be significantly affected with only a small change in catalyst acidity or basicity. When the aldol condensation of acetone is performed over X or Y zeolites containing alkali metal clusters at 350 °C, the major products, mesityl oxide and isophorone, are produced with 80% selectivity at 8–15% conversion (Scheme II) [19,30]. The ratio of the two products can be shifted quite dramatically by the choice of zeolite. A zeolite with smaller pores is more likely to favor the formation of the smaller product, mesityl oxide. With X or Y zeolite the product mole ratio of mesityl oxide to isophorone is 0.74. For the smaller void space sized zeolite L, the ratio increased to 1.87. Another aldol condensation that has been shown to be catalyzed by zeolites is the gas phase reaction between formaldehyde and methyl propionate to form methyl methacrylate (Scheme III). X and Y zeolites were tested for their catalytic activity and various pre–reaction treatments



Scheme II

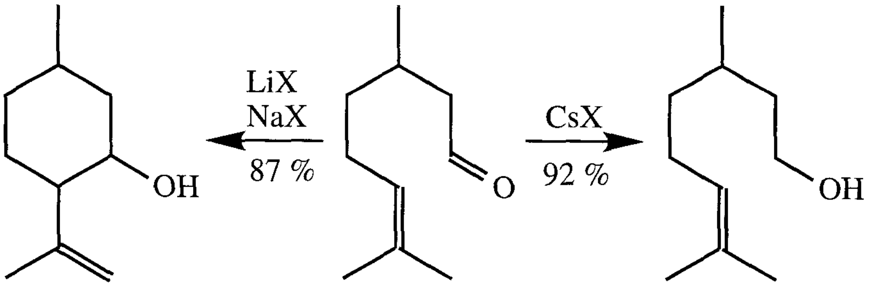


Scheme III

were performed [31]. The highest conversion of substrates was observed using potassium exchanged Y zeolite further treated with potassium hydroxide. This catalyst gave a 69.6% conversion of formaldehyde and a 74.1% selectivity to methyl methacrylate (vs. methyl propionate). Creation of stronger base sites in the zeolite, e.g., by sodium cluster impregnation, decreased the catalytic activity. It was concluded that both acid and base sites were necessary in the condensation reaction.

Zeolites have been found to catalyze reduction reactions. This is another area that could be especially useful in the synthesis of fine chemicals. For example, C5 to C12 aldehydes can be reduced to their corresponding 1–alcohols when reacted with isopropanol over NaX zeolite with selectivities and conversions approaching 98% [32]. Slightly lowering the basicity of the zeolite by exchanging Na^+ with Ca^{2+} alters the reaction between the aldehyde and isopropanol to give the corresponding acetal as the major product.

Another interesting example of a zeolite catalyzed reduction that clearly shows the drastic alteration in reaction pathway by changing the exchanged cation is the reduction of citronellal [32]. When citronellal is reacted with isopropanol at 150 °C over an alkali metal–exchanged zeolite, two major products are formed, as is shown in Scheme IV. If the zeolite is exchanged with Li or Na, the reaction produces 86% isopulegol and 14% citronellol at a conversion of 87%. By simply changing the exchanged ion to cesium, the



Scheme IV

reaction now produces 92% citronellol at a conversion of 77%. The investigators explain their findings by arguing the steric hindrances caused by the larger cesium ion prevent the cyclic compound from being formed. However, Holderich [7] has pointed out that the change in the acidity/basicity relationship in the zeolite must also be considered. These examples again reveal that small changes in the nature of the zeolite acid–base sites can have large effects on activity and selectivity.

As can be seen from the reactions previously discussed, the great majority of studies involving the catalytic activity of basic zeolites have used either alkali–exchanged zeolites or zeolites impregnated with sodium metal clusters. The third method of creating basic sites within the zeolite framework as discussed above involves the formation of nanophase cesium oxide particles in the pores of the zeolite. These particles can be formed by the decomposition of cesium acetate, nitrate, or hydroxide occluded in faujasites. ESR spectroscopy was used to rule out the presence of metallic or ionic clusters of cesium [33,34]. Formation of cesium carbonate was dismissed due to the lack of IR bands associated with carbonate species. By comparing the activity of CsOH loaded onto silica gel and activated carbon, cesium hydroxide was also excluded from the list of possible active sites. Cesium oxide was found to be the most likely candidate for the active base site. Pure cesium oxide showed similar start–up and steady–state reactivities for isopropanol decomposition to the cesium zeolites.

The activity and selectivity of cesium faujasites were tested using a variety of probe reactions. Isopropanol was reacted over alkali–exchanged X and Y zeolites in the presence and absence of occluded exchange salts at 350 °C and atmospheric pressure. This reaction was chosen because there seems to be a consensus that dehydrogenation occurs over basic sites [21–28]. Therefore, a catalyst found to be active for the isopropanol decomposition to acetone should be similarly effective in other base–catalyzed reactions. From studies involving the base–catalyzed alkylation of toluene with methanol [35–37], it was found that

CsNaX was the most effective catalyst for side–chain alkylation over other alkali metal exchanged X and Y zeolites. Cesium exchanged zeolite X proved to be quite active for the isopropanol dehydrogenation reaction, yet it was an order of magnitude less active than for zeolite Y. The effect of loading cesium acetate (followed by calcination) was also investigated. With approximately two cesium acetate molecules added per unit cell before calcination, the activity rose another order of magnitude (over the simply ion–exchanged zeolite) with no change in acetone selectivity. On a surface area basis, the cesium–impregnated CsNaY (referred to as Cs–Ace/CsNaY) had an activity and selectivity approximately equal to that of MgO. Due to the high surface area of the zeolite, the activity of Cs–Ace/ CsNaY becomes five times greater than that of MgO on a volume basis.

Another series of reactions was studied using the cesium acetate impregnated faujasites as catalysts. These zeolites were tested for their ability to catalyze the side–chain alkylation of toluene, ethane, methane, and acetone with methanol. In the toluene reaction, it is generally accepted that methanol is dehydrogenated to formaldehyde which becomes the alkylating agent to produce styrene. Even though strong acid sites have been shown to result in ring alkylations [13,37,38] a certain degree of acidity is thought to aid in the stabilization of the formaldehyde [35,39]. For the alkylation of ethane and methane no conversion was observed even though reaction temperatures up to 465 °C were attempted. Alkylation of acetone with methanol was observed at 425 °C but the majority of the reacted acetone formed products that were thought to arise from acetone aldol condensations. For the toluene alkylation, the impregnated X zeolite showed the highest yield of styrene. With both the X and Y zeolites, impregnation led to higher toluene conversion, however for the Y zeolite, it also led to a lower yield of styrene. The impregnated X zeolite had the highest styrene yield (1.07% at 425 °C), but it was accompanied by the same yield of ethylbenzene. It should be noted that MgO is not able to catalyze the side–chain alkylation of toluene. The fact that MgO, which possesses vitually no Bronsted acidity and high base activity, was inactive may suggest that some acidity is required to stabilize the formaldehyde.

In order to gain a better understanding of the reaction occurring in the zeolite the decomposition products were also studied. It was observed that the yield of CO from CsAce/CsNaY was significantly higher than that obtained over CsAce/CsNaX. For the CsAce/CsNaX zeolite, dimethyl ether and formaldehyde were observed in the product stream, while the CsAce/CsNaY zeolite produced only trace amounts of formaldehyde and dimethyl ether. This led to the conclusion that the more basic CsAce/CsNaY (as defined by acetone formation from isopropanol) decomposed the formaldehyde and gave less styrene while simultaneously having the largest toluene conversion. These results support the theory that the base sites are responsible for the side–chain alkylation yet acid sites are necessary to stabilize formaldehyde. Unland and Barker [35] occluded boric acid within zeolitic pores and showed by infrared spectroscopy that the acid does not influence the adsorbed toluene, yet it significantly influences the adsorption of formaldehyde. They concluded that the boron slows the decomposition of formaldehyde by neutralizing basic sites that break–up formaldehyde or by providing acid sites next to the basic sites that are responsible for the catalytic activity. Itoh et al. [39] showed by quantum chemical calculations that formaldehyde is far more stable when interacting with an acid site than with a base site.

Following the preparation procedure of Hathaway and Davis [15], Tsuji et al. [40] synthesized a number of alkali metal faujasites and studied them as catalysts for the isomerization of 1–butene. TPD experiments were performed on the zeolites using CO_2 as the probe molecule. The zeolite catalysts were prepared in their ion–exchanged form and their "ion–added" form. The latter is used to designate zeolites that have an excess of cations past the exchange level (via Hathaway and Davis). For Rb and K "ion–added" samples a higher temperature TPD peak was observed as compared to the ion exchanged samples. These data were viewed as evidence for the generation of new basic sites that are stronger than the basic sites in simply ion–exchanged zeolites.

1–Butene was isomerized over all the "ion–added" and ion–exchanged zeolites at 273 K and 423 K. At 273 K all the ion–exchanged zeolites showed practically no activity as shown in Table 2.1. The ion–added zeolites showed considerable activity that becomes even more astounding when one realizes that this reaction has never been active over any basic zeolites, alkali oxide, or alkali hydroxide at 273 K. The higher temperature TPD peaks were considered to be the stronger basic sites and these sites were concluded to be the active component of the zeolite at 273 K.

When the reaction was conducted at 473 K, all of the ion–exchanged zeolites did not show activity, except for the CsX. The "ion–added" zeolites became more active, as expected. By comparison of the cis/trans ratios found over the zeolites and the cis/trans ratios found over alkali metal oxides the authors suggested that the active sites within the zeolites were alkali metal oxide clusters. This supports the conclusion drawn by Hathaway and Davis.

Table 2.1 Activity for 1-butene isomerization at 273 and 423 K [a]

Catalyst		# of excess M^+ / unit cell	Reaction Rate [mmol/g•m] at 273 K	Reaction Rate [mmol/g•m] at 423 K	cis/trans ratio at 273 K	cis/trans ratio at 423
NaX	E	—	0	0	—	—
	A	9.9	0	0.011	—	2
KX	E	—	0	0	—	—
	A	11.5	0.024	0.078	3	1
RbX	E	—	0	0	—	—
	A	4.0	0.032	1.3	11	12
CsX	E	—	0.00086	0.13	—	5
	A	12.8	0.14	1.1	10	9

[a] Adapted from ref. [40].

Although this method of preparing basic zeolitic catalysts is rather recent and has not yet been studied in a wide scope of reactions, a variation of this synthesis procedure has already found application in the pharmaceutical industry. This underscores the nature of the fine chemical industry; the high profits and relatively small quantities involved allow fast, major changes in production techniques for improvements in selectivity, activity, or environmental safety. Merck & Co. [41] have investigated the use of a cesium impregnated zeolite in the production of 4–methyl thiazole (4–MT). The compound 4–MT is used as an intermediate in the manufacture of thiabendazole (TBZ). TBZ is a fungicide used to control spoilage of citrus fruit, to prevent and treat Dutch elm disease in trees, to control fungal diseases in seed potatoes and as an anthelmintic. The previous routes to 4–MT typically involve the use of several hazardous chemicals. Figure 2.2 shows the steps involved.

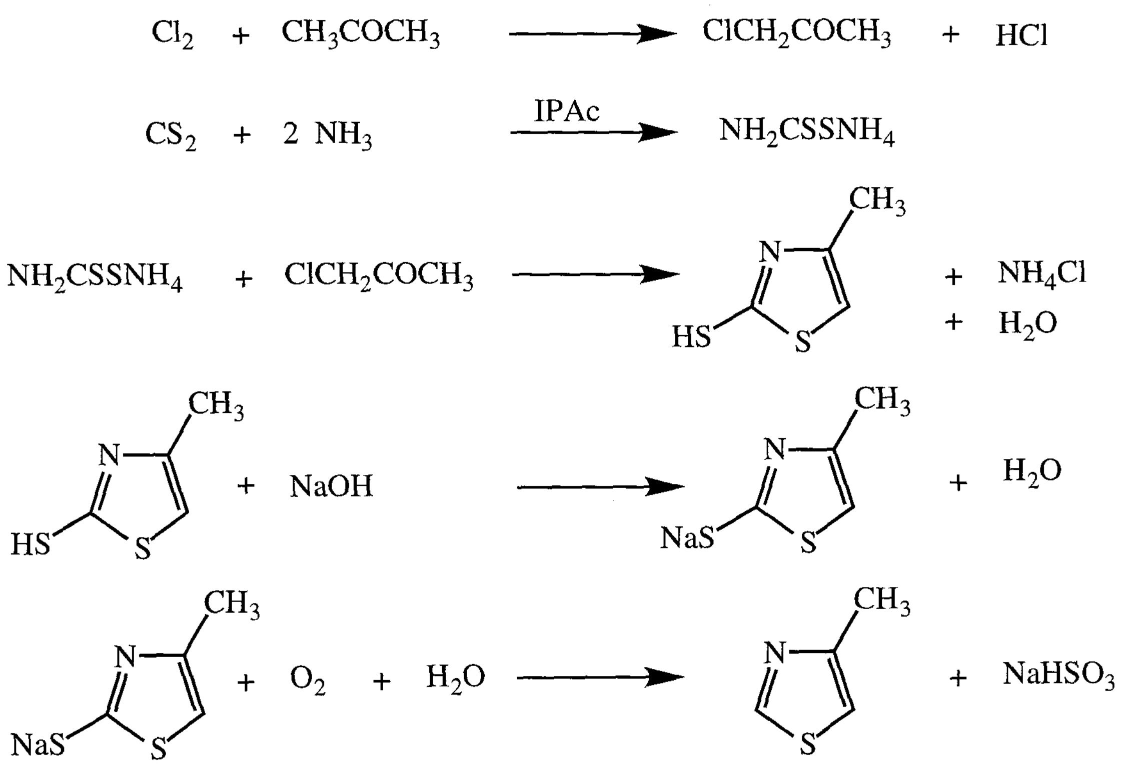
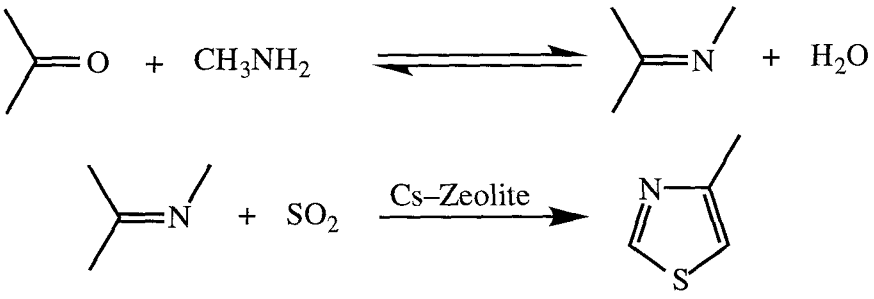


Figure 2.2 Previous route to 4–MT (adapted from ref. [41]).

4–MT has also been produced in a fixed bed reactor using strongly basic solid catalysts such as CaO, MgO, or soda lime [42]. The reaction, performed in the vapor phase, is shown below (Scheme V). The yields were dependent on the starting imine and generally ranged from 20–70%. Acetone-imine gave the highest yield and this particular reaction was studied with the base catalysts mentioned earlier. ZrO_2 doped soda lime gave yields of 70% but the catalyst was totally deactivated after 3 hours. The catalyst could be reactivated a number of times but eventually no regeneration was possible. Stringent environmental regulations would not permit the disposal of this material, and therefore this catalyst could not be used on a commercial scale.



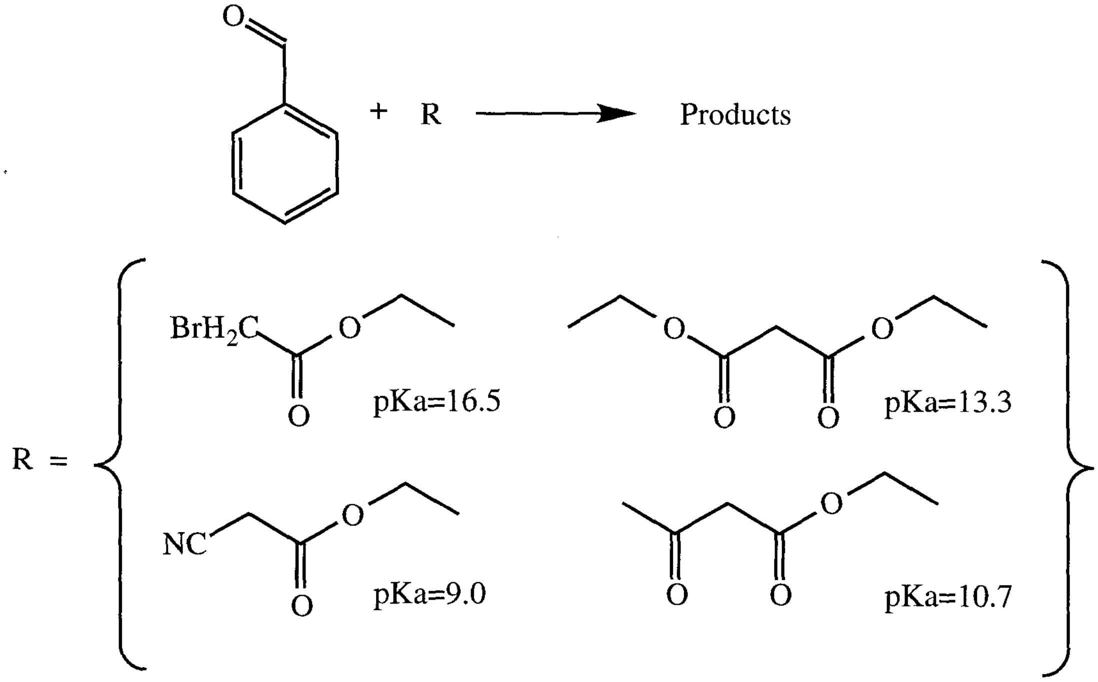
Scheme V

The Merck group turned to the use of basic zeolites as catalysts in the preparation of 4–MT. The thermal stability and regeneration capability of zeolites made them ideal candidates for this study. Alkali metal impregnated zeolites were prepared in a manner similar to that of Hathaway and Davis. Many zeolite types and alkali salts were tested in attempts to maximize yield and time between regenerations. Because the reaction was run in the vapor phase (450–500 °C) and with the presence of water vapor, zeolites with high hydrothermal stability were chosen. The zeolites ZSM–5 and beta were used due to their stability and activity [43]. ZSM–5 was studied most extensively because it was easier to obtain a large variety of commercially available samples. Various alkali salts were occluded within the zeolites and the materials were tested for their activity, selectivity, and lifetime for the preparation of 4-MT. It was found that the activity followed the order: Cs > Rb >> K. When sodium was added, the activity dropped. Therefore, Na was assumed to merely act as a diluent. Of all the cesium salts tested, the best catalytic results were obtained with cesium sulfate. The catalysts studied by Merck typically had cesium concentrations of 20–25 wt%. Higher loadings lead to pore blockage and poor catalytic performance.

Overall, the cesium sulfate impregnated ZSM–5 proved to be an excellent catalyst for the production of 4–MT. The Merck researchers reported very good catalytic regeneration properties, although the zeolites eventually needed to be replaced due to Al migration out of the framework by the prolonged exposure to high temperature steam (water is liberated during the reaction). One catalyst was tested for a total of 20 regeneration cycles and had an overall yield of 55% for 4–MT. Yields as high as 65% were also obtained with catalyst lifetimes as long as two weeks. The catalyst has performed successfully in pilot studies and only time will tell whether this new and exciting discovery will be commercialized.

As a final note in the discussion of basic zeolites as catalysts, the methods used to define the true basicity of basic zeolites are outlined. This is important in characterizing a zeolite as a catalyst for a base catalyzed reaction. Because very strong base sites can catalyze undesirable side reactions, it becomes critical to control the strength and density of base sites. Many schemes have been suggested to characterize basicity. Titration with indicators, adsorption of acids, spectroscopic techniques, and probe catalytic reactions [44] have all been used to determine the overall basicity of zeolites. The use of a single test catalytic reaction can only be used to determine whether or not a catalyst has the required base strength to catalyze a particular reaction. None of the aforementioned techniques are able to measure base site strength and total number of sites, except for the titration method with Hammett indicators. However, this method has inherent limitations such as base site accessibility and equilibrium adsorption considerations.

Corma has introduced a new method which not only gives base site strength but also gives the density of sites with specific strengths [45]. Both pieces of information are important because most often a zeolite will have a distribution of sites with differing strengths. The proposed scheme uses a series of reactants with similar sizes and structures, but each one requiring a different base strength to initiate the reaction by forming the corresponding carbanion. The test reaction used was the condensation of benzaldehyde with ethyl cyanoacetate, ethyl acetoacetate, ethyl malonate, or ethyl bromoacetate (Scheme VI). From the ratio of kinetic rate constants found using reactants with different pKa values, the fraction of sites with a certain base strength can be obtained. The number of sites can be quantified by carrying out the reaction in the presence of increasing amounts of acid. This last procedure is similar to the titration method except the reaction takes the place of the indicator and of course it occurs at temperatures above ambient.



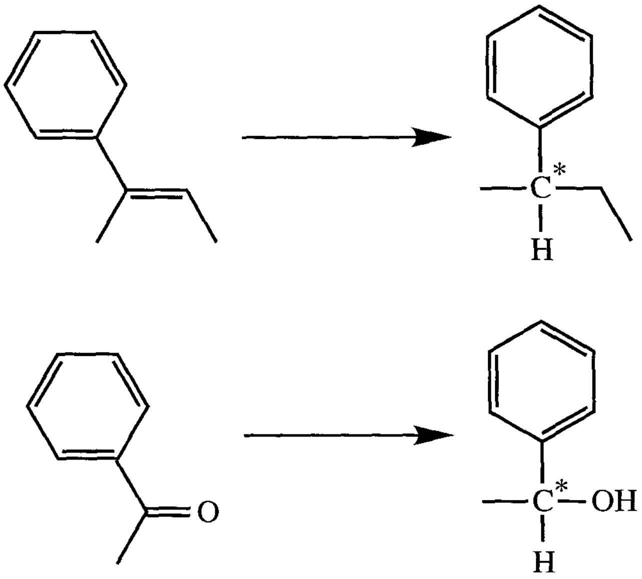
Scheme VI

2.3 Enantioselective Catalysis by Zeolites

The synthesis of a heterogeneous, shape–selective, enantioselective catalyst must be considered as one of the ultimate goals for the production of fine chemicals. It also would be another step closer to a truly enzyme–mimicking catalyst. There are two methods which hold promise for the completion of this goal.

The first method involves the addition of a chiral compound into the cages of a zeolite. This compound could then be the active site or be adjacent to an active site within the zeolite structure. The occluded complex may work in concert with the shape–selective nature of the zeolite cage and pore system.

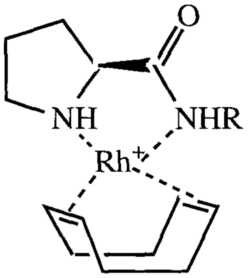
A method of chiral–compound incorporation was first proposed by Dessau [46] in 1985. The patent claims that a chiral hydrogenating catalyst can be prepared by loading an acid zeolite with a metal capable of performing hydrogenation chemistry and an optically active amine. The amine is used to neutralize some of the acidic sites present. Some examples of optically active amines are: (S)–(–)–2–methylbutylamine, (S)–(+)–alanine, (S)–(+)–valine, (S)–(–)–alpha–methylbenzylamine, and (R)–(–)–valine. From the patent examples, one is led to believe that the proposed zeolite is able to catalyze the chiral reduction of 2–phenylbutene and acetophenone to 2–phenylbutane and 1–phenylethanol (Scheme VII), respectively, with an excess of one enantiomer. The hydroformylation of α–methylstyrene to an optically active mixture of aldehydes over the same catalyst is also claimed. This patent has led many researchers to believe the example reactions have been carried out [8,47,48]. In fact, the patent was simply a proposal for chiral compound incorporation into zeolites and no experiments were performed; the examples given were only used to elucidate the concept. The examples cited in the patent were performed [49] and no products were formed. Most likely, the reactants were not able to enter the pores of ZSM–5 after the introduction of the chiral amine. This result does not preclude the synthesis of this type of chiral catalyst. The use of a zeolite with larger pores or with cages may allow both the amine and the reactants molecules to enter and form an optically active product. No results from this type of reaction have been found in the literature to date.



Scheme VII

Although the above procedure has not yet led to a successful catalyst, Corma et al. [50] have recently described the preparation of a chiral heterogeneous catalyst and the asymmetric hydrogenation of prochiral alkenes. These investigators anchored rhodium complexes with nitrogen–based chiral ligands onto modified, ultra–stable Y (USY) zeolites. These catalysts are capable of performing the enantioselective hydrogenation of dehydrophenylalanine derivatives.

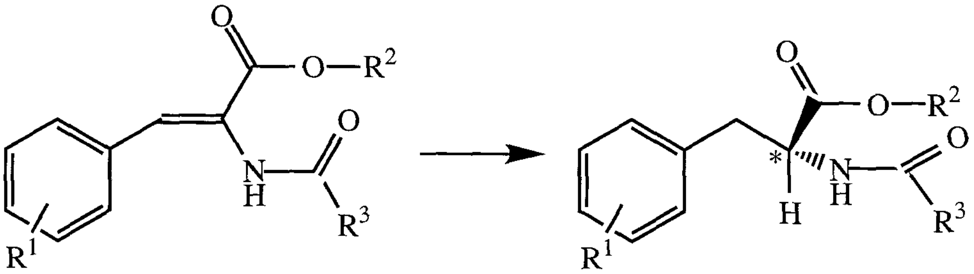
The complex (shown in Scheme VIII) with R=CMe_3 was used as a homogeneous catalyst and with R=$(CH_2)_3Si(OEt)_3$ anchored to a Merck silica and to a modified USY zeolite. By steam calcination to remove aluminum atoms, mesopores (pore diameter > 20 A) were formed in the interior of the zeolite. Extra–framework species (e.g. Al) that may



Scheme VIII

have blocked these pores were then removed by contact with a citric acid solution. These treatments resulted in 2 major modifications: the formation of a supermicropore system and a large number of silanol groups. These silanol groups are proposed to serve as the anchoring sites for the rhodium complexes. The appearance of the supermicropore system provides sufficiently sized voids for the incorporation of the large rhodium complexes.

These catalysts were tested for their ability to perform the chiral hydrogenation of α–acylaminocinnamate derivatives (see compounds i–v in Scheme IX) to the corresponding substituted phenylalanine derivatives. The reactions were run at 65 °C under



Scheme IX i: R^1=R^2=H, R^3=Me
ii: R^1=R^2=H, R^3=Ph
iii: R^1=5-OAc, 3-OMe, R^2=H, R^3=Me
iv: R^1=H, R^2=Et, R^3=Me
v: R^1=H, R^2=Et, R^3=Ph
(adapted from ref. [50]).

5 atm of hydrogen and the results are shown in Table 2.2. In each case, the zeolite supported catalyst had the highest enantiomeric excess (ee). The greatest differences in ee's were observed for the compounds with the less bulky N–acetyl derivatives (i, iii, iv). Corma et al. suggest that this is most likely the result of the steric constraints imposed by the supermicropores in which the catalytic sites are anchored. Since the larger pores are not homogeneous in size, it is doubtful that they contribute to the reaction selectivity. Rather, it is most likely the organometallic complexes dictate the reaction selectivity. Another interesting finding is the lack of an induction period for the catalytic reaction conducted over the zeolite; the silica supported catalyst did show an induction period. This is attributed to the concentration effect of the zeolite and/or the interaction of the substrate due to the electrostatic fields present in the zeolite. The zeolite–supported catalysts were also shown to maintain activity after several batch reactions. No rhodium losses were detected (minimum detection levels were not reported). These results show that zeolite catalysts can perform chiral chemistry.

Table 2.2 Activity of dehydrogenation reactions of N–acylphenylalanine derivatives [a]

Compound	Enantiomeric excess[b] [%]		
	unsupported	silica supported	zeolite supported
i	84.1	88.0	97.9
ii	90.3	93.5	96.8
iii	–	–	94.0
iv	54.4	58.0	94.2
v	85.6	92.2	99.0

[a] Adapted from ref. [50].
[b] All ee's were measured at 100% conversion.

The number of chiral solids that can perform enantioselective catalysis is very limited [51]. This is especially true for inorganic solids. To date, none of the zeolite structures are chiral. Thus, the synthesis of a chiral zeolite would be a monumental discovery. Treacy et al. [52] have shown that zeolite beta is an intergrowth of two distinct but closely related structures, the so–called polymorphs A and B. Polymorph A is chiral. It contains a 3–dimensional pore system consisting of 12 T–atom rings. For this polymorph, the building units may stack in a purely right–handed (RRRR....) or left–handed (LLLL....) manner, forming a helical pore. Polymorph B is obtained when a recurrent alternation of right and left stacking sequences is formed (RLRL....). When zeolite beta is synthesized it appears that each layer formed has an equal chance of being in a right or left stacking sequence. The previous stacking sequences does not seem to have an effect on the following stacking sequence. It has been shown [54] by using lattice energy minimization calculations that the lattice energies of polymorphs A and B are essentially equal, and this is a likely cause of the random stacking.

The problem of synthesizing chiral zeolite beta becomes one of influencing the stacking such that the left stacking is more probable than the right one (or vice versa). The use of a chiral "template" molecule, as suggested by Newsam and Treacy [53], seems to be the most likely route to obtaining one of the enantiomers of pure polymorph A. As discussed by Lobo and Davis [3] the template must be developed according to at least three constraints. First, the molecule must be chiral. Second the length of the molecule must be at least 10 Å. This dimension is used so that the template imposes its chirality over more than one layer of stacking. Third, the organic template molecule must be stable at the synthesis conditions of high pH and temperatures greater than about 110 °C.

Arhancet and Davis [49] performed the synthesis of zeolite beta in the presence of chiral organic molecules. Figure 2.3 illustrates the X–ray powder diffraction pattern of "normal" zeolite beta, beta synthesized in the presence of a chiral molecule, and the simulated pattern of polymorph A. At the lower 2–theta values the X–ray powder diffraction pattern of the sample synthesized in the presence of a chiral organic molecule has, on average, larger domains of

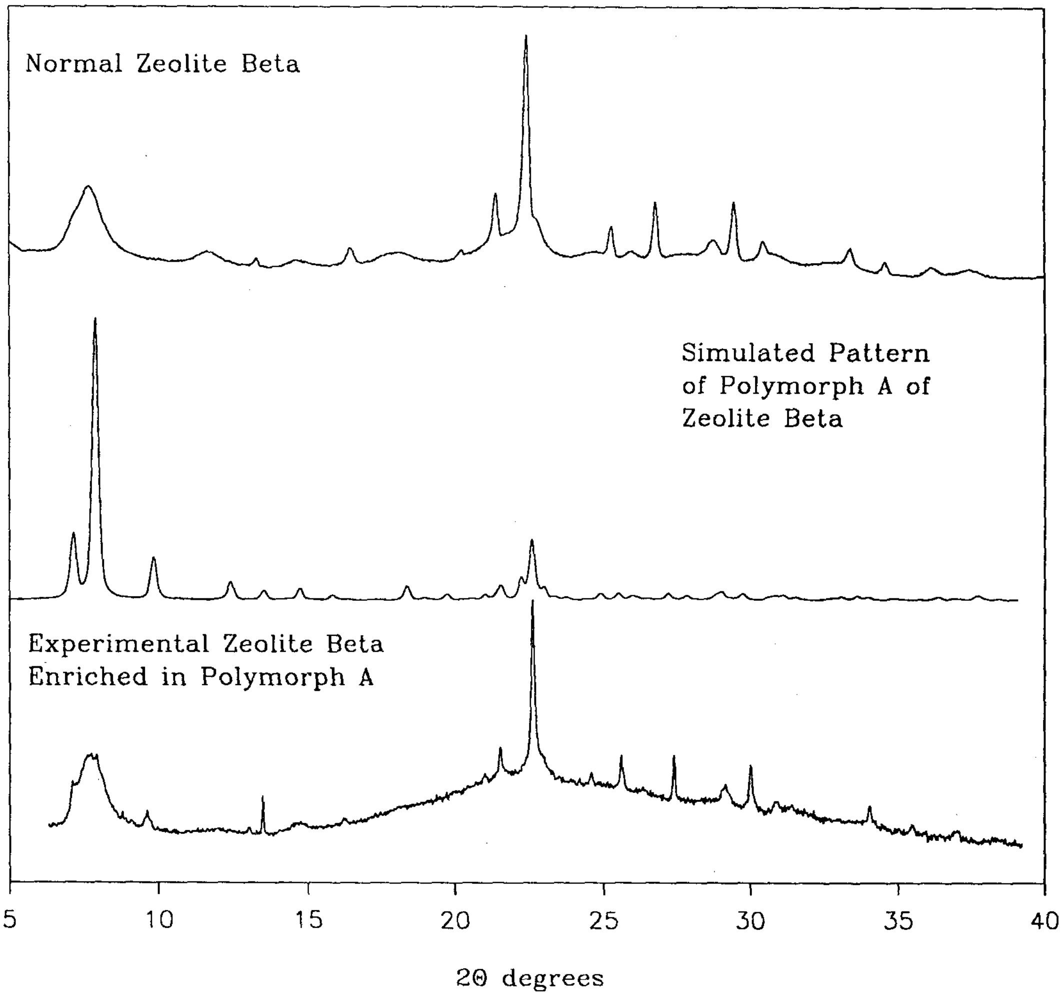
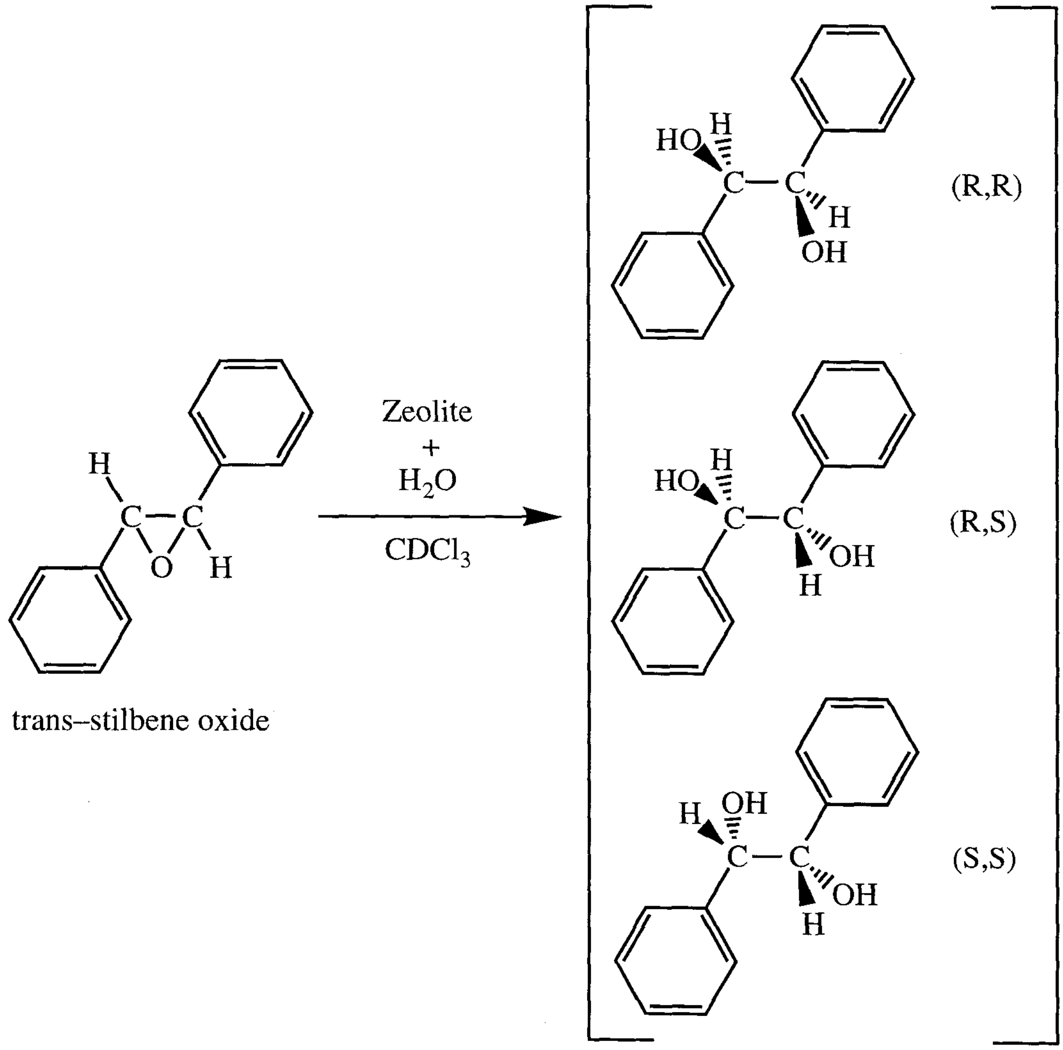


Figure 2.3 X–Ray powder diffraction patterns for various forms of zeolite beta (adapted from ref. [3]).

polymorph A than "normal" zeolite beta. X–ray powder diffraction patterns cannot reveal whether these domains of polymorph A are "racemic" or are enhanced in one enantiomorph. Despite this, it has been shown that the synthesis of pure polymorph A should be feasible. Due to the chirality of the template, if a pure polymorph A sample is synthesized it most likely will be enantiomerically pure as well.

This sample of zeolite beta was then tested for its ability to perform enantioselective adsorption and catalysis. The zeolite was placed in its acid form and contacted with trans–stilbene oxide and then water (Scheme X). The zeolite beta sample enriched in polymorph A gave products which were optically active. An ee of ~5% (R,R–diol) was found, while "normal" zeolite beta gave an ee of zero. To test for enantioselective adsorption, a racemic mixture of the diols ((+/–)–hydrobenzoin) was slurried with the zeolite beta samples. The zeolite beta enriched in polymorph A preferentially adsorbed the R,R isomer.



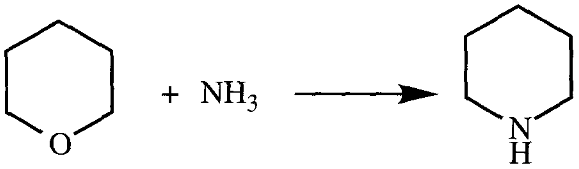
Scheme X (adapted from ref. [3]).

Again the ee was ~5% while "normal" zeolite beta did not preferentially adsorb either isomer. The ee's for these experiments are quite low, yet they are nonzero and outside the error limits of the experiments. Thus, these results suggest that a chiral zeolite could perform enantiomeric separations and syntheses. A suitable chiral template must now be found in order to synthesize pure polymorph A or another chiral zeolite.

2.4 Ring Transformation Reactions

The previously discussed 4–methyl thiazole is a good example of how cyclic compounds, especially those containing heteroatoms, are important in the fine chemical industries. Ring transformation reactions, where nitrogen or sulfur replace oxygen in cyclic compounds, are often used in the production of industrially important chemicals. The synthesis of the oxygen containing compounds will also be discussed. In these zeolite catalyzed reactions, the acidity/ basicity of the zeolite plays a major role.

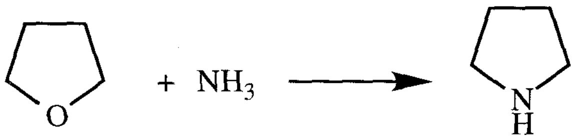
The preparation of piperidine from tetrahydropyran and ammonia (Scheme XI) is an example of a reaction that can be catalyzed by zeolites that contain Bronsted acid sites. Alkali metal exchanged zeolites are unable to catalyze this reaction. It has also been shown that the dealumination of the acidic zeolites HL and HY leads to significant increases in selectivity to piperidine [55]. When the reaction is conducted at 460 °C HL (Si/Al = 3.2) gives a conversion of 24% and a selectivity to piperidine of 58%. If the Si/Al ratio is



Scheme XI

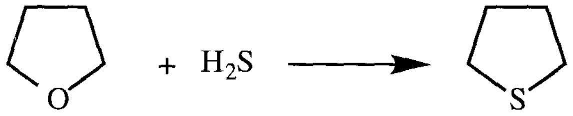
approximately doubled, the conversion remains relatively constant yet the selectivity increases to 80%.

The synthesis of pyrrolidine from tetrahydrofuran (THF) and ammonia (Scheme XII) is another example of a reaction that requires the presence of Bronsted acid sites within the zeolite; alkali–exchanged zeolites were totally inactive. Pyrrolidine is produced with 91% selectivity at 53% conversion over HL, and with 82% selectivity at 61% conversion over HY [56]. The reaction temperature was 350 °C.



Scheme XII

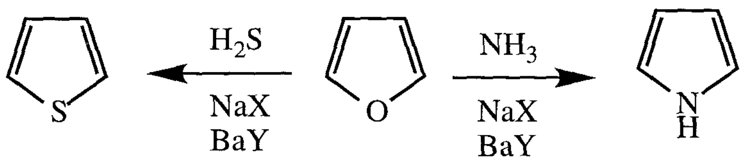
When the corresponding O/S exchange of tetrahydrofuran to tetrahydrothiophene (Scheme XIII) is attempted with acidic zeolites such as HY, HX, or MgY, the reaction



Scheme XIII

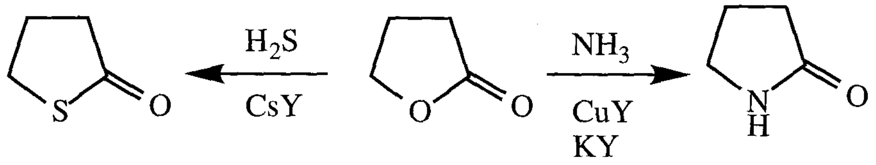
does not proceed [57]. If NaX is used as the catalyst, tetrahydrothiophene is produced with a 97% yield and a selectivity of approximately 100% at a reaction temperature of 350 °C. The sodium exchanged zeolite has significantly lower acidity and has acquired some base character. In the same study, experiments were performed after neutralizing base sites with HCl and neutralizing acid sites with pyridine. The reaction rate was suppressed in both cases. This indicates that both basic and acidic sites must be present within the zeolite.

For the O/N transformation of furan, high Bronsted acidity is no longer required. The reaction of furan with ammonia to form pyrrole (Scheme XIV) only works well over zeolites with low acidity such as NaX [1] or BaY [55]. Over BaY, pyrrole is produced with 100% selectivity at a 14% conversion (reaction temperature of 330 °C). The same conditions of reduced acidity are also best for the reaction of furan and H_2S to thiophene (Scheme XIV) [1].



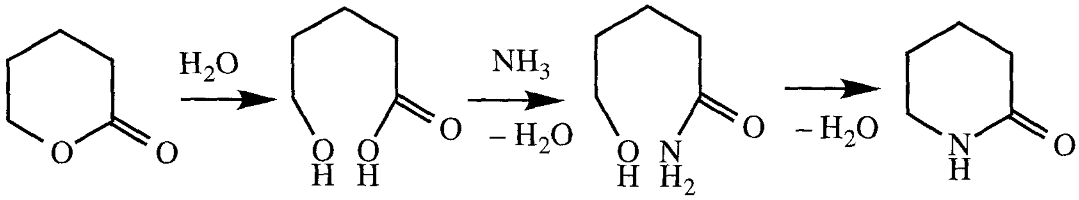
Scheme XIV

The heterocyclic compound 2–pyrrolidinone, formed from γ–butyrolactone and ammonia (Scheme XV), is catalyzed by a variety of exchanged zeolites. CuY, HY, LiY, and NaY were all found to have high activity. They all give similar results, yet CuY gave the best yields with 31% conversion and 80% selectivity at 258 °C [58,59]. Because the highly acidic HY gave comparable results to the alkaline forms, it was concluded that acid sites are not necessary for this reaction to occur. The activity was thought to be caused by the polarization of reactant molecules under the influence of the strong electrostatic field in the zeolite cavities. For the O/S transformation of γ–butyrolactone (Scheme XV), it has been shown that alkali metal exchanged X and Y zeolites are more active than the acidic forms of these zeolites [60]. The activity increased as the basicity of the exchange–ion increased. Correspondingly, CsY at a reaction temperature of 330 °C gave the best results; γ–thiobutyrolactone was produced at a yield of 99% with 100% selectivity. The addition of HCl into the feed stream was used to examine the effects of poisoning the base sites. When HCl was added, ring conversion was almost completely inhibited. Surprisingly, the addition of pyridine to neutralize the acid sites did not poison the catalyst, but rather, actually enhanced the catalysis. These results indicate that the acid sites are not responsible for the catalysis; the active centers are associated with the base sites.



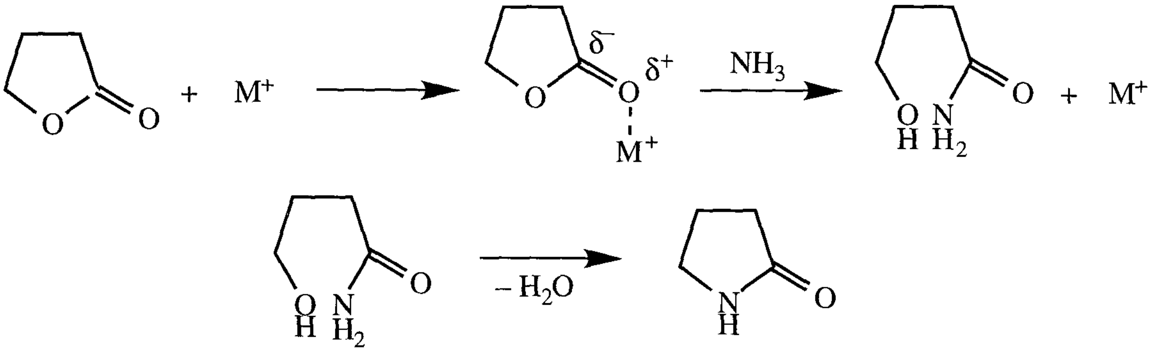
Scheme XV

For the six carbon ring system (δ–valerolactone), the results for the O/N exchange are similar to that of the five carbon ring system [61]. That is, acidic zeolites such as HY are very effective for catalyzing this reaction. Using HY–zeolite at 285 °C, δ–valerolactam yields of up to 80% were observed. Because water was found to facilitate the reaction, the following route was proposed (Scheme XVI):



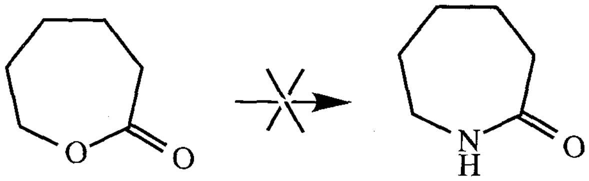
Scheme XVI

This type of ring opening was also proposed for the conversion of γ-butyrolactone into 2–pyrrolidone (Scheme XVII) [58].



Scheme XVII

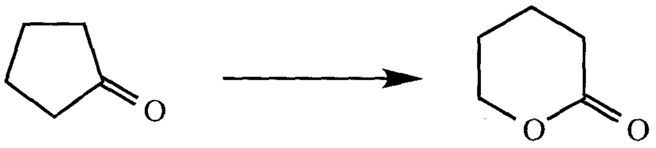
These types of reactions have also been attempted on larger molecules. Using a seven carbon ring system (ε–caprolactone), it is expected that acid zeolites would catalyze the O/N exchange to ε–caprolactam (Scheme XVIII). A patent has been filed that claims that this reaction is indeed possible using ammonia with HY–zeolite [62]. Holderich [63] has found, to the contrary, that no O/N exchange occurs. Instead ring cleavage and dehydration to hexene nitriles takes place. This reaction, when run at 400 °C over weakly acidic boron zeolites or strongly acidic aluminum faujasites, yields selectivities of 86% and 75%, respectively. Acidic aluminum–containing ZSM–5 yields a selectivity of 82%. This



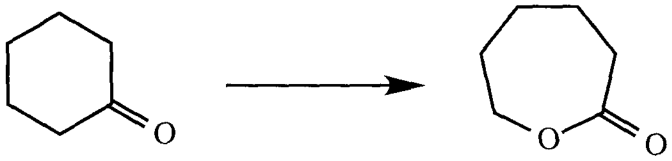
Scheme XVIII

zeolite has pores too narrow to allow ε–caprolactone to enter. Sato et al. [64] have also shown that the similar reaction of cyclopentanone oxime to ε–caprolactam proceeds on the surface of ZSM–5. If the decompostion to hexenenitrile does occur on the surface, shape–selective arguments cannot be used to explain the results.

It has been found that certain zeolites are able to catalyze the oxidation of cyclic ketones to lactones [65]. The production of lactones is in general favored, at low reaction temperatures, short reaction times, minimal amounts of water, and zeolite catalysts with low Constraint Indices and high Si/Al ratios. Typically, zeolite catalysts which fit these conditions would be zeolite beta, mordenite, and ZSM–5. δ–Valerolactone was produced from cyclopentanone (Scheme XIX) using ZSM–5 (in its acid form Si/Al=70) with a selectivity of 63% at 40% conversion. This reaction was carried out at room temperature for five hours. At shorter reaction times higher selectivities at lower conversions were reported. Using the same catalyst, ε–caprolactone was produced from cyclohexanone (Scheme XX) with 75% selectivity at 5.6% conversion. Selectivity to ε–caprolactone is improved when the Si/Al ratio is increased to 500. Aqueous hydrogen peroxide is used as the oxidant for both of these reactions.

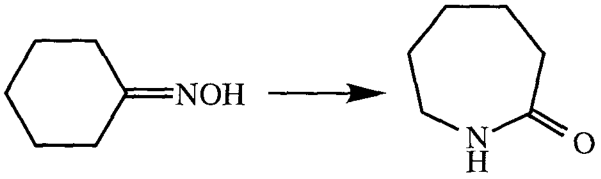


Scheme XIX



Scheme XX

The zeolite–catalyzed conversion of cyclohexanone oxime to ε–caprolactam (Scheme XXI) has been reported [66]. This reaction is thought to best proceed at



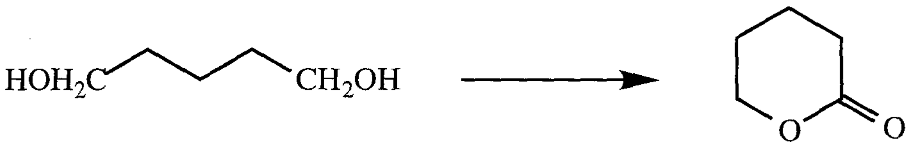
Scheme XXI

approximately 300 °C over dealuminated ZSM–5. The decrease in acidity, by dealumination, increases the selectivity to ε–caprolactam and also decreases the aging rate of the catalyst. Selectivities approaching 95% at 93% oxime conversion were reported.

γ–Butyrolactone can be produced from butane–1,4–diol using oxygen as the oxidant, over Pd supported on zeolites (Scheme XXII) [67]. The effect of zeolite type, ion–exchange, and reaction solvent were studied. The reactions

Scheme XXII

were run in a batch reactor under an oxygen atmosphere. Zeolite L gave the best results. Potassium exchanged zeolites proved to be more effective catalysts than those in the sodium form. The KL–zeolite was tested in two different solvents, N,N–dimethylpropionamide (NPA) and N–methylpyrrolidin–2–one (NMP). Both solvents worked well, but when the reaction was run in NPA higher yields were observed (91.5% selectivity to γ–butyrolactone at 99.4% conversion of diol). When the reaction was conducted in pure butane–1,4–diol, i.e., no solvent, very low conversions and selectivities were observed. The same catalyst was also shown to be effective in the oxidative lactonization of pentane–1,5–diol into δ–valerolactone (Scheme XXIII).



Scheme XXIII

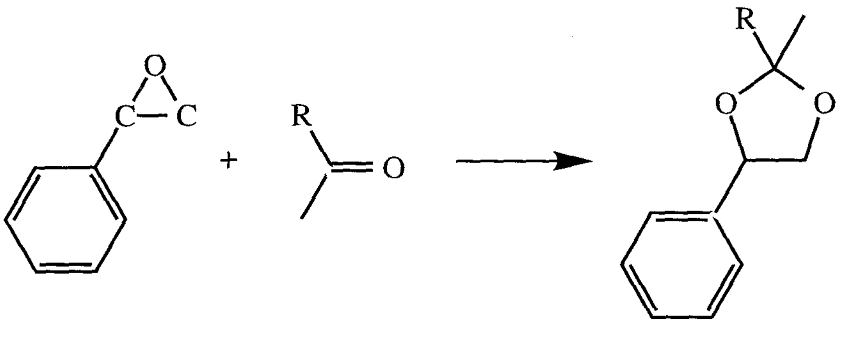
From Table 2.3, one can attempt to identify trends in the requirements for O/N and O/S exchange, yet no definite explanations have been found for determining the acid or base character needed to catalyze a given reaction. These transformations for heterocyclic compounds will most likely find use in the synthesis of fine chemicals.

USY–zeolite in its acid form (Si/Al=5.0) was found to be a suitable catalyst for the synthesis of 2,2–dialkylsubstituted–4–phenyl–1,3–dioxolanes from styrene oxide and an aliphatic ketone (Scheme XXIV) [68]. The acidity appears to play an important role because the alkali-exchanged zeolites were not active. H-USY-zeolite gave greater than 99% conversion of styrene oxide and dioxolane yields of 56%, 30%, 15%, and 44%, respectively for the following ketones: acetone, 2-butanone, 3-methyl-2-butanone, and cyclohexanone. It is interesting to note that mineral acids, such as HCl and H_3PO_4, are not able to catalyze the reaction.

Table 2.3 General requirements for ring transformations [a]

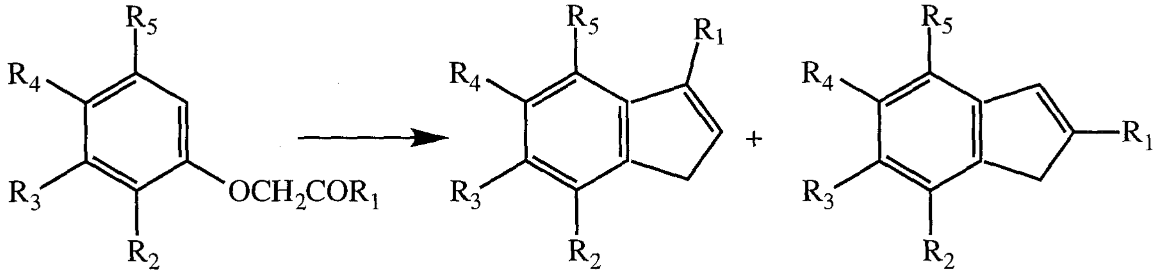
Heteroatom transformation reaction		basic	acidic
saturated	5 ring + NH_3	–	+
saturated	5 ring + H_2S	+	+
saturated	6 ring + NH_3	–	++
unsaturated	5 ring + NH_3	+	–
unsaturated	5 ring + H_2S	+	–
saturated	5 ring lactone + NH_3	+	+
saturated	5 ring lactone + H_2S	+	–
saturated	6 ring lactone + NH_3	–	+

[a] Adapted from ref. [7].



Scheme XXIV

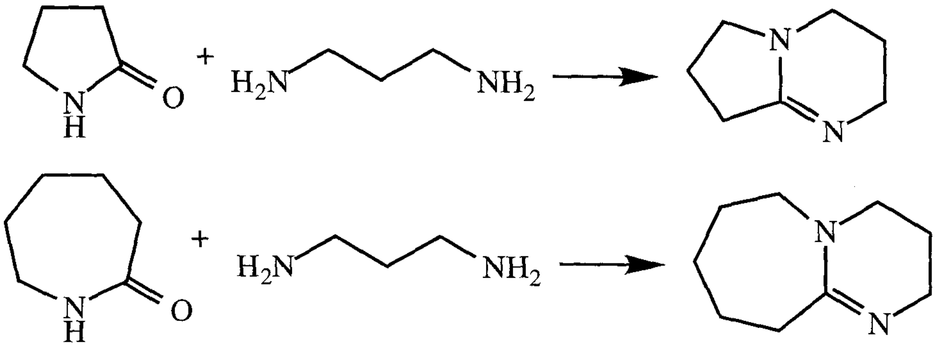
Bicyclic compounds have been formed over zeolites. 3–Substituted benzofurans have reportedly been synthesized by the cyclization of α–aryloxyketones in the presence of HY zeolite (Scheme XXV) [69]. The zeolites afford high selectivity to the 3–substituted over the 2–substituted benzofurans, which are often seen when homogeneous catalysts are



Scheme XXV

used. The reactant molecules are thought to cyclize on the surface of the zeolite because they are too large to enter the pores. It is also pointed out that, on the surface of the zeolite, the acidity is too weak for rearrangement to occur.

Pyrrolidinone and caprolactam have been shown to react in the gas phase with diaminopropane (DAP) over zeolite catalysts to form 1,5–diazabicyclo[4.3.0]non–5–ene (DBN) and 1,8–diazabicyclo[5.4.0]undec–7–ene (DBU) (Scheme XXVI) respectively [70]. HY–zeolite proved to be the most effective catalyst for the caprolactam reaction. At 350 °C, DBU was produced with a selectivity of 53% at 75% conversion of caprolactam. By increasing the ratio of DAP to caprolactam, the conversion was raised to 97% without any change in DBU selectivity. H–USY–zeolite was the most active for the synthesis of DBN (91% selectivity to DBN at 46% conversion of pyrrolidinone).



Scheme XXVI

2.5 Oxidation Chemistry with Ti–Containing Zeolites

The synthesis of a titanium containing zeolite, by Taramaso et al. [71] in 1983, ushered in the use of zeolite catalysts for partial oxidation chemistries. It was shown that titanium occupied framework positions in this material (denoted TS–1, titanium–silicalite–1) [72]. The importance of TS–1 in the catalytic synthesis of fine chemicals makes it extremely noteworthy. Within a short time after its synthesis, TS–1 was employed as a commercial catalyst for the production of catechol and hydroquinone from phenol and aqueous H_2O_2 [73]. Its utility is quite evident in its ability to catalyze a broad spectrum of oxidation reactions (see Figure 2.4). Aqueous H_2O_2 has great advantages over organic oxidants; it is relatively inexpensive, and, more importantly, produces water as its by–product. As environmental standards become more stringent, such "clean" reactions become increasingly desirable. The shape–selectivity and ease of separation and recovery of zeolite catalysts make this type of catalyst even more attractive over some traditional homogeneous processes. Titanium has also been incorporated into ZSM–11 (TS–2) [74], ZSM–48 [75], and zeolite beta [76]. TS–2 behaves similarly to TS–1 as expected [77] and titanium zeolite beta is capable of oxidizing alkanes with aqueous H_2O_2.

The search for large–pore zeolites containing titanium is driven by the desire to perform partial oxidation chemistries on molecules too large to enter into TS–1. Post–synthetic methods have been used in attempts to place titanium into zeolite frameworks. This method holds promise since it has been shown that the catalytic activity for phenol hydroxylation of acid–extracted ZSM–5 treated with gaseous $TiCl_4$ is equal to that of synthetic TS–1 [78]. The physical and chemical properties of the two solids have also been shown to be similar [79].

Ferrini and Kouwenhoven [80] have reported the insertion of titanium into the framework of various zeolites and have tested these materials for the oxidation of phenol with aqueous H_2O_2 to compare with TS–1. An IR absorption band at 960 cm^{-1} appeared

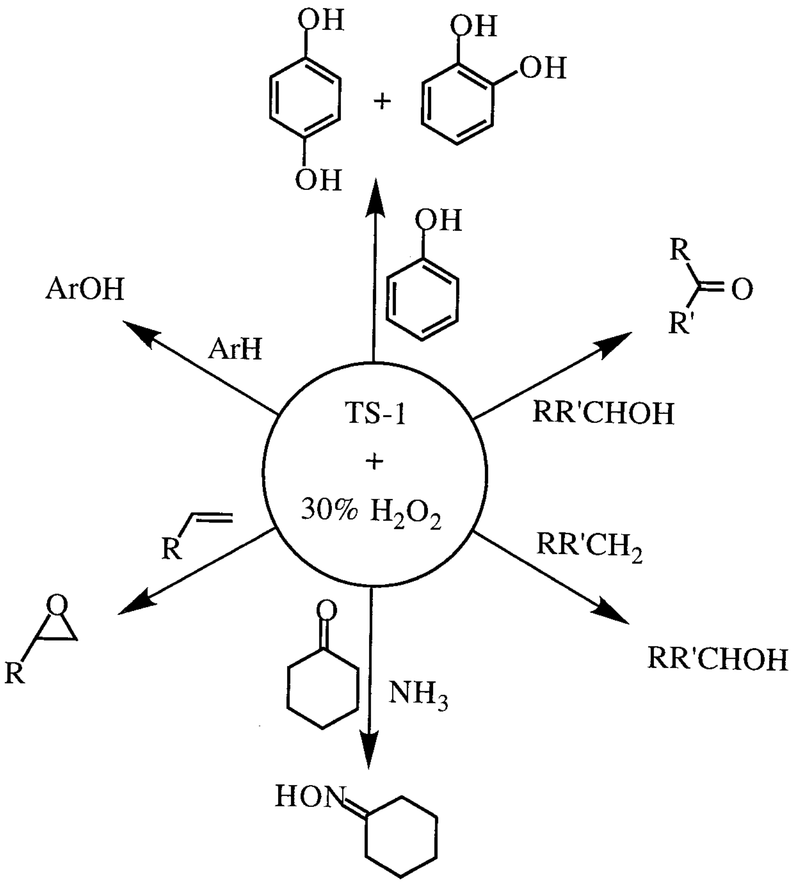


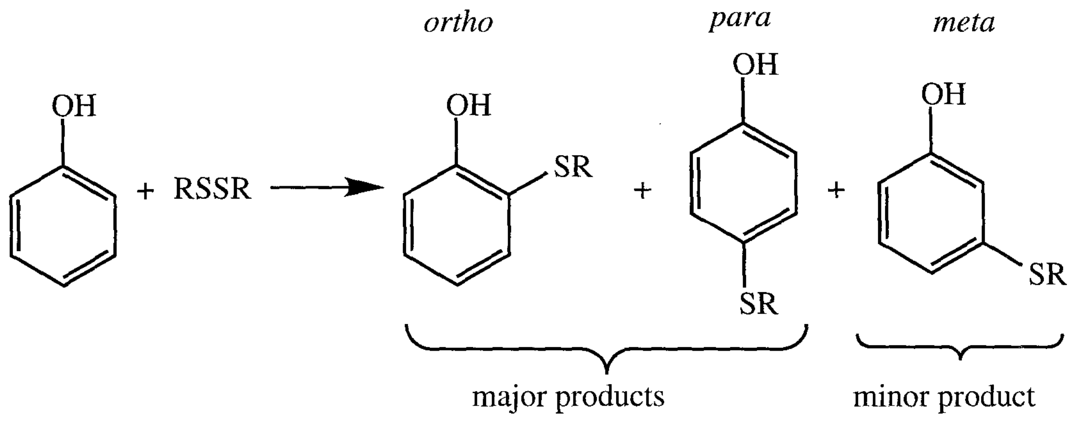
Figure 2.4 Oxidation reactions catalyzed by TS-1 (adapted from ref. [81]).

for ZSM–5 and zeolite USY after treatment with $TiCl_4$, although zeolite beta did not show any new peak in this region. The ZSM–5 sample treated with $TiCl_4$ was active for phenol hydroxylation, yet its activity was less than TS–1. Ti–USY was not active for this reaction. Ti–beta was active for phenol hydoxylation but the conversion was lower than that observed when using the parent material H–beta.

The isomorphous substitution of Si with Ti in the zeolite beta framework by direct synthesis has been reported by Camblor et al. [76]. As evidence for Ti incorporation, the interplanar d–spacings were shown to increase as the Ti content of the zeolite increased. The samples also contained a 960 cm^{-1} band in the IR spectra. The intensity of the band increased with Ti content. The oxidation of cyclododecane with H_2O_2 was used as a test reaction to study the catalytic activity of Ti–beta. It was found that Ti–beta exhibited a higher activity and higher selectivity to the corresponding ketone than a TS–1 reference sample. The Ti–beta contained less titanium (by weight per cent) than TS–1. The same results were observed for the oxidation of cyclohexane. The acid sites (framework Al) catalyzed the side reaction with the solvent, but only at long reaction times. These results are not surprising because the reactant molecules are too large to enter into the pores of TS–1. The activities observed in these experiments were due to the shape–selective nature of the pore system rather than actual catalytic ability. The new Ti–beta may prove to be more useful than TS–1 in the manufacture of fine chemicals. Its larger pores will allow larger, more complex molecules to enter and react.

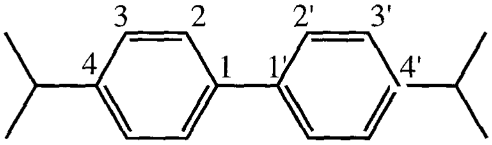
2.6 Miscellaneous Shape–Selective Reactions

The shape selective nature of zeolites has made them widely studied in many alkylation reactions. Because of steric hindrances within the pores, the meta product (often the bulkiest of bi–substituted compounds) is usually a minor constituent. This is indeed the case for the preparation of alkylthio–phenols (Scheme XXVII) [82].



Scheme XXVII

Another interesting case where shape selective alkylation has been investigated is with the 4,4' alkylation of biphenyl. This particular isomer is quite valuable because it is difficult to obtain using previous methods, and its application in liquid crystals and high performance polymers [83,84]. Biphenyl has been alkylated with propene over HY, HL, and H-mordenite [85]. HY and HL zeolites gave conversions and selectivities similar to an amorphous silica–alumina. However, H–mordenite had the highest selectivities for the singly alkylated 4–(isopropyl)biphenyl and the doubly alkylated 4,4'–(isopropyl)biphenyl. With an overall conversion of 48%, the 4–(isopropyl–biphenyl made up 71% of the singly alkylated products, and the 4,4'–(isopropyl)biphenyl composed 78% of the bis(isopropyl)biphenyl products. For the other catalysts tested, the selectivities for the singly (4–) and doubly (4,4'–) substituted products were near 45% and 10% respectively.



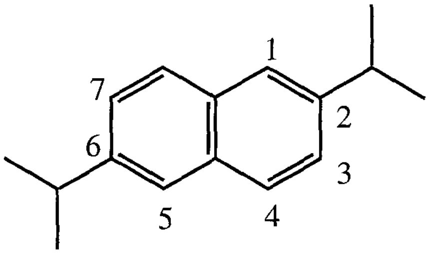
4,4’-(isopropyl)biphenyl (numbers indicate substitution positions)

The oval pore structure of mordenite is speculated to cause the increase in selectivity for the 4– and 4,4'–products. The authors claim that the 2– isomer and many of the bis– isomers are too bulky to escape the pore of H–mordenite. Reaction temperature did not influence product distribution.

Lee et al. [86] have also investigated this same reaction and have observed significantly higher yields than the aforementioned study. Reacting biphenyl and propene over highly dealuminated (Si/Al=2600) H–mordenite (reaction conditions: 523 K, 20 hours, propene pressure 8.43 kg (wt) cm^{-2}) gave a biphenyl conversion of 98% with a selectivity to the 4–4’ isomer of 73.5%. The dealumination results in reduced acidity and increased pore volume. The reduced acidity led to lower coke formation and polymerization reactions as compared to the parent material. The reactant molecules are believed to be packed in the 12 membered ring pores in such a way that there is partial overlap of the aromatic rings. Thus, the shape–selectivity appears to be due to the geometry of the pores and the packing of the reactants. They coined this phenomenon "reactant assisted shape–selectivity." The propene reacts with these packed molecules after diffusing in through the 8 membered rings (which intersect the 12 membered rings). This was described as "molecular traffic control."

In a similar study, the chlorination of biphenyl was attempted in hope of producing the 4,4'– isomer [87]. Many zeolites, with different cations, were used and it was found that KL–zeolite outperformed all the other zeolites tested. In molten biphenyl, using Cl_2 for the chlorination, KL–zeolite gave 100% conversion and 66.5% selectivity for the 4,4'–product. In attempts to improve this selectivity, co–catalysts were added to the molten mixture. Carboxylic acid derivatives proved to be excellent choices as co–catalysts. When chloroacetic acid was added to the reaction mixture with KL–zeolite, the selectivity to the 4,4'– isomer increased to 83.7%. The reaction was then attempted at room temperature using dichloromethane as the solvent. This treatment increased the selectivity to 89.0% at 20 °C. Other solvents were not nearly as effective. The solvent effect was observed on zeolite L alone. Elevating the reaction temperature to 40 °C and introducing a 10% excess of chlorine further increased the selectivity to 96.4% when using KL–zeolite as the catalyst. Under the same conditions, only a LiL–zeolite performed better than the KL–zeolite with 96.7% selectivity.

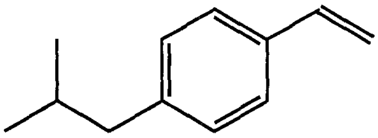
Another polyaromatic compound useful as a starting material for the preparation of polymers is 2,6–diisopropylnaphthalene (2,6–DIPN). This compound is difficult to synthesize using the usual alkylation techniques because of the myriad of substituted products that can be formed. Experiments employing acid zeolite catalysts have shown that the 2,6 alkylation product can be selectively formed over other isomers in the reactions of naphthalene with propene or 2–propanol [88]. As in the case for the 4,4'–alkylation of biphenyl, H–mordenite gave the best results in the selective alkylation of the 2,6–DIPN. The linear, oval channels are thought to be small enough to prevent attack at the 1,4,5 positions (the so–called α positions). The 2,6 and 2,7 isomers (the so–called β positions) are smaller in size than α,β and α,α isomers. After 2 hours in a batch reactor at 240 °C, the conversion was 35.6% and the selectivities for the 2,6– and 2,7– isomers were 51.7% and 24.0% respectively. Allowing the reaction to run 8 hours increases the conversion to 68.3% and the selectivities remain relatively stable. Because the 2,6– and 2,7– isomers are nearly the same size, the shape selective argument cannot be used to explain the higher yield of the 2,6–isomer. The investigators speculated that an activated complex which promotes the production of the 2,6–isomer is more easily formed between naphthalene, propene, and the walls of the H–mordenite channels. For more detailed discussions of polyaromatic alkylations see the relevent chapter of this volume.



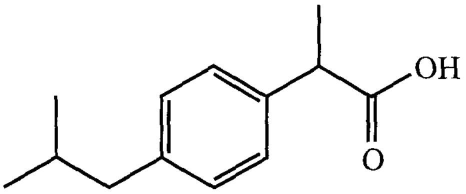
2,6-diisopropylnaphthalene (numbers indicate substitution positions)

Zeolites have been found to be quite effective in the synthesis of pharmaceutical intermediates. For example, HX– and HY–zeolites have been used as disproportionating catalysts to convert o– and/or m–isobutylethylbenzene into p–isobutylethylbenzene [89]. The latter is then dehydrogenated in another process to form p–isobutylstyrene.

p–Isobutylstyrene is an intermediate that can easily be used to manufacture α–(4–isobutylphenyl)propionic acid. This substance is better known as Ibuprofen.



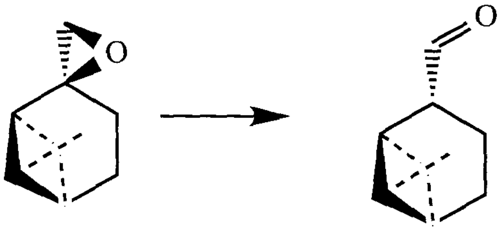
p–isobutylstyrene



Ibuprofen

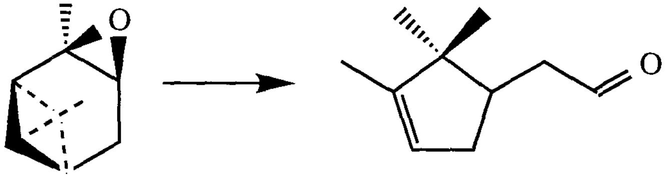
When a mixture of isobutylbenzene and o– and/or m–isobutylethylbenzene reacts at 180 °C over HY–zeolite, some p–isobutylethylbenzene is produced. As mentioned earlier, the ortho isomers are usually not major products when zeolites are used due to steric constraints. Again, this phenomenon is found in the present example. The products are then distilled to obtain nearly pure p–isobutylethylbenzene. The use of the zeolite as a solid acid is also advantageous because less sec–butylethylbenzene is produced than with other acid catalysts. This by–product is undesirable because it is difficult to separate from the desired product using distillation methods.

Another class of reactions for which zeolites have proven to be quite useful is in the ring–opening of epoxides. For the pyrolysis reaction of (+)–2(10)–pinene oxide over ZnZSM–5 zeolite at 300 °C, cis–myrtanal was obtained as the main component (95% conversion, 84% selectivity) (Scheme XXVIII) [90]. The zeolite showed a much higher selectivity than Raney-nickel or acetic anhydride catalysts.



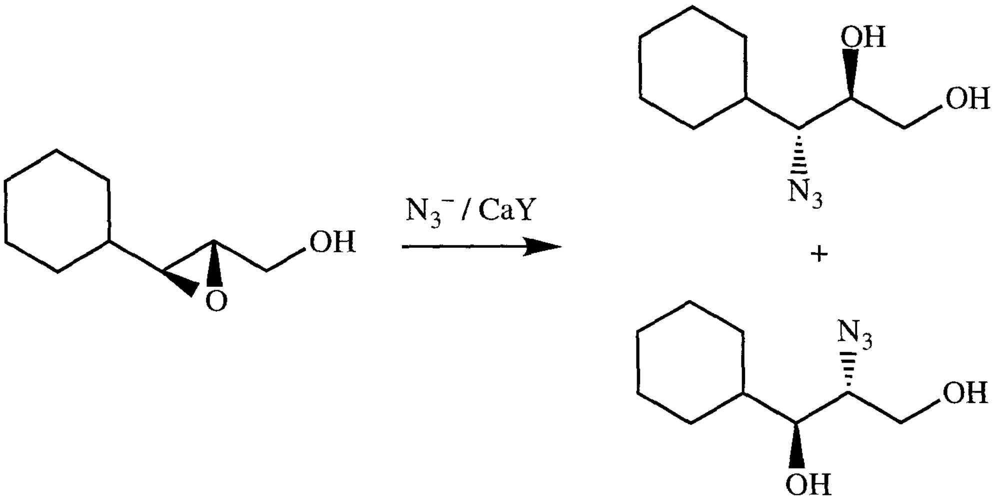
Scheme XXVIII

The same catalyst was also shown to be quite effective for the pyrolysis of (+)–2–pinene oxide to α–campholenic acid (92% conversion, 85% selectivity) (Scheme XXIX).



Scheme XXIX

The ring opening of epoxides has also been reported by using zeolite–supported nucleophiles. In an interesting study by Onaka et al. [91], it was found that CaY–supported nucleophiles induce ring opening in a highly regioselective manner. The reactions were performed with 3–cyclohexyl–2,3–epoxypropan–1–ol as the reagent and NaN_3 as the nucleophile. Various cationic forms of zeolite Y were used as the support. CaY–zeolite demonstrated unusual catalysis. Using this catalyst, all the epoxide was converted in 1.5 hours at 80 °C and an 85% yield of the diol was reported (Scheme XXX).



Scheme XXX

The unusual result was that 94% of the diol was formed from a C–3 opening. Different cationic forms of zeolite Y exhibited varying degrees of reactivity and selectivity. The data was taken to suggest that the ring opening was highly influenced by the interaction between the substrate and the cations within the zeolite. This argument appears more reasonable than a pure shape–selective argument since the two diols are nearly identical in size. Previous reports [92,93] describe a peculiar affinity between calcium ions and polyoxygenated compounds. Onaka et al. suggest that the epoxy alcohol forms a coordinated structure around a calcium ion in the zeolite (see Figure 2.5b). This type of structure is known to exist with Ti compounds (see Figure 2.5a). If the nucleophile attacks the C–3 position, the C–O bond cleavage results in a five–membered chelation structure. It is believed that the reason for the C–3 attack results from the greater stability of this C–3 chelation compound than the analogous C–2 chelation compound.

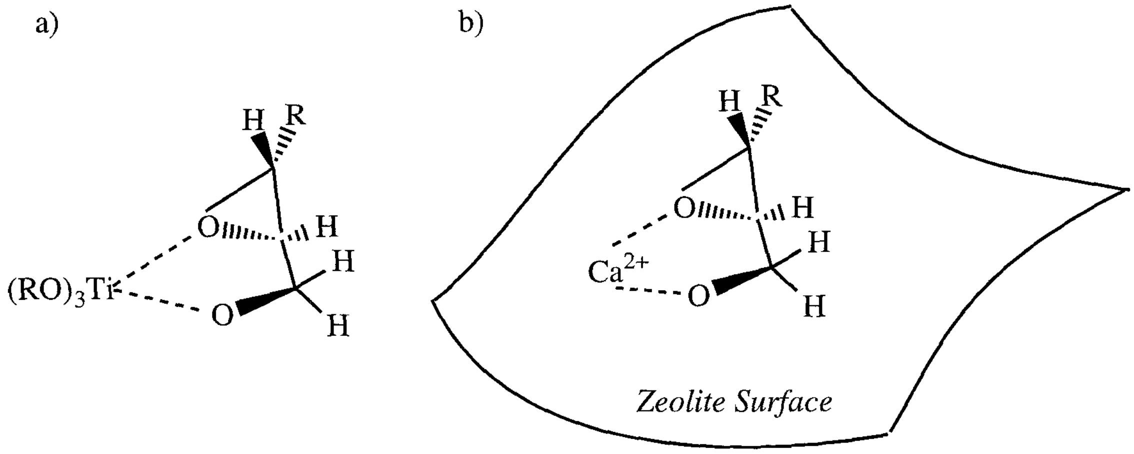
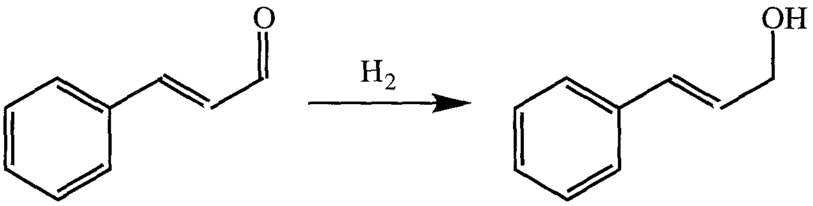


Figure 2.5 Proposed chelate complexes of 2,3-epoxy alcohol (adapted from ref. [91]).

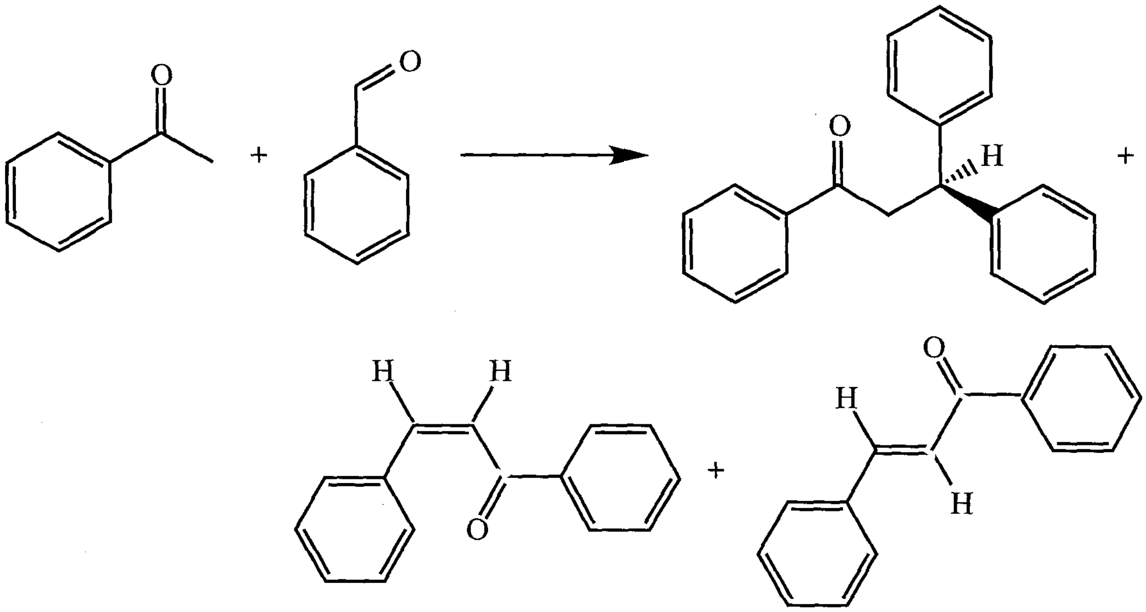
The hydrogenation of cinnamaldehyde (Scheme XXXI) was performed over Y–zeolites containing either platinum or rhodium particles by Gallezot et al. [94]. It was found that extremely high selectivities to cinnamyl alcohol could be obtained using a Y–zeolite in which platinum particles occupy the entire supercages. The pore structure was small enough to keep the aromatic ring from adsorbing onto the particles and catalyzing the hydrogenation of the C=C bond. Only end–on adsorption was then possible, i.e., via the C=O group. A selectivity of 96% to cinnamyl alcohol was observed at a conversion of 75%. Another Y–zeolite that contained smaller platinum particles showed a selectivity to the alcohol of 82% at a conversion of 75%. The authors believe that a few supercages may have platinum clusters so small that cinnamaldehyde may be able to enter the supercage and react at the aromatic ring. The rhodium–containing Y–zeolite showed a selectivity to the alcohol of 22% at a conversion of 75%. The selectivity is quite small compared to that of the platinum containing zeolites, but it is much higher than rhodium supported on carbon. Rhodium is well–known to have a high activity for C=C bond hydrogenation. The geometric constraints imposed by the zeolite pores and the metal particles effectively force the reaction to occur at the C=O bond giving the desired product.



Scheme XXXI

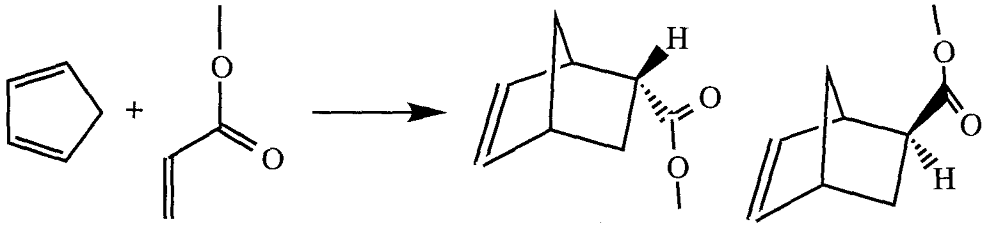
2.7 Miscellaneous Organic Reactions

As was discussed earlier in this review, zeolites possessing base character have been shown to catalyze aldol condensations. Acidic zeolites have also proven to be active catalysts for the Claisen–Schmidt condensation (a type of crossed Aldol condensation) [95]. It was found that HY–zeolite catalyzes the crossed aldol condensation of acetophenone with benzaldehyde in a suitable solvent at 80 °C (Scheme XXXII). The two expected products were formed, cis– and trans–chalcones and 3,3–diphenylpropiophenone was also produced. No other products were detected. The ratio of trans– to cis– for the chalcones was approximately 11. The formation of 3,3–diphenylpropiophenone in the acidic medium was an interesting result since the normal preparation of this compound involves the use of strong basic reagents. This study shows how acidic zeolites may be used to catalyze certain aldol condensations in mild environments (liquid phase, moderate temperatures). This is an important class of reactions due to the fact that many useful synthetic procedures include condensation reactions [96].

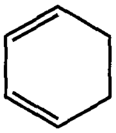


Scheme XXXII

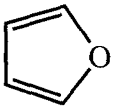
Diels–Alder reactions are also extremely important in the manufacture of valuable intermediates. Rate acceleration and control of stereochemical outcome are two major goals that will further expand the use of zeolites as catalysts for these reactions. In a study by Narayana Murthy and Pillai [97], various zeolites were studied for their ability to catalyze the Diels–Alder reactions of cyclopentadiene, cyclohexadiene, and furan with less reactive dienophiles. For the reaction of cyclopentadiene with methyl acrylate (Scheme XXXIII), zeolites such as NaY, ZnY, CeY and NaZSM–5 all gave yields and endoselectivities greater than 90%. However, it was observed that when a combination of CeY–zeolite and $ZnBr_2$ was employed as the catalyst, the Diels–Alder product was formed with a yield of 96% and 100% endoselectivity (reaction time of 1 hour at 0 °C). For similar reactions involving cyclopentadiene and cyclohexadiene with other dienophiles such as acrolein, acrylamide and methyl acrylate, the combination of CeY–zeolite and $ZnBr_2$ gave very good yields with total endoselectivity. Similar reactions were then attempted using furan. Because of its aromaticity, furan is a poor Diels–Alder diene and generally requires high pressures



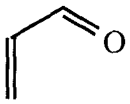
Scheme XXXIII



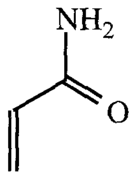
cyclohexadiene



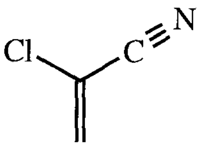
furan



acrolein



acrylamide

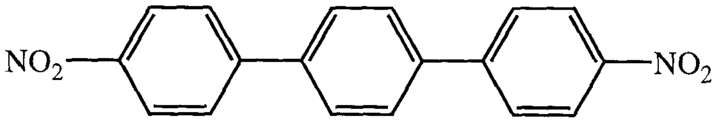


chloroacrylonitrile

(10–20 kbar) to effect cycloaddition [98]. In the reaction of furan with methyl acrylate, CeY gave a yield of 45% with 70% endoselectivity (reaction time: 24 hours). With no catalyst present, the reaction takes more than one month to achieve a yield of 20% with 60% endoselectivity. The use of added $ZnBr_2$ hardly had any effect on yields or endoselectivities. When chloroacrylonitrile was used as the dienophile, an unwanted by–product (2–chloropropionitrile) was formed with NaY, $ZnBr_2$ and NaY, or CeY. The use of ZnY–zeolite eliminated this side–product. Overall, excellent rate enhancement and total endoselectivity were reported for the Diels–Alder reactions of cyclopentadiene and cyclohexadiene with various dienophiles when a combination of $ZnBr_2$ and CeY–zeolite was used as the catalyst. Substantial rate enhancement was also observed for Diels–Alder reactions involving furan.

Smith has reported complete exoselectivity for the Diels–Alder reaction of cyclopentadiene and acrylonitrile over a zeolite catalyst (the type of zeolite was not mentioned) [9]. Although the yield was low (35%), the high selectivity to the exo–product is quite remarkable since the endo–product almost always predominates in Diels–Alder reactions. It was also observed that when the zeolite catalyst was dissolved in acid, the only product that was liberated was the endo–compound. The zeolite was assumed to separate the stereoisomers and only allow the exo–product to exit the pore structure.

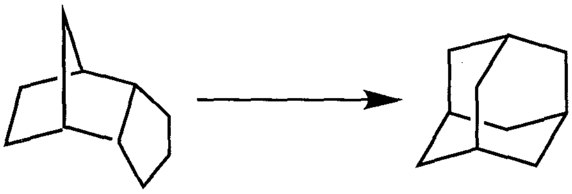
Similar to the reactions on biphenyl, the synthesis of para,para–prime-dinitroterphenyl at high selectivities and yields would be quite important. A patent on the



para, para–prime–dinitroterphenyl

production of this material is reported to give only 31% of the desired product [99]. Smith has reported a final yield of 52% of the desired product from the nitration of terphenyl with benzoyl nitrate over aluminum exchanged mordenite [9].

An interesting example of a skeletal rearrangement that certain zeolites are able to catalyze is the transformation of tetrahydrodicyclopentadiene to adamantane, in the presence of H_2 and HCl (Scheme XXXIV) [100]. Rare Earth Y–zeolites, REY–zeolites, are active for this reaction and the addition of Co or Ni increases the catalyst's activity. These catalysts deactivate rapidly within 20 hours. Further doping with Pt and Re increases activity and catalyst lifetime but brings about a decrease in selectivity to adamantane. The reasons for these results are not yet understood.



Scheme XXXIV

2.8 Final Remarks

The number of patents and articles dealing with organic syntheses catalyzed by zeolites has increased dramatically over the past ten years. This will continue as the demand for fine chemicals grow and as the profits in the petrochemical industry dwindle. It has been noted [101] that only 3% of all heterogeneous catalysts used are for the synthesis of fine chemicals yet this 3% generates 20% of the profits. It is not difficult to see why this field is growing so quickly! This growth will probably have the greatest impact on processes not normally utilizing heterogeneous catalysts, i.e., shape selective base catalysis, stereo– and enantio–selective catalysis, and partial oxidation catalysis.

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CHAPTER THREE

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

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

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Abstract

Titanium containing pure-silica ZSM-5 (TS-1) materials are synthesized using different methods. The activity of the titanium containing 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 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.

3.1 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 the octahedral titanium-containing silicate molecular sieve (ETS-10) *(5)* have been studied. The effect of the presence of aluminum and/or sodium on the catalytic activity of TS-1 is also discussed.

3.2 Experimental

3.2.1 Samples

TS-1 samples were synthesized by modifications of the preparation methods reported in the patent literature *(6,7)*. As shown in Table 3.1, samples TS-1(A) and TS-1(B) were crystallized from clear solutions prepared by mixing titanium butoxide (TNBT), tetraethylorthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH, 1 M) and double distilled water *(6)*. 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 co-precipitate (Type III no.2, obtained from W.R. Grace) with the TPAOH solution *(7)*. Aluminum and/or sodium containing titanium silicate (TAS-1, NaTS-1) were prepared by adding $Al(NO_3)_3$ and/or $NaNO_3$ (from Aldrich) into the TiO_2-SiO_2 co-precipitate/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 distilled H_2O with subsequent calcination at 500 °C. ETS-10, which is a titanium silicate molecular sieve with titanium in octahedral coordination, was provided by Engelhard, Co. 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.

3.2.2 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-Kα 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.

3.2.3 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 an 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.

3.3 Results and Discussion

3.3.1 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 3.1 shows the IR spectra of TS-1(A), TS-1(B), TS-1(C), TiO_2-SiO_2 co-precipitate and pure-silica ZSM-5. The absorption band at 960 cm^{-1} is characteristic of TS-1 *(8)*. All of TS-1 samples used in this study show this band. The band is not present in TiO_2 and ETS-10 (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 3.2.

The catalytic activity of the materials used in this study are shown in Table 3.2. 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. *(9)*. 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 ETS-10, TS-1(A), TS-1(B) and anatase are shown in Figure 3.2. 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), TS-1(C) (not shown in the figure) and ETS-10. 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 3.3 illustrates the UV-VIS diffuse reflectance spectrum of TS-1(A). The spectrum shows two bands at ~220 nm and ~270 nm, which can be assigned to framework *(10)* and extra-framework nanophase *(11)* titanium species, respectively. The other TS-1 samples do not show the band for extra-framework 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 3.3 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.

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 3.2). 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 co-precipitate 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.

ETS-10 shows no catalytic activity. This observation indicates that titanium in octahedral coordination in ETS-10 is not active for selective oxidation and epoxidation using either aqueous hydrogen peroxide or non-aqueous alkyl hydroperoxide as the oxidant.

3.3.2 Effect of sodium and aluminum on TS-1

The catalytic activities of aluminum and/or sodium containing TS-1 are depicted in Table 3.4. The data show that the addition of aluminum during the synthesis of TS-1 yields a material (TAS-1(D)) that has a lower conversion of 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/TAS-1(D)). Therefore, the addition of aluminum into the synthesis mixture most likely reduce 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). It has been shown *(12)* 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 3.4.

3.4 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. Octahedral titanium in ETS-10 and titanium species in the TiO_2-SiO_2 co-precipitate 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.

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Table 3.1 Sample Preparations.

Sample	Composition Si/Al	 Si/Na	 Si/Ti	Crystallization 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
TAS-1(D)[b]	50	-	56	175	7
TAS-1(E)[b]	200	-	56	175	7
NaTS-1[b]	-	10	56	175	7
NaTAS-1[b]	50	10	56	175	7

[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 3.2 Catalytic hydroxylation of n-octane, 1-hexene and phenol with aqueous H_2O_2.

Catalyst	Si/Ti[a]	Conversion[b] (%) n-octane[c]	1-hexene[d]	phenol[e]	IR peak ratio[f]
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	-
ETS-10	5	0 (0)[g]	0 (0)[g]	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, 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 3.3 Influence of TiO_2 on the activity of TS-1(C) and pure-silica ZSM
phenol hydroxylation.

Catalyst	PhenolConversion (%)[a]
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 3.4 n-Octane oxidation on aluminum and/or sodium containing TS-1.

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

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

[b] TAS-1(D) exchanged with 1 M solution of $NaNO_3$.

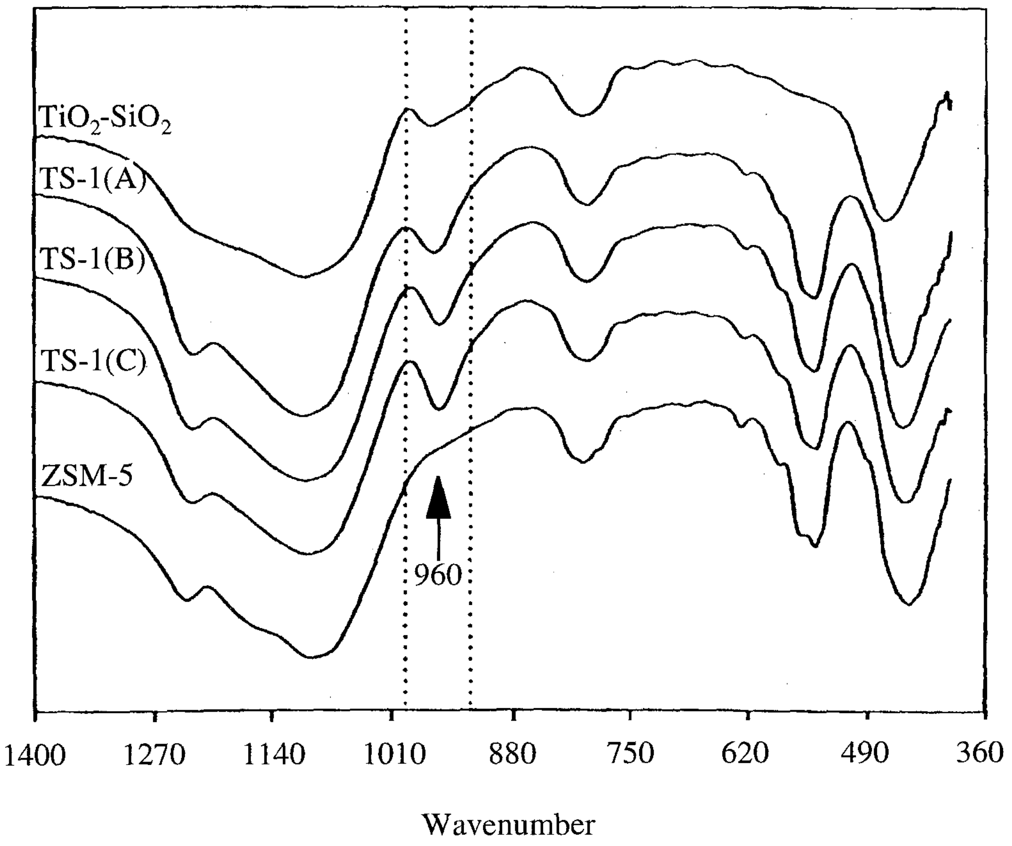

Figure 3.1 Infrared spectra of titanium containing materials and pure-silica ZSM-5.

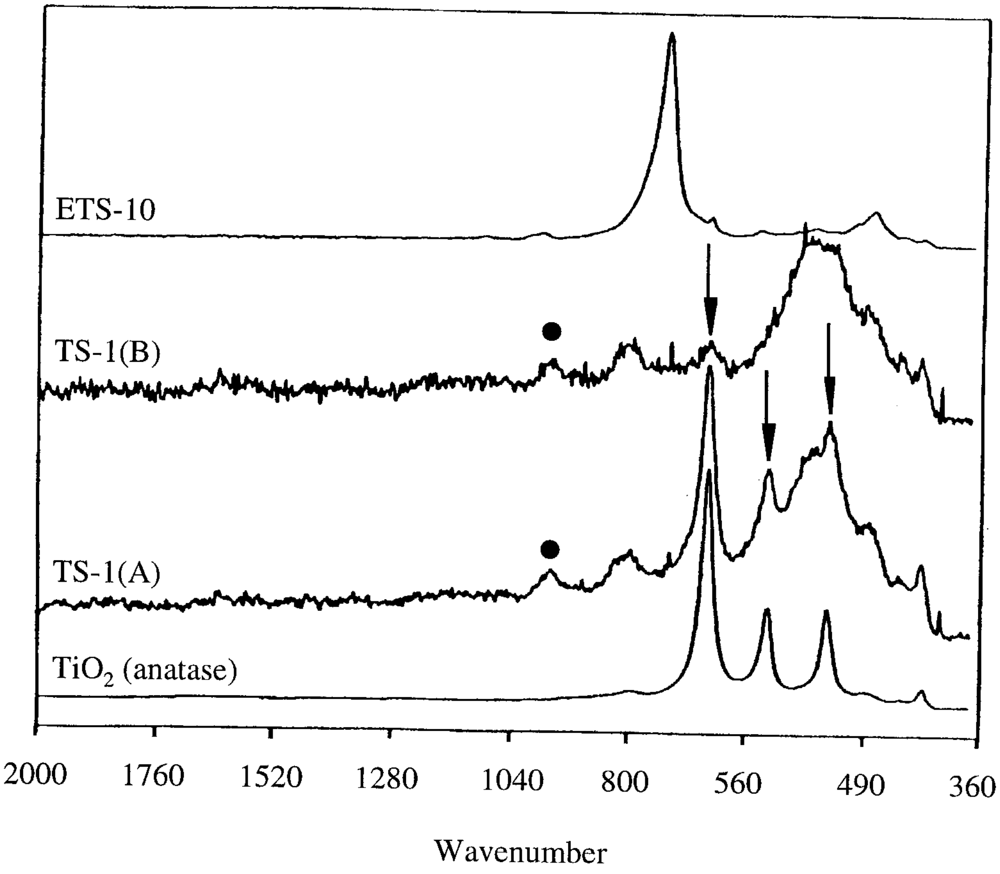

Figure 3.2 Raman spectra of titanium containing materials. Band marked by ● is at 960 cm-1.

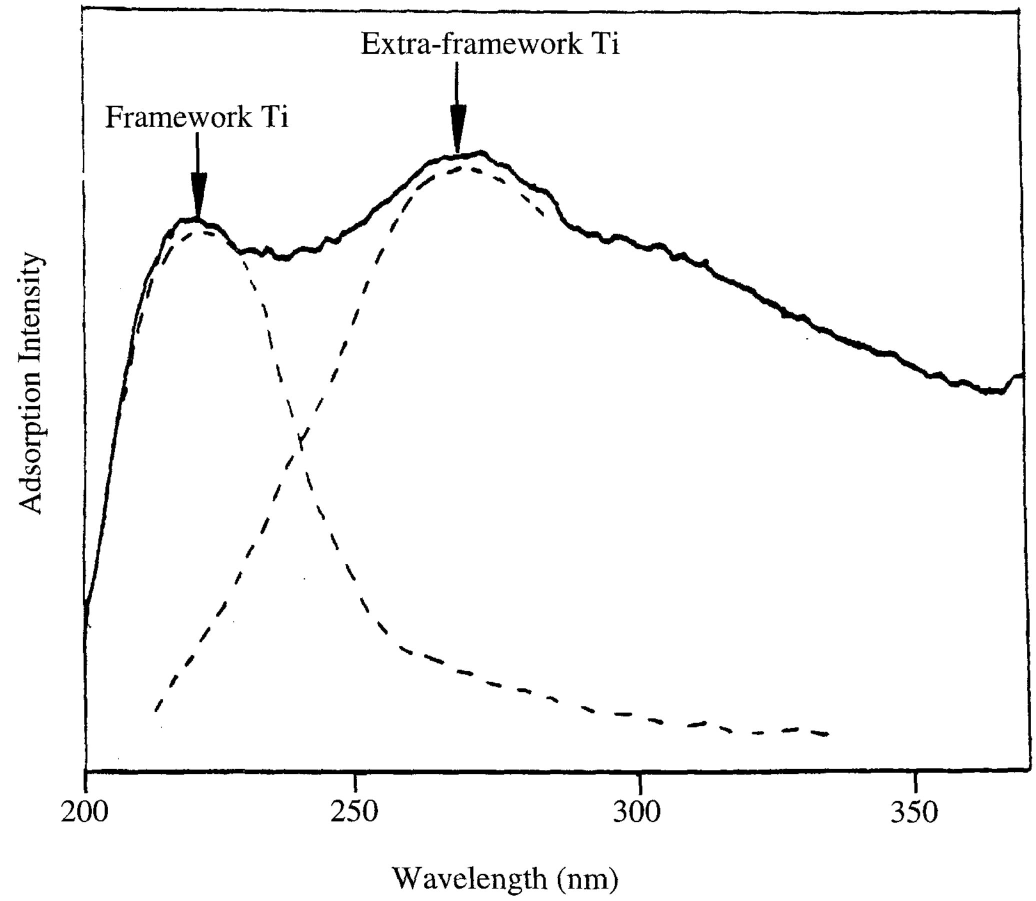

Figure 3.3 UV-visible diffuse reflectance spectra of TS-1(A).

CHAPTER FOUR

Synthesis And Physicochemical Properties Of Zeolites Containing Framework Titanium

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Synthesis And Physicochemical Properties Of Zeolites Containing Framework Titanium

by

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Abstract

Titanium containing pure-silica ZSM-5 (TS-1), pure-silica ZSM-48 (Ti-ZSM-48) and zeolite beta (Ti-Al-beta) are synthesized and characterized by X-ray powder diffraction, elemental analysis, physical adsorption of N_2, FT-IR, FT-Raman, and UV-VIS spectroscopies. TS-1 is synthesized by five different methods. All materials are evaluated for their ability to oxidize 1-hexene and n-octane using aqueous H_2O_2 as the oxidant. The relationships between the physicochemical and catalytic properties of these titanium-containing zeolites are discussed. TS-1 samples synthesized at high pH are catalytically active and framework titanium is shown to be necessary for olefin epoxidation and alkane hydroxylation to occur. The existence of anatase in active TS-1 samples results in decreased hydrogen peroxide efficiencies in the epoxidation reaction. TS-1 produced at pH=7.4 and Ti-ZSM-48 each contain anatase and are not active. Ti-beta is found to contain framework titanium and be free of anatase. However, at the conditions used in this study these samples are not able to activate 1-hexene or n-octane.

4.1 Introduction

Titanium substituted molecular sieves have become one of the most important discoveries in the field of zeolite catalysis. The initial report of TS-1 in 1983 led to a remarkable volume of work devoted to the use of titanium-silicalites as partial oxidation catalysts. The utility of these materials is evident from their ability to catalyze a broad spectrum of oxidation reactions using aqueous hydrogen peroxide as the oxygen source. The list of possible reactants includes alkanes, alkenes, and aromatics. Additionally, all of these reactions are operated at moderate temperatures (< 100°C) and pressures.

In view of increasing environmental regulations, catalytic chemistries involving TS-1 and analogues of it appear especially well situated for future technologies; the by-product from these oxidation reactions is water and total combustion products are not formed. TS-1 is used commercially in Italy for the production of hydroquinone and catechol from phenol [1]. Additionally, the conversion of cyclohexanone into cyclohexanone oxime with TS-1 is operating at pilot-plant scale. The oxime is a valuable intermediate in the production of nylon. Interestingly, this pilot plant (12,000 tons/year) is larger than the commercial phenol plant (10,000 tons/year) [2].

After the synthesis of TS-1, several years elapsed until other titanium containing molecular sieves were synthesized. The next molecular sieve to be synthesized with titanium in the framework was ZSM-11 [3]. This material was designated TS-2 and has the MEL structure that is very similar to that of MFI. Actually, ZSM-11 is an intergrowth of the true MEL structure and the MFI structure. Due to the structural similarities, it is not surprising that TS-1 and TS-2 have similar catalytic properties [4,5].

Recently, two other molecular sieves with framework titanium have been reported, Ti-ZSM-48 and Ti-Al-beta [6,7]. Ti-ZSM-48 differs from TS-1 and TS-2 because it consists of a one-dimensional, 10-ring pore system, rather than a three-dimensional, 10-ring pore system. Ti-ZSM-48 was claimed to have a unit cell expansion with increasing titanium in framework positions. An infrared band at 960 cm^{-1} was present in the titanium material that was absent in the pure-silica analogue. Additionally, the same claim was made for the Raman spectra (960 cm^{-1} band for the titanium containing sample). No reports of catalytic activity were mentioned. For Ti-Al-beta, X-ray powder diffraction and infrared spectroscopy were used to prove that titanium resides in the framework. The advantage of the beta structure over MEL, MFI, and ZSM-48 is the larger pore size (7 Å vs. 5.5Å.) However, the beta sample required the presence of aluminum in order to crystallize. The framework aluminum gives Brønsted acid sites upon calcination. The material was reported to be active for alkane oxidation using aqueous hydrogen peroxide as the oxidant.

The objective of this work is to investigate the structure-property relationships in titanium containing zeolites. The physical properties of titanium containing ZSM-5, ZSM-48, and beta are correlated to their ability to oxidize alkanes with H_2O_2 as the oxidant.

4.2 Experimental Section

4.2.1 Synthesis

Five samples of TS-1, designated TS-1(A) through TS-1(E), were synthesized in this study. Table 4.1 shows the gel compositions for all the syntheses used here. TS-1(A) was synthesized from a clear gel prepared by the dropwise addition of an aqueous solution of tetrapropylammonium hydroxide (TPAOH) (Alfa) to an organic solution containing tetraethylorthotitanate (TEOT) (Alfa) and tetraethylorthosilicate (TEOS) (Aldrich). This preparation was carried out entirely at room temperature. TS-1(B) was prepared by mixing TEOT into the appropriate amount of water with the subsequent addition of aqueous hydrogen peroxide (Janssen Chimica). After several hours of agitation at room temperature, a homogeneous, yellow mixture was obtained. TPAOH was then added and finally colloidal silica (Ludox AS-40) was combined with this solution to give the total reactive slurry. This mixture was stirred overnight before being charged into autoclaves. These first two synthesis procedures closely follow the examples given in the original patent [8]. The third sample, TS-1(C), was prepared as in the preceding example, only fumed silica (Cab-O-Sil M5) is employed as the silica source. TS-1(D) was synthesized using a freshly prepared silica/titania coprecipitate. This solid was added to an aqueous solution of TPAOH and stirred overnight at room temperature. The silica/titania coprecipitate was made by hydrolyzing TEOS in a 0.05 M HCl solution (mass ratio=1:5). Hydrolysis is complete when one phase is obtained. TEOT dissolved in isopropanol (mass ratio=1:10) was then added dropwise. The resulting solution was heated at 90°C until a very thick gel remained. This material was then heated overnight at 110°C to remove the remaining water and alcohols. This solid was then crushed into a fine powder. The coprecipitate was found to be amorphous by X-ray powder diffraction, yet Raman spectroscopy confirmed the presence of anatase. TS-1(E) was prepared by adding a TEOT/isopropanol solution to an aqueous TPAOH solution. Fumed silica was then slowly added. An aqueous HF solution was then added and the entire mixture was heated to 75°C for 2 hours. The thick, milky gel was then charged to an autoclave. The pH of this gel was 7.4.

All the TS-1 reaction mixtures were charged into Teflon-lined autoclaves and allowed to crystallize at 175°C. The first four TS-1 samples (A-D) were removed after 3 days of heating while TS-1(E) was allowed to crystallize for 10 days. The autoclaves were rotated at 50 RPM. After cooling, all these materials were centrifuged and washed with water several times. Calcination to remove occluded organics was conducted at 550°C for 7 hours in an air atmosphere. Two pure-silica ZSM-5 samples were prepared as reference materials for their titanium counterparts. One material was synthesized in the same fashion as TS-1(A) with no titanium being added. This material will be designated Silicalite-1. The second pure-silica ZSM-5 was synthesized in the same manner as TS-1(E) with no titanium being added. This material will be denoted Silicalite-1(HF).

Ti-ZSM-48 was prepared by adding diaminooctane directly to a solution containing the peroxytitanates species (formed from the reaction of TEOT, water, and H_2O_2). Fumed silica was then added slowly and the mixture was allowed to stir overnight at room temperature. This gel was charged into autoclaves as described above, and the crystallization time was 10 days at 175°C. After cooling the autoclaves, the product was collected by filtration, dried, and calcined in air at 600°C for 10 hours. The pure-silica ZSM-48 was prepared in the manner described for Ti-ZSM-48, only no titanium was added to the synthesis medium.

Ti-beta was synthesized by adding a solution of TEOT dissolved in isopropanol to an aqueous solution containing tetraethylammonium hydroxide. Fumed silica was then added with stirring. Finally, a solution of aluminum nitrate dissolved in aqueous TEAOH was added, and the final mixture was stirred for 1 hour at room temperature. The reactive gel was charged to an autoclave, as above, and heated at 135°C for 3 days while being rotated at 50 RPM. The solid product was recovered by centrifugation and then slurried in distilled water. This procedure was repeated until the pH of the solution was less than 9. Calcination was performed in an air atmosphere using a heating rate of 0.75 °C/min to the final temperature of 540 °C and then maintained at this temperature for 4 hours. Two Ti-beta samples were prepared, each with a different Si/Ti ratio. Ti-beta(B) contained twice as much titanium in the gel as did Ti-beta(A). The "parent" material containing no titanium was also prepared following the same procedure.

4.2.2 Analysis and Characterization

Fourier Transform Infrared (FTIR) spectra were obtained using a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) with KBr pellets containing 2.5 wt% sample. Raman spectra were recorded on the Raman accessory to the system described above. A CaF_2 beamsplitter was used for the Raman spectra along with a liquid-nitrogen-cooled germanium detector. X ray powder diffraction (XRD) patterns were collected on a Scintag XDS-2000 diffractometer equipped with a liquid-nitrogen-cooled germanium detector using Cu-Kα radiation. Silicon was used as an internal standard with all samples. Spectra were taken with a step size of 0.02 degrees and with a step time of 15 seconds. Nitrogen adsorption isotherms were collected at 77 K on an Omicron 100 analyzer. All samples were activated by heating to 250°C under vacuum. Diffuse reflectance 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. Light from this lamp was directed upon ca. 10 mg of powdered sample with a fused silica lens fiber optic assembly. The reflected light was detected at a 90^{o} geometry with a second fiber optic assembly that directed the light to the polychrometer before the diode array. The spectra were ratioed to a reference spectrum obtained from powdered MgO. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Scanning electron micrographs were recorded on a CamScan Series 2-LV SEM.

All epoxidation reactions were performed in a 25 mL glass reactor immersed in a constant temperature oil bath using 35% hydrogen peroxide as the oxidant. 2-Butanone was used as the solvent unless otherwise stated and all reactions were conducted for 2 hours at 50°C with vigorous agitation. A typical reaction mixture would contain 100 mg of catalyst, 9.0 mL 2-butanone, 20 mmol olefin, 6.85 mmol H_2O_2, and 0.25 mL mesitylene (as an internal standard). After the reaction, the mixture would be transferred to a flask and the reactor would be washed with 40 mL ethyl acetate. The ethyl acetate was added to the reaction mixture in order to obtain one liquid-phase. The solution was shaken vigorously and 5 mL were removed and transferred to a vial. The vial was spun in a centrifuge to separate the catalyst from the solution. Injections were made into a HP 5890 Series II GC equipped with a 25 m HP-FFAP (polar) capillary column and a flame ionization detector. Products were identified using standards and GC/MS analysis. Hydrogen peroxide conversions were measured by titration with 0.1 N $Ce(SO_4)_2$ using a ferroin indicator.

n-Octane oxidation reactions were performed in a 10 mL glass reactor with 35% aqueous hydrogen peroxide as the oxidant at 80 °C for 6 hours. 2-Butanone was used as the solvent. A typical reaction mixture would contain 20 mg of catalyst, 0.5 mL 2-butanone, 3 mmol n-octane and 3 mmol H_2O_2. The product analysis and the hydrogen peroxide conversions were analyzed following the procedures outlined above.

4.3 Results and Discussion

4.3.1 Characterization

The only phase observed in the XRD patterns of TS-1(A-E) is ZSM-5. Table 4.2 shows the unit cell parameters calculated from the X-ray powder diffraction analysis. The two pure-silica ZSM-5 samples have nearly identical unit cell volumes as expected. However, the unit cell volumes of the first four TS-1 samples (A-D) show a dramatic increase over the volume of pure-silica ZSM-5 indicating the substitution of titanium into the framework. This phenomenon is due to the relatively long length of the Ti-O bond as compared to the Si-O bond. All of the four samples (A-D) have nearly identical unit cell expansions suggesting that equal amounts of Ti have been substituted into each sample. It has been shown that for Si/Ti ratios as low as 39, the correlation between unit cell expansion and framework titanium content is linear [9,10]. TS-1(E), synthesized in the presence of fluoride ions, has the same unit cell volume as its "parent" material that contains no titanium. This indicates that TS-1(E) is not likely to contain framework titanium.

The Ti-ZSM-48 sample synthesized here did not show a significant unit cell expansion relative to the pure-silica analogue. The ZSM-48 structure is difficult to index due to the fact that there are only a small number of peaks, and these peaks are weak and quite broad. However, Serrano et al. have shown that Ti-ZSM-48 can reveal an increasing unit cell expansion with increasing titanium content [6]. The unit cell volume reported for a Ti-ZSM-48 sample with a Si/Ti ratio of 49.5 was 2433 $Å^3$. This is an increase of 17 $Å^3$ over the titanium-free ZSM-48.

Accurate unit cell measurements for zeolite beta samples are difficult to obtain due to the heavily faulted nature of the structure. However, unit cell expansion can be inferred from the shift in d-spacing of the most intense peak in the XRD pattern. This method was used to infer framework siting of titanium in the original paper describing the synthesis and characterization of Ti-beta [7]. Very small shifts were observed, indicating that titanium may be incorporated into the framework. We believe that little faith can be placed in these measurements and that alternative methods should be used to confirm framework siting.

Elemental analyses were performed on all the materials synthesized and the data are presented in Table 4.3. All the samples contain a significant amount of titanium. Large differences in titanium contents are observed among the TS-1 samples. For example, sample D has twice as much titanium as samples A and B. From the unit cell measurements, it appears that TS-1 samples A, B, C, and D have equal amounts of framework titanium. Thus, the elemental analysis implies that samples C and D (with Si/Ti ratios lower than 53) contain extra-framework titanium. The titanium contents of the Ti-ZSM-48 and Ti-beta samples, are similar to the range of compositions found for the TS-1 samples. Notice that the Si/Ti ratios of the two Ti-beta samples are nearly the same even though Ti-beta(B) was synthesized from a gel containing twice as much titanium.

The Si/Al ratios for the zeolite beta samples are also reported in Table 4.3. The samples synthesized with titanium in the gel had significantly less aluminum in the resulting zeolite relative to the sample synthesized in the absence of titanium. From this result it seems reasonable to conclude that titanium is substituting for aluminum in the framework. This is supported by the fact that the slight decrease in Si/Ti ratio of Ti-beta(B) is accompanied by an increase in Si/Al ratio. The same observations and conclusions were first reported by Camblor et al. [11,12].

Nitrogen adsorption isotherms were measured from all samples to determine microporosity. Isotherms from the TS-1 samples are shown in Figure 4.1. As expected, similar isotherms were observed for all samples. Silicalite-1, and TS-1 A, B, and C have essentially identical isotherms while TS-1 samples D and E have capacities lower than the other materials. This is presumably due to the existence of extra-framework material (vide infra) in these samples. The capacity of sample D is only slightly lower than the capacity of the Silicalite-1 sample. However, the capacity of sample E is significantly lower than the Silicalite-1(HF) sample, consistent with the assertion that sample E contains a higher percentage of extra-framework material than sample D (vide infra). The adsorption of nitrogen occurs at the same P/P_0 for all samples with the ZSM-5 structure. This indicates that all these materials have equivalent pore diameters [13]. All extra-framework titanium must, therefore, be located on the surface of the crystals or as separate particles.

Isotherms from the ZSM-48 samples (Figure 4.2) indicate a slightly larger adsorption capacity for the titanium containing material. This is most likely due to residual carbon in the pure-silica material as previously observed by Serrano et al. Full removal of the organic occurs much more readily from Ti-ZSM-48. This observation was also noted previously [6]. The isotherms from the zeolite beta (Figure 4.3) samples show identical final capacities, indicating that large amounts of extra-framework material can not be present in these samples.

Since the first report of TS-1 in 1983, infrared spectroscopy has been employed to characterize titanium-containing zeolites. Figure 4.4 shows the FT-IR spectra of the TS-1 samples. In the 400-1500 cm^{-1} range, one distinct peak is present for the titanium samples that is absent in the pure-silica materials. This band occurs at approximately 960 cm^{-1}. Actually, Silicalite-1 samples produced in the same manner as TS-1(A) without adding titanium have a very weak band at this position but the addition of titanium dramatically enhances it. Only TS-1(E) does not have a distinct band at 960 cm^{-1}. In fact, the infrared spectrum from TS-1(E) is exactly the same as Silicalite-1(HF). The intensity of the 960 cm^{-1} band has been shown to correlate with the increase in unit cell volume and has thus been associated with the incorporation of titanium into the framework [10,14]. If this is true, the infrared spectra shown here lead to the conclusion that samples A-D have framework titanium while sample E may not. However, some studies reveal that this band is more likely due to a Si-O vibration [15,16]. Here, the ratios of the area of the peak at 960 cm^{-1} to the peak at 800 cm^{-1} are 1.50, 1.05, 1.15, and 1.12 for TS-1 samples A, B, C, and D, respectively. These values do not correlate with the unit cell volumes and this result suggests that the relationship may only hold for materials prepared in the same fashion. Huybrechts et al. have suggested that the 960 cm^{-1} band is a necessary, but not sufficient condition for catalytic activity [17]. Below we confirm this suggestion.

Like TS-1, a 960 cm^{-1} band is observed in the Ti-ZSM-48 sample (Figure 4.5) that is absent in pure-silica ZSM-48. Additionally, the Ti-beta samples show a band in the same region (Figure 4.5). However, the beta sample containing no titanium also reveals this band. We have observed this band in dealuminated zeolite beta samples as well. Thus this vibration can not be conclusively used to assign framework siting of titanium in zeolite beta. Interestingly, Camblor et al. reported that their non-titanium containing beta sample did not have a 960 cm^{-1} band.

The methods discussed to this point have provided indications of titanium framework substitution but have not addressed the problem of extra-framework titanium. Here, Raman spectroscopy is used to probe the existence of anatase in these samples. Figure 4.6 shows the Raman spectra of the TS-1 samples. Anatase has very strong Raman bands that are discernible at low concentrations. These bands occur at 386, 513, and 637 cm^{-1} in the region studied. As can be seen from the spectra for the TS-1 materials, samples A-D possess a band at approximately 960 cm^{-1}. This band is not present in Silicalite-1. As with the infrared spectra, this band has been taken as evidence of titanium incorporation into the framework [14]. Deo et al. have reviewed the Raman bands associated with various titanium compounds and conclude that the 960 cm^{-1} band does not provide direct structural informational of the titania species [18]. Instead, this band was assigned to the vibration of two non-bridging oxygens bonded to a single silicon. In sample D, the 960 cm^{-1} band is present along with peaks indicative of anatase. Thus, sample D contains both framework and extra-framework titanium. This is expected since anatase is present in the coprecipitate that was used for the synthesis of TS-1(D). In sample E, the 960 cm^{-1} band is not observed while the bands corresponding to anatase are quite intense. This result further supports the conclusion that the titanium in sample E is present only as anatase.

For Ti-ZSM-48, only Raman bands from anatase are observed in addition to those from pure-silica ZSM-48; no 960 cm^{-1} band is present (Figure 4.7). Thus, Ti-ZSM-48 is different from TS-1 in that all the samples that contained the 960 cm^{-1} IR band also contained the 960 cm^{-1} Raman band. The 960 cm^{-1} band is observed in the IR but not the Raman for Ti-ZSM-48. The presence of anatase peaks in the Raman spectrum, however, indicate that some (if not all) of the titanium is located outside the framework. From the FT-IR spectra, the zeolite beta samples have the 960 cm^{-1} band present in both the titanium and non-titanium materials. While this band is more intense in the titanium containing samples, the fact that the non-titanium containing sample contains the band prohibits one from assigning this band to any effect from the titanium in the beta samples. Ti-beta(A) shows one Raman band indicative of anatase while the sample containing more titanium, Ti-beta(B), is free of this band. Thus, sample A contains a small amount of anatase.

In addition to Raman spectroscopy, diffuse-reflectance ultraviolet (DR-UV) spectroscopy has been used to probe the existence of framework and non-framework titanium [14-16,19]. The DR-UV spectra for the TS-1 samples are shown in Figure 4.8. The band at 220 nm has been assigned to isolated framework titanium in tetrahedral coordination [16]. The broad shoulder between 270 and 350 nm has been attributed to anatase [16]. TS-1(E) clearly shows the characteristic signal for anatase. TS-1 samples B, C, and D show the framework titanium band at 220 nm along with the anatase band of varying intensities. The broad shoulder for anatase appears most intense for sample D suggesting that this sample has more extra-framework titanium than samples B and C. The anatase band for samples B and C is weak compared to the 220 nm band. The amount of anatase is presumably quite small and is not observed by Raman spectroscopy in the spectral region of greater than 200 cm^{-1}. From the DR-UV evidence, TS-1(A) appears to be the only TS-1 sample free of extra-framework titanium; the spectrum contains only the band at 220 nm indicating all the titanium is in the zeolite framework.

The Ti-ZSM-48 sample shows the broad signature of anatase in the DR-UV spectrum (Figure 4.9). The DR-UV spectra of the Ti-beta samples indicate that anatase is not present in these samples. The strong peak for framework titanium at 220 nm is observed for both Ti-beta samples. A very weak shoulder at 270 nm can be seen in both spectra. Because the "parent" beta sample (containing no titanium) does not show any peaks in its DR-UV spectrum, the shoulder at 270 nm is most likely due to an electronic transition localized on a different type of titanium site. The intensity of this shoulder is quite low, and it is reasonable to suspect that the number density of this type of site is much lower than that of the framework titanium.

In summary, the physicochemical properties of several titanium molecular sieves have been investigated. The TS-1 samples have similar amounts of framework titanium from powder X-ray diffraction data. Raman spectroscopy shows the existence of anatase in TS-1 samples D and E while diffuse reflectance UV spectroscopy provides indications that anatase is also present in samples B and C. Sample E contains no framework titanium. Large differences in particle size and morphology are observed between TS-1(A) and the other TS-1 samples (Figure 4.10). The Ti-ZSM-48 material synthesized here does not appear to contain framework titanium after calcination. Anatase is detected by both Raman and DR-UV spectroscopies in Ti-ZSM-48 but not in Ti-beta. Ti-beta samples are difficult to analyze for framework titanium using IR and Raman spectroscopies because the 960 cm^{-1} band is present in the titanium-free sample. However, the DR-UV spectra contain the 220 nm peak from isolated, titanium (IV) in tetrahedral coordination indicating framework siting of titanium.

Figure 4.10 shows scanning electron micrographs of the titanium zeolites synthesized here. All TS-1 syntheses produced homogeneous batches of crystals, with the exception of sample D. Sample A is the smallest of all TS-1 synthesis products and is composed of single, nearly cubic crystallites. Samples B and C consist of twinned crystallites of approximately 3-4μ. Sample D has crystallites from 1 to 5μ, with both single and twinned morphologies. Sample E is comprised of long needle-like crystals. Ti-ZSM-48 is made up of 6μ spheres, that are in turn made of very small needles. All zeolite beta samples synthesized here are composed of very small (1μ), homogeneous crystallites. No differences in size or morphology were observed between zeolite beta samples.

4.3.2 Catalytic tests

All materials were tested for their ability to epoxidize 1-hexene and hydroxylate n-octane. The catalytic results from these reactions are shown in Table 4.4. For the epoxidation reaction, only the epoxide was formed. Conditions were such that overall conversions were low. This was purposefully done to ensure that the reactions were not H_2O_2 limited. For all of the catalysts tested, significant amounts of hydrogen peroxide remained after the reactions were terminated. With n-octane activation, 2 and 3 alcohols and ketones were produced. The most striking result from the catalytic data is that TS-1(E), Ti-ZSM-48, and Ti-beta are inactive for both hydrocarbon oxidation reactions at the conditions used in this study. The results from TS-1(E), and Ti-ZSM-48 are expected since anatase itself is not active for these reactions [20] and no framework titanium is present in these samples. However, the Ti-beta samples did not show evidence of appreciable amounts of extra-framework titanium. Thus, the lack of catalytic ability is surprising and may be due to the hydrophilic nature of the beta structure. From thermogravitametric studies on these materials, it was found that all the beta samples lose ≈20 wt% water, while the TS-1 samples lose only 4 wt % water. Pure-silica materials are well-known to be hydrophobic while alumino-silicates are generally hydrophilic. In other titanium-catalyzed systems, water is known to inhibit catalytic ability. For example, the well-known Sharpless homogeneous epoxidation catalysts do not function if water is present, even in small amounts [21]. In order to test this hypothesis, we used non-aqueous H_2O_2 as oxidant for both the n-octane and 1-hexene reactions. The catalysts were dried at 175°C for 8 hours before the tests. No activity was observed indicating that water is not the cause of the inactivity. At this time we are at a loss to explain why our samples of Ti-beta are not active oxidation catalysts.

Despite the lack of activity in the four samples mentioned above, TS-1 A, B, C, and D showed excellent activity for both the 1-hexene and n-octane oxidation. As shown in Table 4.4, the differences in the n-octane conversion between samples A through D are quite small. For all cases only small amounts of hydrogen peroxide were found when the reaction was stopped. These reactions were most likely peroxide limited and thus the similar substrate conversions are not surprising. However, notice that framework titanium is necessary for the alkane activation to proceed (TS-1(A-D) vs. TS-1(E)). The 1-hexene reaction data show more interesting behavior. Sample A is the most active for epoxidation. We believe that TS-1(A-D) all contain approximately the same amount of framework titanium from the unit cell volumes. Thus, the increase in activity for TS-1(A) over the other TS-1 samples is likely due to the smaller crystal size of TS-1(A). In addition to revealing the highest substrate conversion, sample A also gives the highest hydrogen peroxide efficiency. From the DR-UV spectra, sample A is the only catalyst free of extra-framework titanium. The small amounts of anatase in samples B, C, and D most likely convert H_2O_2 to water and O_2 and diminish the H_2O_2 efficiency since anatase is known to decompose H_2O_2 faster than framework titanium [14]. Thus, it is conclusively demonstrated that framework titanium is responsible for the selective epoxidation of olefins.

Acknowledgments

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Table 4.1 Gel compositions (mole ratios) used for the synthesis of molecular sieves.

Sample	Si/Ti	Si/Al	R/Si[a]	H_2O/Si	H_2O_2/Ti	iPrOH/Ti	Si/F^-
TS-1(A)	33.3	-	0.44	30	-	-	-
TS-1(B)	33.3	-	0.44	30	10	-	-
TS-1(C)	33.3	-	0.44	30	10	-	-
TS-1(D)	30.7	-	0.44	30	-	-	-
TS-1(E)	33.3	-	0.44	50	-	25	2
Silicalite-1	-	-	0.44	30	-	-	-
Silicalite-1(HF)	-	-	0.44	50	-	-	2
Ti-ZSM-48	33.3	-	0.44	65	16.7	-	-
ZSM-48	-	-	0.44	65	-	-	-
Ti-beta(A)	33.3	194	0.57	16	-	20	-
Ti-beta(B)	16.7	194	0.57	16	-	10	-
beta	-	194	0.57	16	-	-	-

[a] R = the appropriate structure-directing agent

Table 4.2 Unit cell data of titanium molecular sieves.

Sample	Sym.[a]	a [Å]	b [Å]	c [Å]	Volume [Å^3]
Silicalite-1	O	19.885(4)	20.087(2)	13.374(2)	5341.7
Silicalite-1 (HF)	M	19.878(2)	20.197(3)	13.367(2)	5339.7
TS-1(A)	O	19.912(4)	20.096(3)	13.398(2)	5361.3
TS-1(B)	O	19.914(4)	20.102(3)	13.395(3)	5361.9
TS-1(C)	O	19.919(3)	20.096(2)	13.398(2)	5362.9
TS-1(D)	O	19.917(3)	20.102(2)	13.396(2)	5363.5
TS-1(E)	M	19.883(3)	20.105(4)	13.358(7)	5339.6
ZSM-48	O	8.386(2)	14.279(7)	20.09(1)	2406.3
Ti-ZSM-48	O	8.3758(3)	14.2929(1)	20.143(2)	2411.4

[a] O = orthorhombic; M = monoclinic

Table 4.3 Molar ratios of solids determined from elemental analyses.

	<--------------TS-1 Samples ----------->						<------Beta Samples------>	
	A	B	C	D	E	Ti-ZSM-48	beta	A	B
Si/Ti	53.5	53.4	38.3	28.2	49.1	38.4	-	48.7	42.0
Si/Al	-	-	-	-	-	-	24.3	40.9	42.6

Table 4.4 Reaction data from titanium molecular sieves.

Sample	Particle Size [μ][a]	1-Hexene Conversion [%][b]	H_2O_2 Efficiency [%][c]	n-Octane Conversion [%][d]
TS-1(A)	0.2	8.5	75.6	20.2
TS-1(B)	4	6.3	67.0	21.7
TS-1(C)	5	7.2	62.1	20.4
TS-1(D)	1-5	6.0	61.9	21.2
TS-1(E)	10 x 50	0.3	56.2	3.7
Ti-ZSM-48	4-6	≈ 0	-	≈ 0
Ti-Beta(A)	0.1	≈ 0	-	≈ 0
Ti-Beta(B)	0.1	≈ 0	-	≈ 0

[a] Particle size determined by SEM

[b] Reaction conditions: 100 mg catalyst, 20 mmol 1-hexene, 6.85 mmol H_2O_2 (35% in H_2O, stabilized), 9 ml 2-butanone, stirred at 50°C for 2 hr.

[c] H_2O_2 Efficiency (for 1-hexene experiments) =
moles epoxide formed / moles H_2O_2 consumed

[d] Reaction conditions: 20 mg catalyst, 3 mmol n-octane, 3 mmol H_2O_2 (35% in H_2O, stabilized), 0.5 ml 2-butanone, stirred at 80°C for 6 hr.

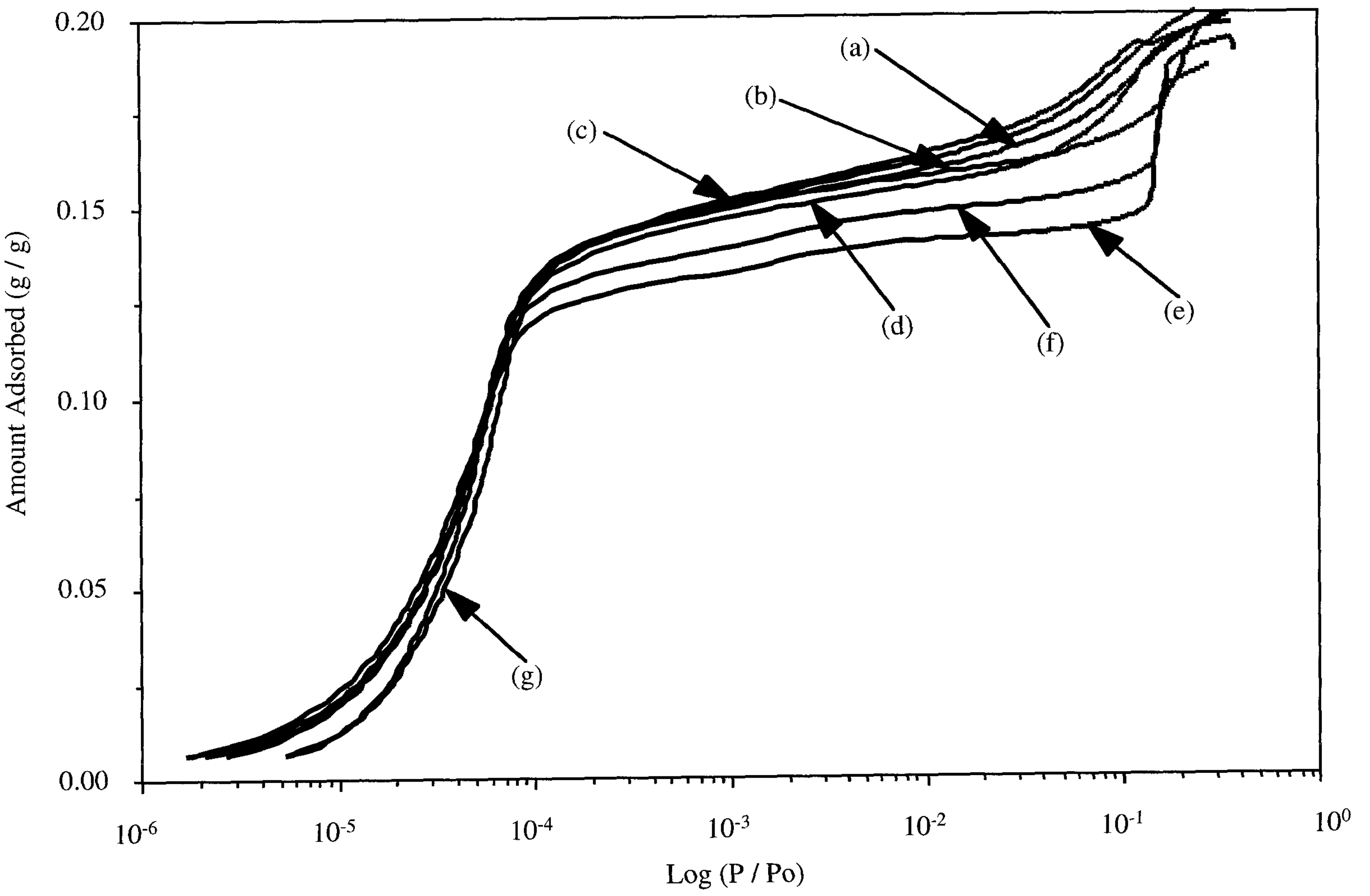

Figure 4.1 Nitrogen adsorption isotherms of TS-1(A) (a); TS-1(B) (b); TS-1(C) (c); TS-1(D) (d); TS-1(E) (e); Silicalite-1(HF) (f); Silicalite-1 (g).

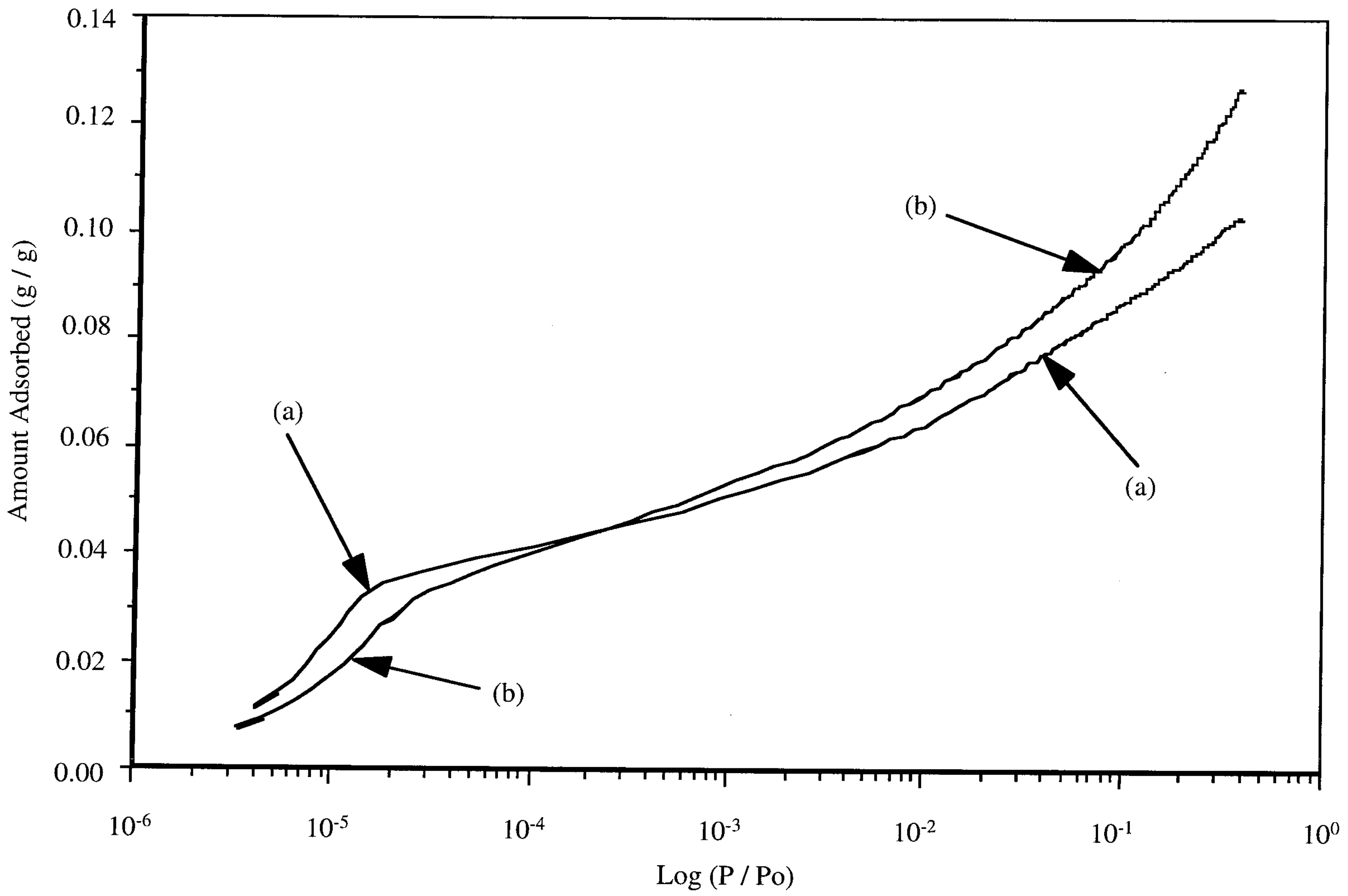

Figure 4.2 Nitrogen adsorption isotherms of ZSM-48 (a); Ti-ZSM-48 (b).

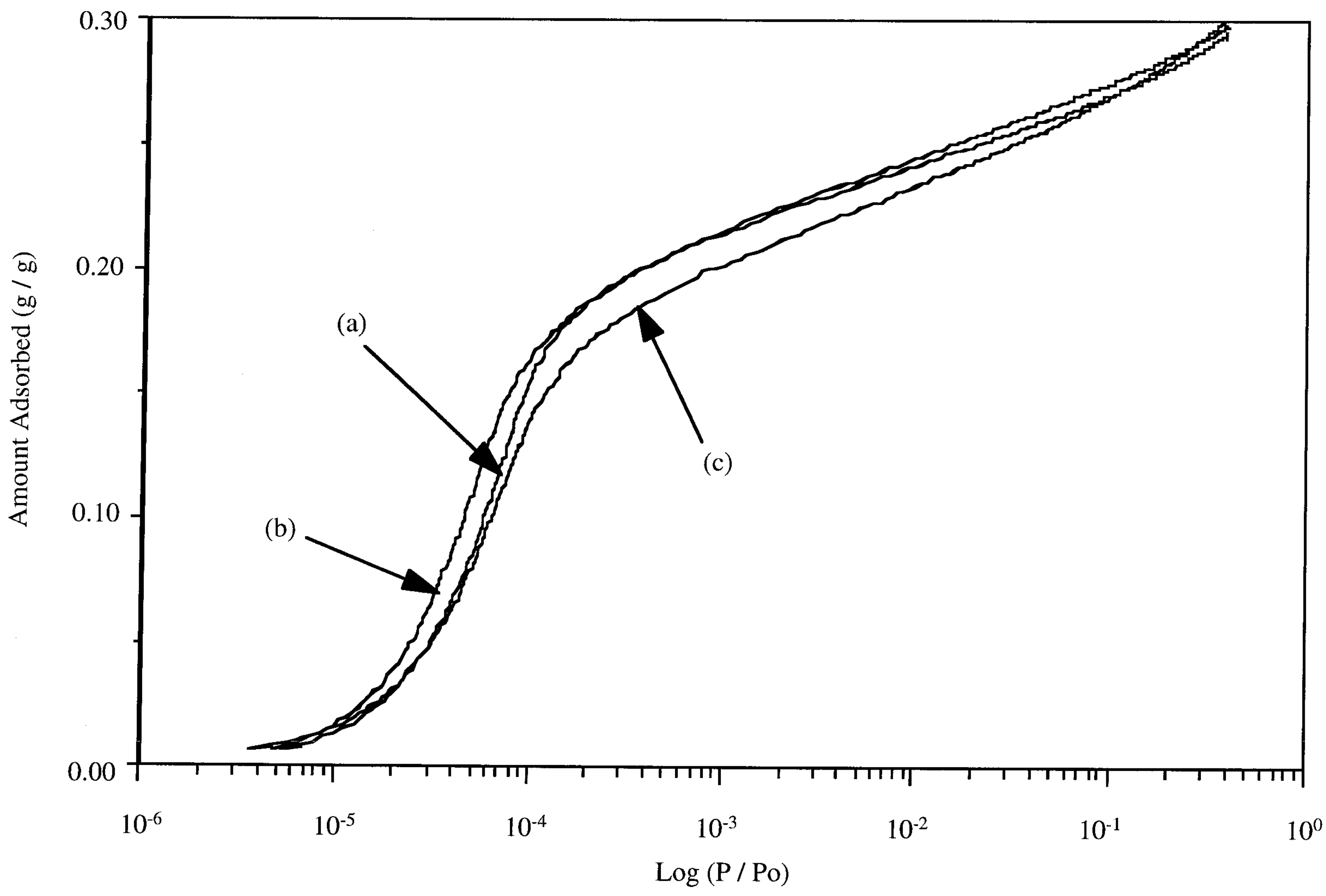

Figure 4.3 Nitrogen adsorption isotherms of zeolite beta (a); Ti-beta(A) (b); Ti-beta(B) (c).

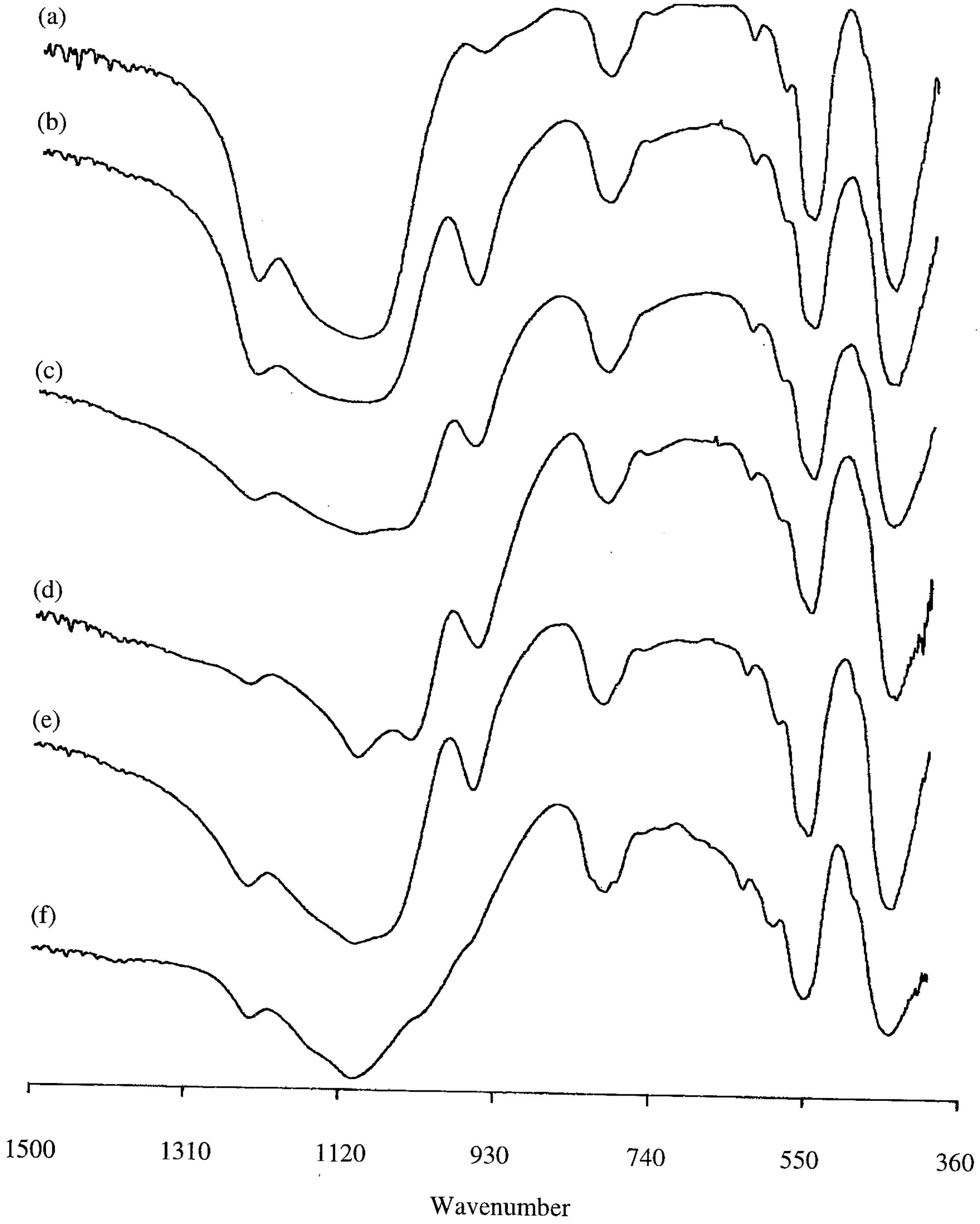

Figure 4.4 Infrared spectra of Silicalite-1(a); TS-1(A) (b); TS-1(B) (c); TS-1(C) (d); TS-1(D) (e); TS-1(E) (f).

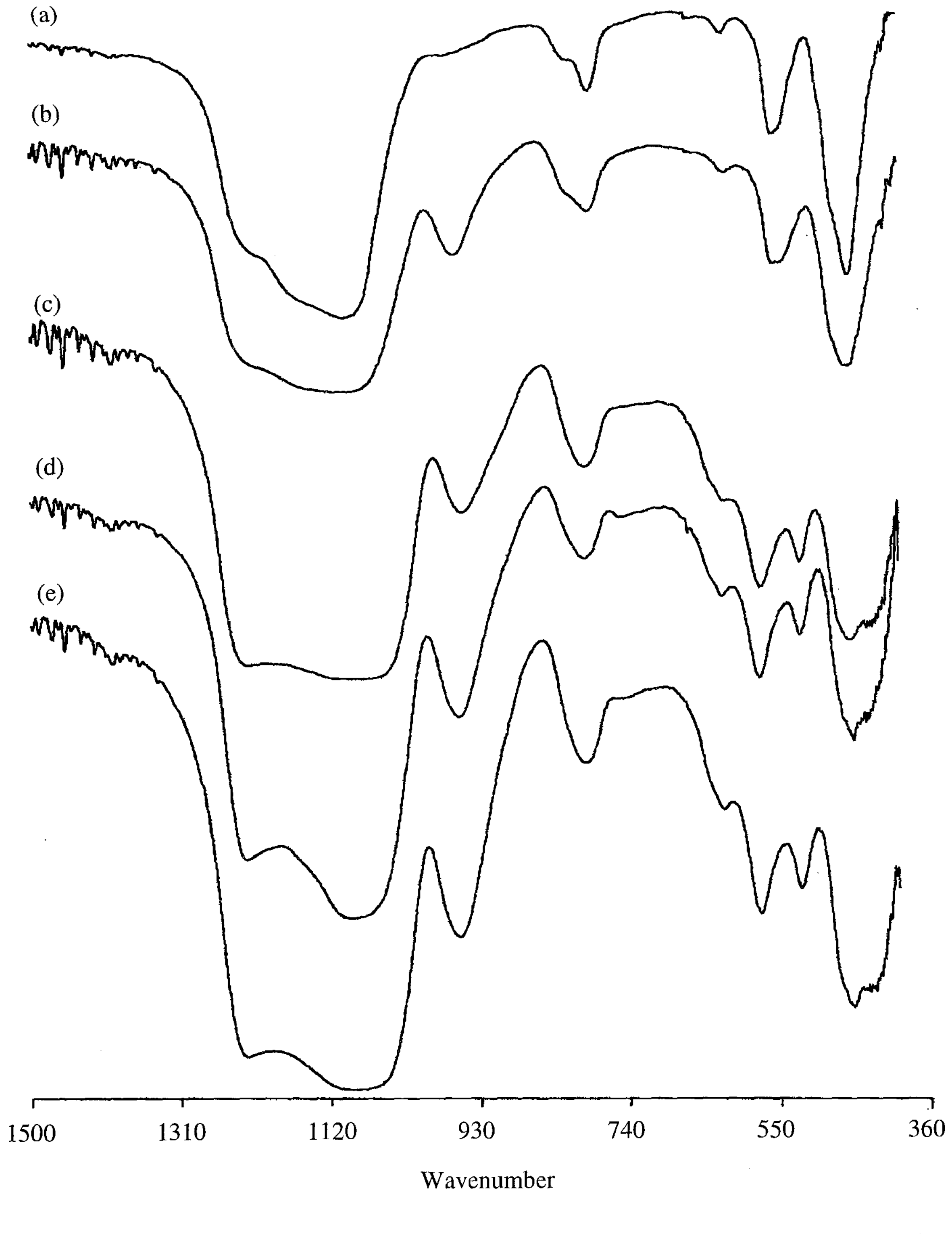

Figure 4.5 Infrared spectra of ZSM-48 (a); Ti-ZSM-48 (b); beta (c); Ti-beta(A) (d); Ti-beta(B) (e).

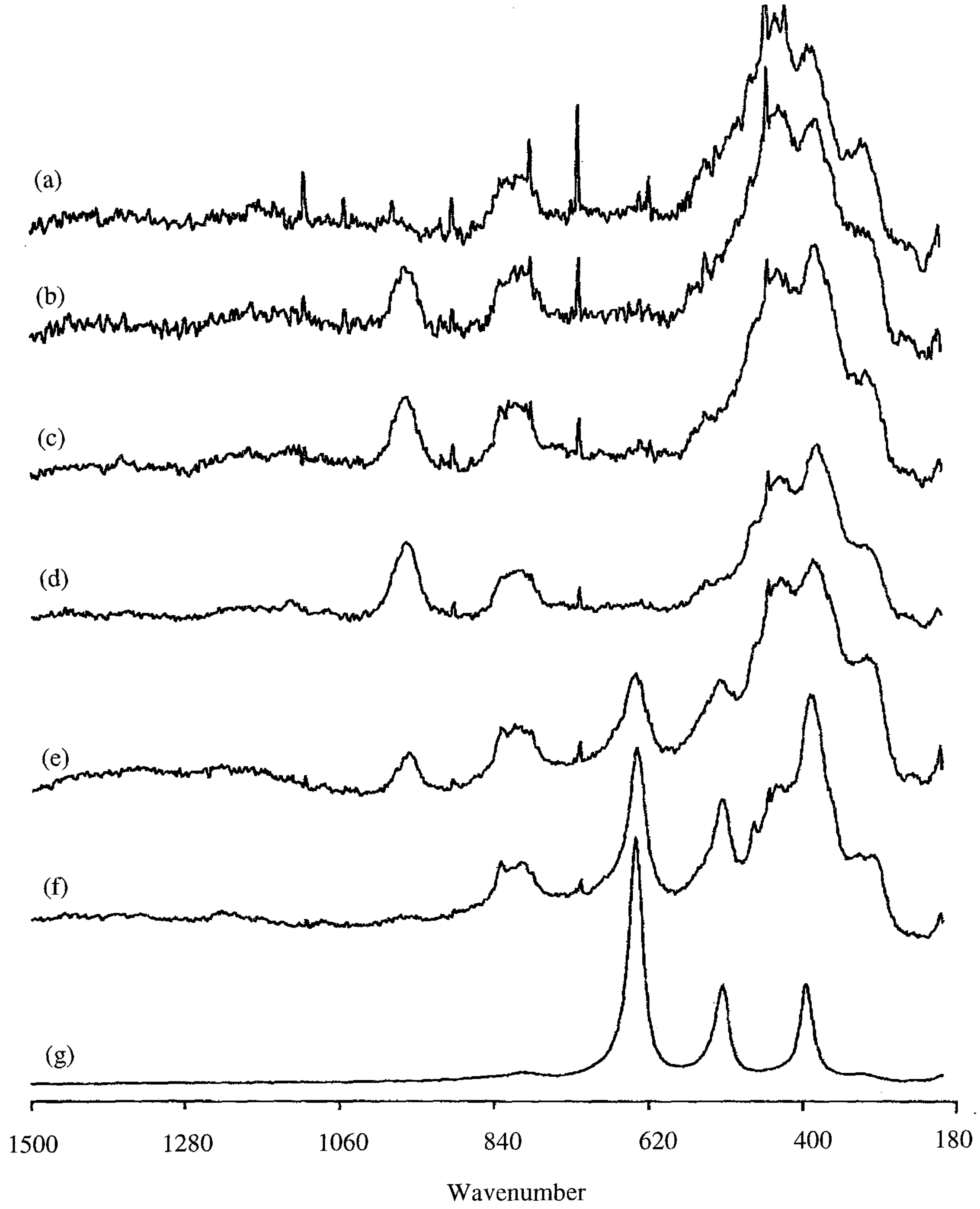

Figure 4.6 Raman spectra of Silicalite-1(a); TS-1(A) (b); TS-1(B) (c); TS-1(C) (d); TS-1(D) (e); TS-1(E) (f); anatase (g).

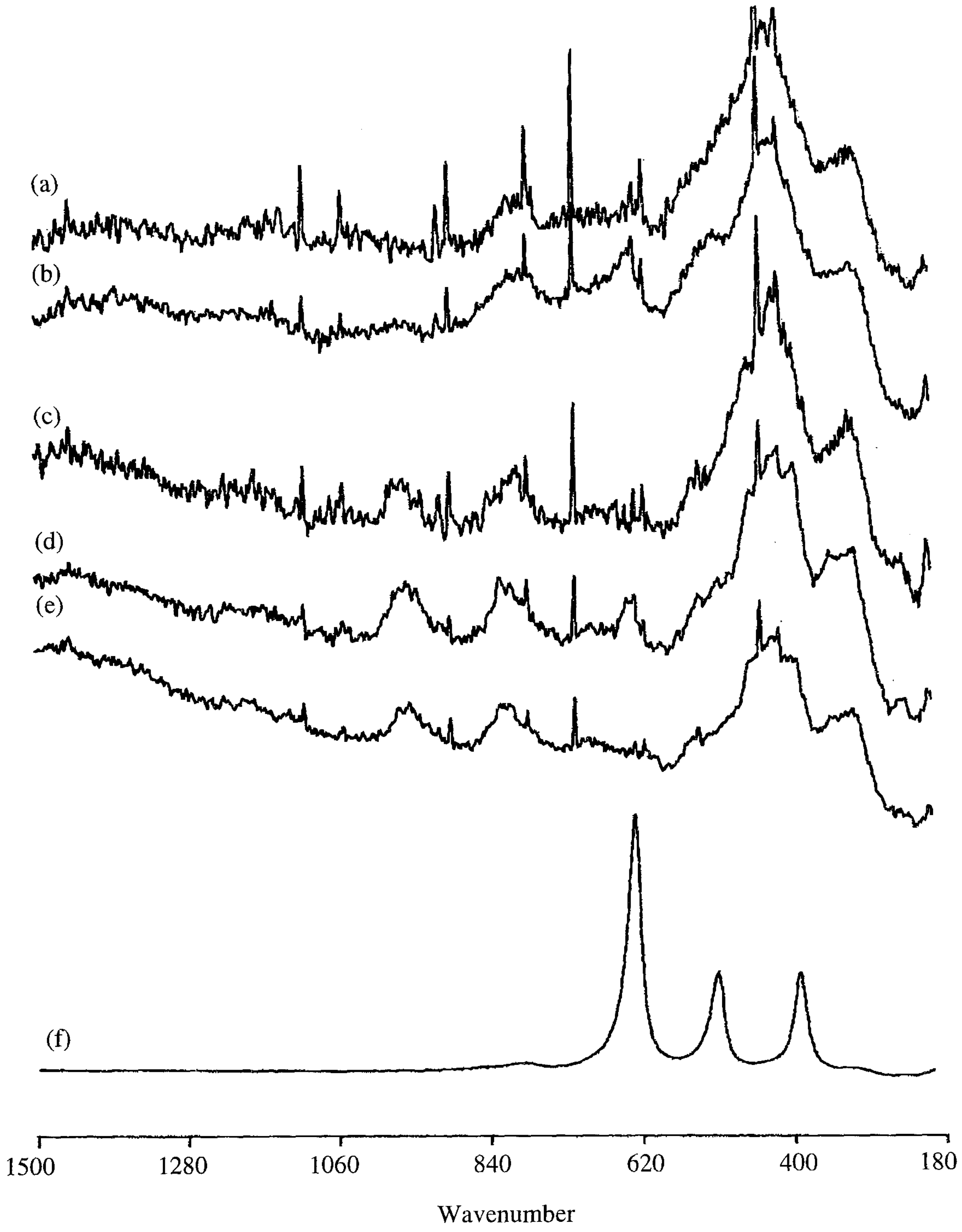

Figure 4.7 Raman spectra of ZSM-48 (a); Ti-ZSM-48 (b); beta (c); Ti-beta(A) (d); Ti-beta(B) (e); anatase(f).

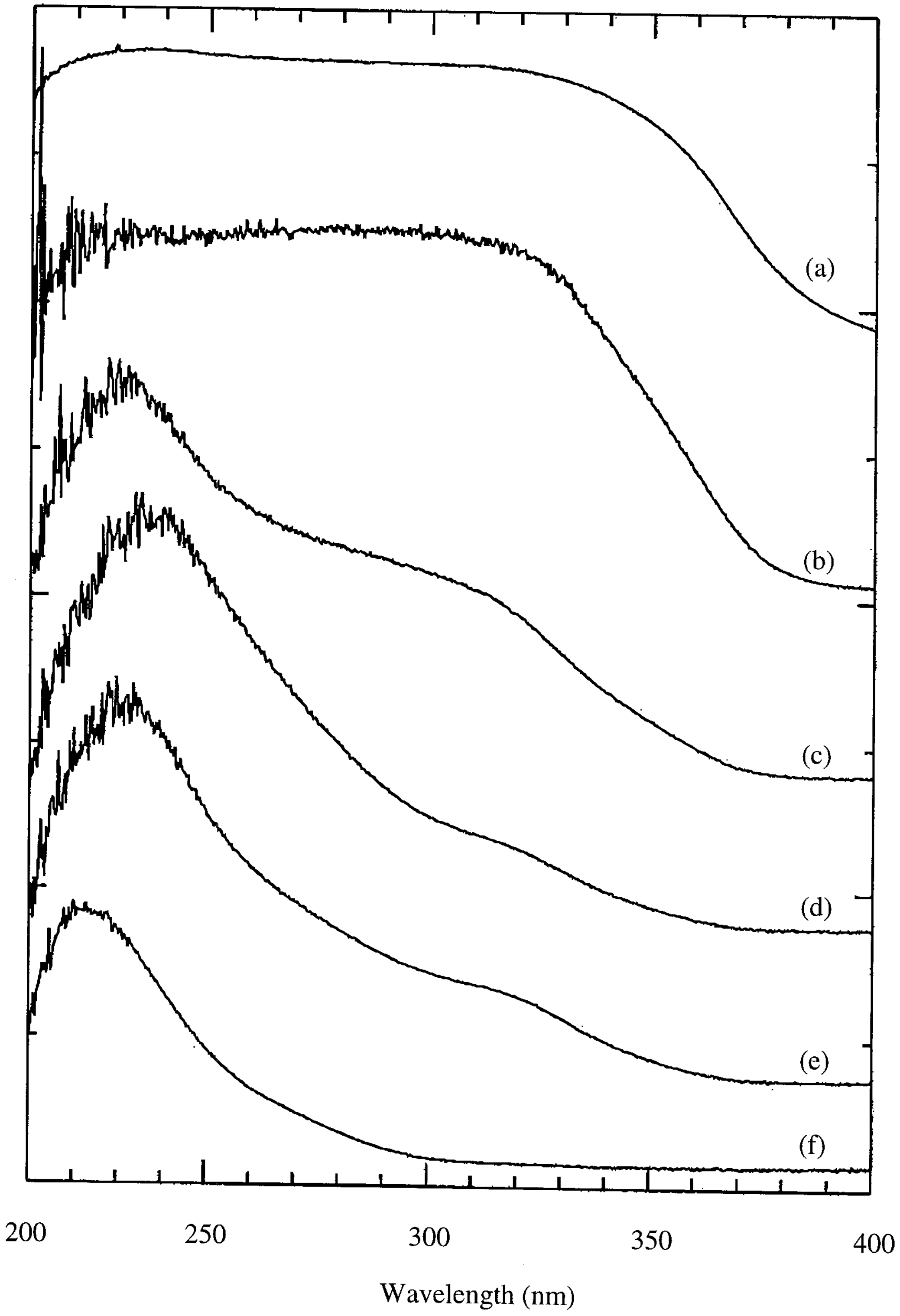

Figure 4.8 Diffuse-reflectance ultraviolet spectra of anatase (a); TS-1(E) (b); TS-1(D) (c); TS-1(C) (d); TS-1(B) (e); TS-1(A) (f).

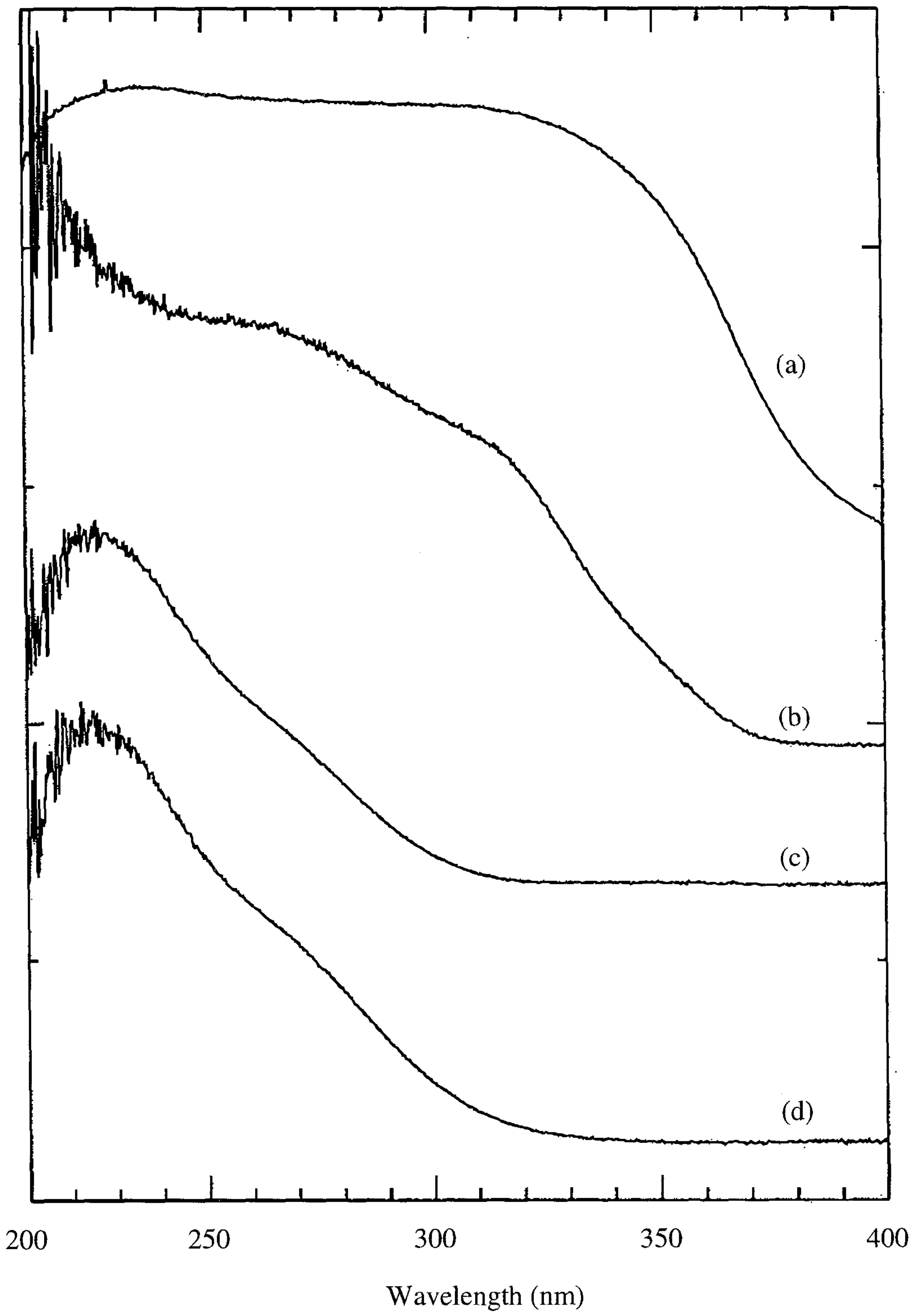

Figure 4.9 Diffuse-reflectance ultraviolet spectra of anatase (a); Ti-ZSM-48 (b); Ti-beta(A) (c); Ti-beta(B) (d).

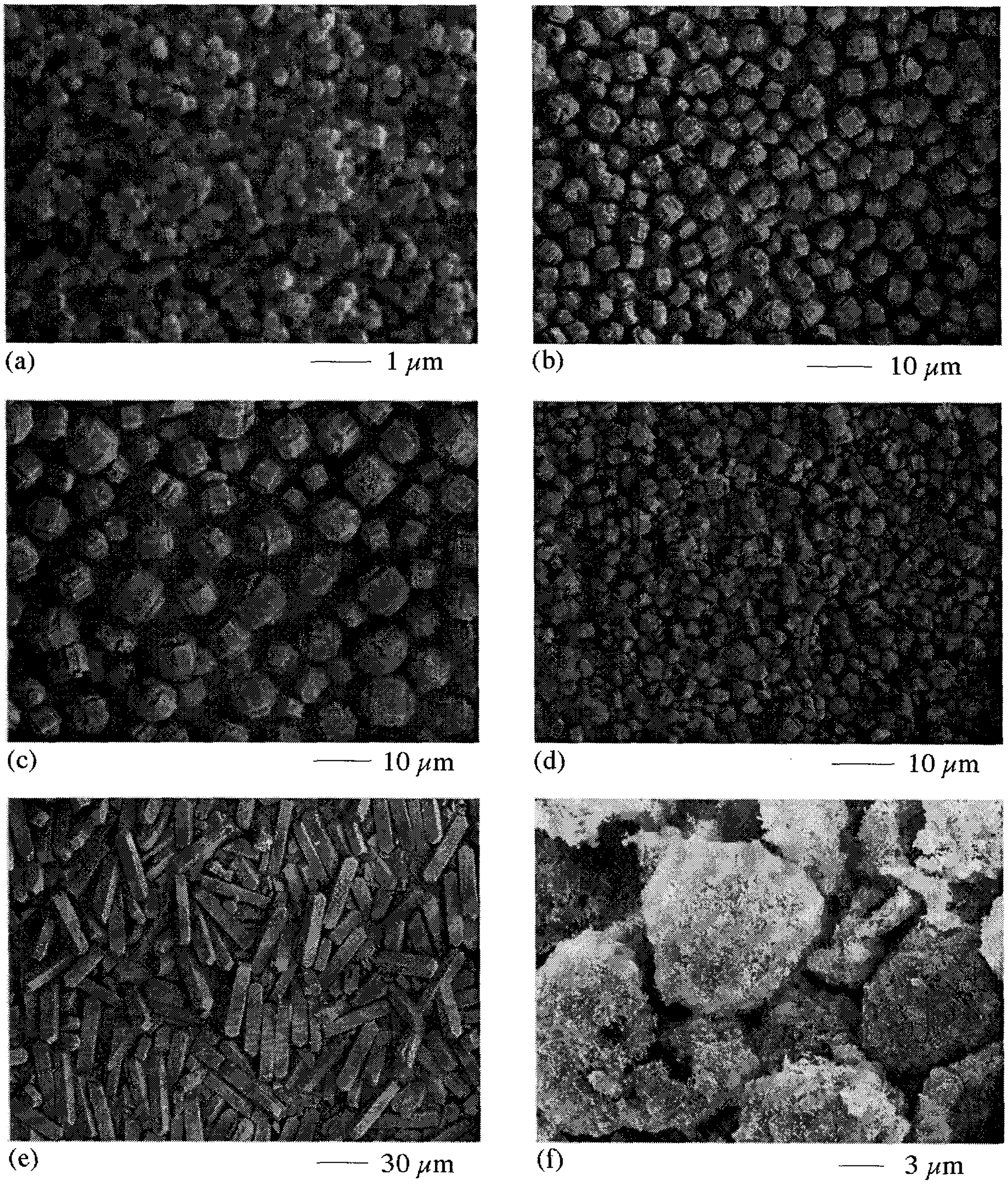

Figure 4.10. Scanning electron micrographs of TS-1(A) (a); TS-1(B) (b); TS-1(C) (c); TS-1(D) (d); TS-1(E) (e); Ti-ZSM-48 (f).

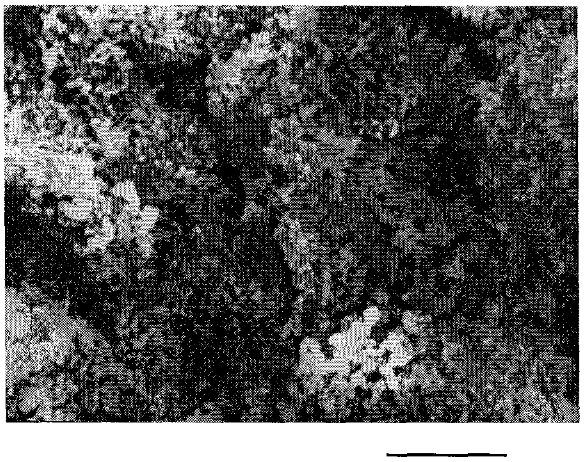

Figure 4.10 (continued) Scanning electron micrograph of Ti-Beta (A).

CHAPTER FIVE

Characterization And Catalytic Activity of Titanium Containing SSZ-33 and Aluminum-Free Zeolite Beta

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Characterization And Catalytic Activity of Titanium Containing SSZ-33 and Aluminum-Free Zeolite Beta

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Abstract

The post-synthetic incorporation of titanium in the borosilicate SSZ-33 and the direct synthesis of an aluminum-free titanium-containing zeolite Beta (Ti-Beta) are reported. These materials are characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), FT-Raman, and diffuse reflectance ultraviolet (DR-UV) spectroscopies. The molecular sieves are shown to catalyze the epoxidation of various olefins using aqueous hydrogen peroxide as the oxidant. The physicochemical properties as found by the characterization methods are correlated to the catalytic data and the results compared to a high quality sample of TS-1. The modified SSZ-33 samples contain titanium primarily in the form of isolated tetrahedrally coordinated Ti atoms, although some extra-framework Ti is observed by Raman and DR-UV spectroscopies. Ti-Beta samples show no evidence of extra-framework titanium. For the epoxidation of cis-cyclooctene, the Ti-Beta catalysts give quantitative conversion to epoxide, and both the Ti-Beta and Ti-SSZ-33 catalysts are able to epoxidize substrates too large to be oxidized by TS-1.

5.1 Introduction

The catalytic oxidation of hydrocarbons is an industrially important process for both the bulk and fine chemical industries. While many industrially practiced oxidations are performed using homogeneous catalysts, several oxidation reactions employing solid catalysts have proven to be quite useful. Two examples of selective partial oxidation by solid catalysts are the Shell propylene epoxidation catalyst (an amorphous TiO_2/SiO_2) [1] and the silver supported on alumina catalysts for ethylene epoxidation [2]. The synthesis of titanium-containing Silicalite-1 (denoted TS-1) by researchers at Enichem ushered molecular sieve technology into the area of oxidation chemistry. The discovery that TS-1 was active for a wide variety of partial oxidations of small organic molecules has initiated a new field of zeolite catalysis.

The utility of TS-1 for oxidation reactions is significant for at least two reasons: 1) TS-1 is active for a broad spectrum of partial oxidation reactions including hydroxylation, epoxidation, ammoxidation, and aromatic oxidation, and 2) aqueous hydrogen peroxide is used as the oxidant. Although relatively expensive, hydrogen peroxide is attractive due to the fact that its by-product is water. It is expected that future regulations will force industrial processes to become more environmentally benign, and for oxidation chemistries the choice of oxidant plays an important role in determining the environmental impact of the process. TS-1 is currently used by Enichem for the production of hydroquinoine and catechol from phenol [3] and for the synthesis of cyclohexanone oxime from cyclohexanone [4].

TS-1 has proven to be quite active in the oxidation of a number of different substrates [5-9]. More importantly, the efficiency of the hydrogen peroxide (defined here as the total moles of oxidized product divided by the total moles of H_2O_2 consumed during the reaction) is nearly quantitative when the reaction conditions are optimized [10]. These results have been shown to arise from the fact that the titanium atoms in TS-1 are located in lattice positions where the second coordination shell is entirely silicon, and not in the form of TiO_2 clusters [6]. While the catalytic achievements of TS-1 are quite impressive, TS-1 does possess several limitations. The void volume of TS-1 is comprised of intersecting pores composed of ten tetrahedral atoms bonded through oxygens (10 membered rings or 10MR) with a diameter of approximately 5.5 Å. Therefore, substrates composed of highly branched hydrocarbons or multicyclic ring systems are excluded from use.

Subsequent to the discovery of TS-1, other structures have been synthesized with titanium occupying framework positions. Some of these structures have pores equal to or smaller than TS-1 and show no real advantage over TS-1 from a catalytic standpoint. These materials (Ti-ZSM-48 [11,12], Ti-ZSM-11 [13,14]) are nonetheless important because they demonstrate that the syntheses of other crystalline titanosilicates are feasible. In 1992, Camblor et al. [15,16] synthesized zeolite Beta with both titanium and aluminum in the framework (Ti,Al-Beta). This structure contains intersecting 12MR pores. The pore diameter of zeolite Beta is approximately 7.5 Å. While active for the oxidation of larger hydrocarbons when using hydrogen peroxide as the oxidant, the aluminum in the sample leads to some difficulties. The framework aluminum results in Brönsted acidity that may perform side reactions on either the substrate or the oxidized product. For example, in the epoxidation of olefins, the epoxide ring is opened with the solvent over the acid site [17]. Moreover, the yield of zeolite from the starting synthesis gel is quite low (less than 30%). Recently, Tuel has reported the synthesis of Ti-ZSM-12 using a novel structure directing agent [18]. Another new structure directing agent has given zeolite Beta from a gel containing only silicon and titanium [19]. This work from ARCO researchers allows the preparation of zeolite Beta without the need for aluminum and/or alkali-metal cations in the starting gel. Davis and coworkers have used EXAFS and XANES to show that in this preparation of zeolite Beta, the titanium occupies framework sites and is structurally similar to the titanium in TS-1 [20].

More recently, mesoporous materials including MCM-41 [21] and the hexagonal mesoporous silicas (HMS) [22, 23] have been synthesized in the presence of titanium. The titanium is claimed to occupy isolated sites in the walls of solid products and these materials have been reported to be active for partial oxidation reactions utilizing both aqueous hydrogen peroxide and organic hydroperoxides.

In addition to the preparation of titanium containing molecular sieves by direct synthesis, post-synthetic treatments (or secondary syntheses) have shown promise for preparing active oxidation catalysts with large pore materials. These techniques all operate on the same principle: titanium atoms are inserted into lattice sites previously occupied by heteroatoms such as boron and/or aluminum. Various titanium compounds have been used to accomplish the insertion reaction. Zeolite Beta has been the primary choice for a large pore catalyst when using these techniques. Reddy et al. have transformed an aluminum containing zeolite Beta sample into a catalyst with oxidation activity similar to the original Ti,Al-Beta reported by Camblor et al. by employing ammonium titanyl oxylate in a secondary synthesis [24,25]. These authors conclude that the titanium is occupying tetrahedral framework positions. Another promising treatment involves the reaction of titanium tetrachloride with boron containing zeolite Beta. Rigutto et al. have shown that when $TiCl_4$ is contacted with zeolite Beta prior to the removal of the boron, a catalyst with high epoxidation activity is formed [26].

The objective of this work is to investigate the physicochemical properties of Ti-Beta prepared by direct synthesis and the post-synthetically modified boron SSZ-33 (our attempts to produce an active Ti-SSZ-33 material by direct synthesis have thus far failed). SSZ-33 is a borosilicate molecular sieve with a multidimensional pore system formed by intersecting 10 and 12 membered ring pores [27]. This type of void volume gives SSZ-33 unique adsorption properties that are intermediate between those of ZSM-5 and zeolite Beta [28]. SSZ-33 is also a more stable structure than zeolite Beta. Here, modification of this boron-containing zeolite has been performed through both liquid and vapor phase titanium treatments. To study the efficacy of the direct and secondary syntheses of these materials, epoxidation activity is tested using aqueous hydrogen peroxide and olefins as reactants.

5.2 Experimental

5.2.1 Synthesis

Aluminum-free, titanium-Beta was synthesized by a modified procedure adapted from reference 20. Samples of this titanosilicate were synthesized from reaction mixtures of molar composition:

$$SiO_2 : x\ TiO_2 : 0.28\ R^{++}\ (OH^-)_2 : 60\ H_2O$$

where R^{++} is 4,4'-trimethylenebis(N-benzyl-N-methylpiperidinium). In a typical synthesis, 0.31g of tetrabutylorthotitanate (TBOT) was added to 6.38g of tetraethylorthosilicate (TEOS). While this solution was stirred vigorously, 25.47g of a 15 wt% aqueous solution of the dihydroxide structure directing agent was added dropwise. After stirring for 3 hours, 10.76 g of deionized water was added under agitation. This mixture was then allowed to stir overnight and the resulting clear solution was heated to 40°C under vacuum to remove the alcohols formed by the hydrolysis of TBOT and TEOS. The solution (still clear) was then transferred to a Teflon-lined autoclave and heated to 135°C for 9 days with rotation (40 RPM). The resulting crystallized solids were recovered by centrifugation. The solids were dried at 110°C overnight and calcined to 550°C in air. For this study, two samples with different titanium contents were synthesized. Ti-Beta(1) and Ti-Beta(2) had Ti/Si molar ratios in the synthesis gel of 0.015, and 0.03, respectively.

Three samples of boron-SSZ-33 were synthesized for use as "parent" materials for the study on secondary syntheses. All of these solids were synthesized using the structure directing agent N,N,N-trimethyltricyclo[5.2.1.$0^{2,6}$] decaneammonium (R') hydroxide. The reactive gels had composition:

$$SiO_2 : x\,B_2O_3 : 0.2\,R'OH : 0.1\,NaOH : 40\,H_2O$$

A typical synthesis involves the addition of 0.363 g of 50 wt% aqueous sodium hydroxide to 0.139 g boric acid dissolved in 17.47 g of a 11 wt% aqueous solution of R'OH. 16.71 g of deionized water was then added and the mixture was stirred until the solution was homogeneous. 2.7 g of fumed silica (Cab-O-Sil M5) was then added under agitation and the mixture was allowed to stir for 1 hour. This gel was then transferred to a Teflon-lined autoclave and heated to 160°C for 10 days under rotation (40 RPM). The resulting crystalline solid was then recovered by filtration and washed with water. After allowing the solid to dry overnight at 100°C, it was calcined to 590°C for 4 hours in air to remove occluded organic material. For this study, three samples with varying boron content were synthesized. SZ33(1), SZ33(2), and SZ33(3) were prepared from synthesis gels where x=0.0125, 0.0175, 0.025, respectively.

A TS-1 sample used for comparison with the aforementioned materials was synthesized according to the procedure described in Example 1 of the patent by Taramasso et al. [29]. The sample was allowed to crystallize for two days rather than the ten days described in the patent. Calcination was performed in air at 550°C for 4 hours.

5.2.2 Post-synthetic treatments

The titanium-containing materials Ti-Beta(1), Ti-Beta(2), and TS-1 prepared by direct synthesis were not modified after calcination in air. The SSZ-33 samples were subjected to various post-synthetic treatments before use. The primary treatment studied in this work employs subtle changes from the procedure used by Rigutto et al. [26]. Here, 300 mg of calcined zeolite were loaded into a quartz reactor and heated to 300°C in a flow of dry argon. The dehydrated samples (still at 300°C) were then exposed to a flow (40 ml/min) of argon bubbled through a vessel containing $TiCl_4$ (Aldrich, used as received) maintained at 22°C. The $TiCl_4$ flow was continued for 1 hour unless otherwise noted. The sample was cooled to 100°C and the argon stream was then redirected through another bubbler containing methanol at room temperature. Rigutto et al. claim that this "methanolysis" step involves the reaction of methanol with framework boron to produce trimethyl borate which is volatilized out of the crystals. As depicted in Figure 5.1, the titanium is speculated to insert into the vacancy created by the loss of the boron. Here, the methanol treatment was conducted for 12 hours. The flow was then switched to dry air, and the sample was calcined to 400°C. As a final precaution to remove any extra-framework boron, the sample was removed from the quartz reactor and refluxed in methanol for 1 hour and recovered by filtration. A final calcination at 590°C in air was performed prior to characterization and catalysis. The samples resulting from this treatment will be referred to with -Ti after the "parent" material name, e.g., SZ33(3)-Ti. In a separate experiment, sample SZ33(1) was first treated with a solution of 0.005 M HCl to remove the boron from the lattice and leave empty silanol nests (confirmed by ^{11}B NMR). The $TiCl_4$ in argon was then contacted with the sample for 1 hour as described above. The steps involving methanol treatment were omitted. This sample will be denoted SZ33(1)-HCl-Ti.

To test for the incorporation of titanium into samples prepared by liquid phase secondary syntheses, a calcined sample of SZ33(2) was contacted with a 40 mM aqueous solution of ammonium titanyl oxylate (ATO) for 9 hours at 60°C. In this experiment, 400 ml of the ATO solution were used per gram of molecular sieve. The solid was recovered by filtration and calcined to 590°C. This sample will be referred to as SZ33(2)-ATO. Here, we employed a more concentrated ATO solution and a higher treatment temperature than used by Reddy et al., who recently published a study on the effects of ATO concentration on catalyst preparation [24,25]. Another method of titanium insertion via a liquid phase secondary synthesis involved the contact of a dehydrated sample of SZ33(2) with $TiCl_4$:2THF dissolved in methanol (200 mg per 150 g methanol). 40 g of the solution were transferred to a flask containing 300 mg of dehydrated SZ33(2). The mixture was heated to reflux for 2 hours under an argon atmosphere. The solid was filtered, washed with methanol, and then calcined to 590°C in air prior to testing. This sample will be referred to as SZ33(2)-THF.

5.2.3 Analysis and characterization

Fourier Transform Infrared (FTIR) spectra were obtained using a Nicolet System 800 Spectrometer (KBr beamsplitter and DTGS detector) with the KBr pellet technique. Raman spectra were recorded on a Nicolet System 950 Raman Spectrometer. A CaF_2 beamsplitter was used for the Raman spectra along with an InGaAs detector. X-ray powder diffraction (XRD) patterns were collected on a Scintag XDS-2000 diffractometer equipped with a liquid-nitrogen-cooled germanium detector using Cu-Kα radiation. Fluorophologopite mica (Standard Reference Material 675, National Bureau of Standards) was used as an external standard for all samples. Data were collected with a step size of 0.02 degrees and a step time of 10 seconds. Diffuse reflectance UV spectra were obtained on a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance accessory. Spectra were referenced to a powdered sample of barium sulfate. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

5.2.4 Catalytic tests

All epoxidation reactions were performed in a 25 mL glass reactor immersed in a constant temperature oil bath and used 30% hydrogen peroxide as the oxidant. The 1-hexene reactions were carried out in methanol for 2 hours at 50°C with vigorous stirring. Each reaction experiment utilized 50 mg of catalyst, 6.0 g solvent, 8.25 mmol 1-hexene, and 2.08 mmol H_2O_2. The cyclohexene and cyclooctene reactions were performed in methanol for 3 hours at 70°C with vigorous stirring. Each reaction experiment utilized 50 mg of catalyst, 6.0 g methanol, 9 mmol olefin, and 3 mmol H_2O_2. Mesitylene was used as an internal standard for all reactions. Reaction solutions were analyzed by gas chromatography using a HP 5890 Series II GC equipped with a 50 m HP-FFAP (polar) capillary column and a flame ionization detector. Products were identified using commercial standards and GC/MS analysis. The amount of hydrogen peroxide left unreacted was determined by titration with $Ce(SO_4)_2$.

5.3 Results and Discussion

5.3.1 Characterization

The XRD patterns of the samples SZ33(1-3) revealed no peaks attributable to impurities. As is shown in Table 5.1, the boron content of the SSZ-33 samples increased with increasing boron concentration in the synthesis gel. It is well known that for SSZ-33 there is a lower limit to the amount of boron that can be incorporated into framework positions. With the structure directing agent used here, extremely low boron contents will yield mixtures of SSZ-33 and SSZ-31 [28]. Thus, the samples SSZ33(1-3) cover a significant portion of the compositional range possible for SSZ-33.

For TS-1, it has been found that there exists a maximum in the amount of titanium that can be inserted into framework positions. Researchers at Enichem have found that attempts to produce TS-1 with Ti/Si molar ratios above 0.025 produce samples with extra-framework titanium. The presence of extra-framework is undesirable because it is able to promote the decomposition of hydrogen peroxide to dioxygen and water. The ratio found for TS-1 was used as a guideline for the preparations of our boron containing samples.

For the $TiCl_4$ substitution method with zeolite Beta, Rigutto et al. [26] found that increasing boron contents led to increased titanium contents. However, it was observed that as the titanium content rose, so did the amount of extra-framework titanium. For these preparations of zeolite Beta, Ti/Si ratios above 0.06 were reported.

In an attempt to prepare titanium containing molecular sieves from large-pore borosilicates with ultimately lower Ti contents (and presumably less extra-lattice TiO_2), the parent materials used here were synthesized with small boron contents. In addition, these samples were used in the calcined form without modification. Because sodium is present in the synthesis gels of SSZ-33, these samples will contain some Na^+. Therefore, boron sites will be balanced by Na^+ and protons. The data in Table 5.1 show that the sodium content in the SSZ-33 materials increases with lower boron incorporation.

Data concerning the elemental analysis of various titanium treated samples are shown in Table 5.1. The calcined SSZ-33 materials show an increase in unit cell volume with decreasing boron content. This effect is due to the relatively short B-O bond as compared to the Si-O bond. The unit cell volume of sample SZ33(1) expands further after treatment with dilute HCl, indicating removal of boron from the framework. The elemental analysis data show that nearly 85% of the boron in the zeolite is extracted by the acid. All boron-containing samples treated with $TiCl_4$ and methanol in the vapor phase show a large increase in unit cell volume over their respective "parent" material. The incorporation of titanium into other molecular sieve frameworks has been shown to produce unit cell volume expansions on the order of those given here for the SSZ-33 samples [11,30].

As expected, the relative unit cell volume increase is largest for titanium-containing samples that had high amounts of boron. After the vapor phase treatments, boron contents of the resulting materials are approximately 10% of the parent materials. The amount of titanium in these materials (from elemental analysis) indicates that the number of Ti atoms present after the treatment outnumber the maximum number of boron vacancies by 39, 42, and 12% for samples (1), (2), and (3), respectively. Rigutto et al. observed excess titanium after similar treatment with boron-Beta, and surmised that it results from reactions of $TiCl_4$ with silanol groups associated with defect or surface sites. A unit cell expansion indicates that for sample SZ33(1)-HCl, the titanium treatment does indeed place Ti atoms into lattice positions. The elemental analysis shows that while titanium is present, the titanium content is less than 25% of that from the material that was treated with $TiCl_4$ before removal of boron. Thus, it appears that titanium insertion is more efficient with $TiCl_4$ when the boron is still present in the framework.

To test the effect of $TiCl_4$ exposure time, a second sample of SZ33(2) was allowed to react for 20 rather than the typical 60 minutes. The titanium content of the material (denoted SZ33(2)-Ti(*)) is approximately one-third that of SZ33(2)-Ti. It appears that at the conditions used for this study the titanium uptake is linear within the first hour. Assuming that the titanium occupies boron vacancies alone, only 41% of the open sites are incorporated with titanium. The unit cell volume increase for the material treated for 20 minutes is less than that observed for the sample treated for 1 hour.

Samples SZ33(2)-ATO and SZ33(2)-THF show very little titanium incorporation by both elemental analysis and unit cell expansion. The success of the ammonium titanyl oxylate treatment for aluminum-containing zeolite Beta by Reddy and Sayari [25] was not realized for SSZ-33 at the conditions used here. These researchers have shown that the cationic form of the parent zeolite is crucial in the incorporation of titanium. They found for zeolite Beta that the Na^+ and K^+ forms contained much more titanium than samples in the H^+ or NH_4^+ form after ATO treatments. Because the SZ33(2) sample was used without modification after calcination, the lack of full Na^+ exchange may be the reason for the low level of titanium insertion. It was hoped that the relative ease of boron removal compared to aluminum would allow the ATO treatment to be successful without full alkali-metal exchange of the molecular sieve. It now appears that the alkali-metal content of the sample may be more important than whether the molecular sieve is a borosilicate or an aluminosilicate.

As is shown from the data in Table 5.2, the Ti-containing Beta samples prepared by direct synthesis contain titanium in amounts similar to the Ti/Si ratio of the gel. Ti-Beta(1) is slightly enriched in titanium over the gel composition while Ti-Beta(2) is depleted in titanium, indicating that the maximum Ti/Si for this system may be close to that of TS-1. A similar result was observed for Ti,Al-Beta [16]. The heavily faulted nature of the Beta structure makes unit cell measurements difficult, but many have used the d-spacing of single peaks to base inferences on lattice expansion [16,25]. By observing changes in the (302) plane, it appears that the unit cell of the Ti-Beta samples increases with increasing titanium content (see Table 5.2). The relative changes in d-spacing between the materials is smaller than the change reported for the Ti,Al system of Camblor [16], but the presence of aluminum in the latter system makes direct comparison difficult. The very small shifts reported here for only one relatively broad peak present from the XRD pattern of zeolite Beta does not allow for the determination of extent of titanium insertion.

The presence of a band at approximately 960 cm^{-1} in the IR spectra of molecular sieves prepared by direct or secondary synthesis with titanium has been used to infer Ti insertion into the framework [15,18,29]. Silicalite-1 shows a small band in this region but the addition of titanium into the framework dramatically enhances its intensity [6]. For TS-1 samples prepared in the same manner, the intensity of this band correlates with the amount of framework titanium [31]. This result was also observed for Ti,Al-Beta (the Beta sample prepared without titanium was claimed to be free of this band) [15]. Reddy et al. report an absorption at 960 cm^{-1} for the aluminum containing zeolite Beta samples treated with ATO, but no correlation between intensity and titanium content was observed. Scarano et al. have investigated the appearance of the 960 cm^{-1} band in Ti-substituted silicalites and rule out the assignment of a titanyl stretching mode for the origin of the 960

cm^{-1} peak. They conclude that this mode predominantly involves the stretching between the silicon and oxygen of tetrahedral $[O_3Si–O]^{\delta-}$ units surrounding the titanium atoms.

FTIR spectra of the calcined SSZ-33 "parent" materials are almost identical (see Figure 5.2). There is an increase of intensity in the band at 1400 cm^{-1} with increasing boron content. This band has been ascribed to trigonal boron formed during calcination [28]. The band at $\approx$930 cm^{-1} (due to boron in tetrahedral coordination) shows a smaller increase in intensity with boron content. For samples SZ33(1-3), the vapor phase treatment with $TiCl_4$ and methanol have a pronounced effect on the FTIR spectra (see Figure 5.3). In all three cases, the band at 1400 cm^{-1} disappears and the small shoulder at 930 cm^{-1} becomes a distinct band with much higher intensity at 954 cm^{-1}. The intensity of the band in all three materials is nearly identical. Sample SZ33(2)-Ti(*), treated with $TiCl_4$ for only 20 minutes also shows the 954 cm^{-1} band but at half of the intensity of those shown for SZ33(1-3)-Ti.

SZ33(1)-HCl shows a band in the same position as the $TiCl_4$ treated samples although less intense. After $TiCl_4$ treatment of SZ33(1)-HCl, the band at $\approx$950 cm^{-1} almost disappears. This result suggests a plausible explanation as to why less titanium is incorporated in SSZ-33 if the boron is removed prior to $TiCl_4$ contact. After acid treatment, silanol nests would be present at the boron vacancies. At the elevated temperatures used to perform the titanium insertion, these silanol nests may anneal leaving less sites for the $TiCl_4$ to react. Rigutto et al. use thermogravimetric results to show water is liberated from the partial self-condensation of these nests at 300°C in zeolite Beta [26]. They propose that this process is enhanced by the release of HCl during the $TiCl_4$ treatment. The reaction of $TiCl_4$ with water would lead to extra-framework TiO_2 moieties.

The IR spectrum for SZ33(2)-THF does not contain the 954 cm^{-1} band. This result agrees with the elemental analysis data that indicate very little titanium is incorporated and almost all of the boron is removed (see Table 5.1). It appears that the methanol used in this experiment did indeed assist in the removal of lattice boron. However, titanium did not react into the boron vacancies at the temperature employed here. After contact with the titanium compound, the material was calcined, which may have led to the same type of silanol loss as argued above (results in the disappearance of the 954 cm^{-1} band).

The B-SSZ-33 sample treated with ATO has an IR band located at 946 cm^{-1}. Although the sample lost more than two-thirds of the boron, it still contained much more boron than any of the other treated samples. It is difficult to assign this IR peak to the result of metal insertion simply because elemental analysis shows very little titanium in the sample.

All of the zeolite Beta samples synthesized here showed an intense IR band at 955 cm^{-1} (see Figure 5.4). This was true even for the pure-silica Beta synthesized without titanium in the gel. The intensity of the 955 cm^{-1} band is slightly larger for the two titanium containing Beta samples than for the Si-Beta sample, and is equally intense for Ti-Beta(1) and Ti-Beta(2). Therefore, titanium incorporation into pure-silica Beta has no pronounced effect on the IR spectra.

Raman spectroscopy is a powerful tool for investigating titanosilicates because it can identify the presence or absence of extra-framework TiO_2 anatase. Crystalline forms of TiO_2 are very strong Raman scatterers while molecular sieves, even when containing heteroatoms, are weak scatterers. This allows the presence of very small amounts of TiO_2 to be detected within a sample. A disadvantage of Raman spectroscopy is the susceptibility of sample fluorescence that can be caused by residual carbon deposits that remain after calcination.

Samples SZ33(2-3) have identical Raman spectra in the region from 100-1500 cm^{-1} (only sample (2) is shown in Figure 5.5). Sample SZ33(1) fluoresced after calcination in air at 590°C. The TS-1 sample shown in Figure 5.5 is free of anatase due to the absence of a strong peak at 144 cm^{-1} (the intensity of the anatase spectrum included in Figure 5.5 has been reduced by more than 3 orders of magnitude). The band at approximately 960 cm^{-1} in the IR spectra of titanium-containing molecular sieves is also Raman active as observed in the TS-1 sample. As shown in Figure 5.5, a weak, broad band is found in this region for the boron-containing samples. After vapor-phase $TiCl_4$ treatment, an intense peak at 952 cm^{-1} appears in the spectrum for SZ33(2-3)-Ti (see Figure 5.5). Analogous to the IR data, this peak occurs after the titanium treatments. Scarano et al. [32] have shown that this band in the Raman spectrum is like the band found at approximately the same value in the IR spectrum in that it is assigned to the same structural unit (vide supra). The strong peaks at 144 and 640 cm^{-1} are caused by extra-framework TiO_2 in the form of anatase. As mentioned earlier, this type of titanium is detrimental to the catalysis because it is able to decompose H_2O_2 into water and oxygen thereby decreasing the efficiency of partial oxidation reactions. While the band at 952 cm^{-1} has nearly the same intensity for samples SZ33(2)-Ti and SZ33(3)-Ti, the anatase peaks are approximately four times more intense for sample (3). Although not obvious from the IR spectra, the Raman spectra clearly show the presence and relative amount of anatase in these samples. When SZ33(2) is exposed to $TiCl_4$ for 20 minutes rather than the typical treatment of one hour, the Raman spectrum shows a peak at 952 cm^{-1} which is only slightly higher in intensity than the parent material. The intensity of the anatase peaks for this sample are nearly half of that for the sample treated for one hour. All of these spectra contain another spectral feature not observed in the titanium-free "parent" samples; a weak band at 1120 cm^{-1}. Scarano et al. [32] and Deo et al. [33] have observed this band for TS-1 and the assignment of this peak involves the stretching mode of the three Si–O bonds in the group $[O_3Si–O]^{\delta-}$ not polarized by the framework titanium.

The Raman spectra of the SSZ-33 sample treated with ammonium titanyl oxylate shows only one new peak compared to the "parent" material. A small peak at 144 cm^{-1} indicative of anatase is observed. From the small unit cell volume expansion, it can be concluded that the small amount of titanium in this sample is in the form of extra-framework TiO_2. Unfortunately, the sample treated with $TiCl_4$:2THF dissolved in methanol fluoresced. Thus, no Raman data could be acquired from this material.

As shown by the spectra in Figure 5.6, the titanium-containing zeolite Beta samples prepared by direct synthesis reveal very little differences in their Raman spectra from the pure-silica Beta sample. A peak present at 979 cm^{-1} in the Si-Beta sample increases in intensity and shifts to lower wavenumbers with titanium incorporation. For Ti-Beta(2), the sample with the greatest amount of titanium, the peak shifts to 965 cm^{-1} but is no more intense than the peak at 971 cm^{-1} for Ti-Beta(1). A very small absorption at 1120 cm^{-1} appears in the spectra from the titanium-Beta samples that is absent in the spectrum of the pure-silica material.

Zecchina et al. have assigned absorption edge frequencies from DR-UV spectra of titanium containing materials to various titanium species [34]. Figure 5.7 shows the DR-UV spectra of TS-1, anatase, and some of the titanium containing SSZ-33 materials. TS-1 is characterized by having a relatively narrow peak at 205 nm and an absorption edge beginning at 300 nm. The absorption edge of anatase is at 380 nm. Zecchina et al. assign the peak at 205 nm to isolated Ti(IV) in tetrahedral coordination. Samples SZ33(1-2)-Ti both show an intense absorption maximum at approximately 220 nm and the corresponding peak for SZ33(3)-Ti is at 210 nm. The adsorption edge for all SZ33 samples is shifted towards higher wavelengths (>330 nm). Davis et al. [20] have shown this shift to be indicative of titanium in an octahedral environment. The shift in absorption edge for samples SZ33(2-3)-Ti is expected since anatase is present in these samples (detected from Raman spectra). For sample SZ33(2)-Ti(*) the absorption edge occurs at the same wavelength as SZ33(2)-Ti but is shifted to slightly lower wavelengths. This is most likely due to the smaller size of the anatase TiO_2 clusters. The strong absorption shoulder at 310 nm indicates that samples SZ33(1)-Ti and SZ33(1)-HCl-Ti most likely have the highest amount of anatase (fluorescence from these samples prevented conclusive determination of the presence of anatase via Raman spectroscopy).

The titanium contents of the samples treated with Ti compounds in the liquid phase are very low (by elemental analysis) and thus give weak DR-UV spectra. In addition to a broad absorption maximum between 200 and 250 nm, the sample treated with ATO shows an absorption edge in the region where anatase appears. The DR-UV spectrum of the sample treated with $TiCl_4$:2THF in methanol gives only negligible intensity from background.

The DR-UV spectra of the titanium-containing Beta samples are very similar to the spectrum recorded for TS-1 (see Figure 5.8). The absorption edge of TS-1 and both Ti-Beta samples begins at approximately 300 nm. This value closely matches that of the sample with similar Ti/Si ratio reported by Davis et al. [20]. The absorption maximum for all three materials is approximately 210 nm, which combined with the similar absorption edge location gives a clear indication that the titanium in all three materials is situated in tetrahedrally coordinated lattice positions with silicon in the second coordination shell.

5.3.2 Catalytic tests of titanium treated SSZ-33 samples

All materials were tested for their ability to epoxidize 1-hexene, cyclohexene, and cis-cyclooctene. The results of the catalytic tests are summarized in Table 5.3. Of the three substrates tested, 1-hexene is known to be the least reactive. Over titanium-containing molecular sieves, epoxidation is believed to occur through an electrophilic attack by the active titanium site [35]. Therefore, increasing electron density at the double bond results in higher reactivity. For TS-1, this effect is often masked by steric constraints. Based on electron density, cyclic olefins will be more reactive than α-olefins yet severe diffusion limitations within TS-1 result in very low conversions. Results from Ti,Al-Beta catalysts show higher reactivity for internal linear olefins and cyclic olefins than for α-olefins [17].

The titanium containing SSZ-33 samples prepared from $TiCl_4$ treatments show activity for the partial oxidation of 1-hexene with aqueous hydrogen peroxide. The level of conversion increases with the total titanium content, although the Raman and DR-UV data indicate differences in the percentages of extra-framework Ti. Sample SZ33(1)-Ti, found to contain relatively high levels of anatase, has the lowest conversion of the three, along with the lowest selectivity to the epoxide. When using 1-hexene as the substrate, all catalysts tested here produced only the epoxide and products derived from the ring opening of the epoxide with the solvent, i.e., methanol. Hydrogen peroxide efficiencies were 49% for samples (2) and (3) while sample (1) had a higher value of 74%. No Raman spectrum was available for sample (1) so it is difficult to correlate H_2O_2 efficiency to anatase content. DR-UV results and the high amount of "extra" titanium from elemental analysis indicate that sample (1) contains some amount of anatase. Even if one assumes that sample (1) contains the highest amount of anatase, the results can still be rationalized; the larger particles of TiO_2 in sample (1), as indicated by a shift in the DR-UV spectrum, may yield less available surface sites of Ti to accomplish the decomposition reaction. The sample treated with $TiCl_4$ for only 20 minutes shows low conversion for the epoxidation even when normalized on titanium content. The sample leached of boron before Ti insertion also gives low catalytic activity. The TS-1 sample studied here, while having a Ti/Si ratio less than half of those found in the $TiCl_4$ treated samples, is a far superior catalyst in terms of conversion, H_2O_2 efficiency, and epoxide selectivity.

The three active samples show poor selectivity to the epoxide (due to ring-opening) when compared to TS-1. The ring opening of epoxides with protic solvents and/or water has been well documented for some titanium containing molecular sieves [17,21]. This phenomenon is typically encountered because the catalyst contains acid sites, in the form of framework aluminum, which are responsible for solvolysis. For the Ti-Beta samples, the use of very pure synthesis reagents makes this explanation unlikely. This very low boron content of the Ti-SSZ-33 samples also tends to rule out the possibility of an acidic framework.

When cyclic olefins are reacted with hydrogen peroxide over these Ti-SSZ-33 catalysts, the activities and selectivities rose dramatically. The relative order of conversion and H_2O_2 efficiency between the catalysts remained nearly constant. With a maximum possible olefin conversion of 33.3% (substrate/ H_2O_2 initially = 3), sample SZ33(3) is the most active with a conversion above 25 % for both substrates. Hydrogen peroxide efficiencies are high even though anatase is present in the samples. Sample SZ33(2)-Ti(*) performed exceptionally well if one considers the low titanium content. Nearly all of the H_2O_2 reacted over this catalyst is used to form the epoxide and ring opened products in the reaction of both cyclic olefins.

While the conversions and efficiencies of the SSZ-33-based catalysts are very high for the epoxidation of cyclic olefins, there is almost no reactivity with TS-1. While TS-1 can epoxidize linear α-olefins, the cyclic molecules are too large to easily enter the pores of TS-1. These results show the utility of the SSZ-33 modified catalysts. By switching from the 10-MR pore system of TS-1 to the 10/12 MR system of SSZ-33 an order of magnitude increase in conversion for the cyclic olefins is observed.

Although the two cyclic olefins have similar activity over the SSZ-33-based catalysts, they are different when the ring-opening reaction is considered. For the epoxidation of cyclohexene, the ring-opening products of the epoxide are observed almost exclusively. Even TS-1, well known for its lack of ring-opening [35], has an epoxide selectivity of only 36% in this study. Cyclohexene oxide was found to undergo methanolysis in neat methanol (without the addition of a catalyst) at the conditions used here. Thus, the ring opening products from cyclohexene are most likely due to the uncatalyzed methanolysis of the epoxide at reaction conditions. In the epoxidation of cyclooctene the ring opening products account for only a few percent of the product distribution at most. Cyclooctene oxide is a very bulky molecule and steric factors have been shown to hinder its methanolysis [36].

The SSZ-33 samples treated with titanium compounds through the liquid phase do not show activity for the epoxidation of any olefin studied here. This result is expected since there is an extremely low titanium insertion observed in these materials.

5.3.3 Catalytic tests of titanium-containing zeolite Beta samples

For the epoxidation of 1-hexene, the Ti-Beta catalysts show conversion levels near those of the Ti-SSZ-33 samples. The relatively small amount of titanium in the zeolite Beta samples could account for the differences in conversion. The selectivities to the epoxide, and the hydrogen peroxide efficiencies are both unexpectedly low from the Ti-Beta catalysts. Because these zeolite Beta samples are synthesized in the absence of heteroatoms such as boron and aluminum, it is expected that no acid sites strong enough to cause methanolysis of the epoxide would be present.

The titanium-containing zeolite Beta samples proved to be excellent catalysts for the epoxidation of the cyclic olefins. Higher cyclic olefin conversions are observed when compared to the SSZ-33 samples even though the Ti-Beta samples contained half the titanium of the latter catalysts.

As is found for the Ti-SSZ-33 catalysts, the epoxidation of cyclohexene over Ti-Beta produces only the ring-opened products. Hydrogen peroxide efficiencies of 85 and 90% for Ti-Beta(1) and (2), respectively, are also similar to those found with the titanium treated borosilicate materials. The conversion of cyclohexene is higher for Ti-Beta(2) than for Ti-Beta(1) presumably due to its larger amount of titanium. Both Ti-Beta samples contain titanium only in isolated tetrahedral coordination sites so valid comparisons can be made between samples of different total titanium content.

Full quantitative conversion of cyclooctene to the epoxide is found for both Ti-Beta catalysts when the reaction is analyzed after four hours at 70°C. The nearly perfect efficiency of the H_2O_2 to yield the epoxide suggests that this catalyst will be very attractive for the partial oxidation of other hindered olefins where steric factors may prevent the epoxide from undergoing solvolysis.

5.4 Conclusions

Catalysts capable of epoxidizing olefins with aqueous hydrogen peroxide can be prepared by contacting boron-containing SSZ-33 with vapor phase $TiCl_4$ at 300°C following a modified procedure first elaborated by Rigutto et al. [26]. No special calcination or ion-exchange treatment is needed before reaction with $TiCl_4$. The samples prepared here contain primarily titanium in lattice positions as evidenced by DR-UV and Raman spectroscopies. Titanium-containing zeolite Beta prepared by the use of a novel structure-directing agent developed by researchers at ARCO [19] is also found to be active for the epoxidation of olefins with aqueous hydrogen peroxide. Both catalysts are able to epoxidize cyclic olefins too large to enter the pores of TS-1.

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Table 5.1 Elemental analyses and unit cell volumes of the SSZ-33 samples.

Sample	B/Si in solid (gel)	Na / B	Ti / Si	UC Volume [$\AA^3$]	% Change from parent
SZ33(1)	0.031 (0.025)	0.46		3474.0	
SZ33(2)	0.035 (0.035)	0.24		3460.2	
SZ33(3)	0.044 (0.050)	0.19		3456.5	
SZ33(1)-HCL	0.005	-		3480.1	0.18
SZ33(1)-Ti	0.003	-	0.039	3515.8	1.20
SZ33(2)-Ti	0.004	-	0.044	3519.0	1.70
SZ33(2)-Ti(*)	0.001	-	0.014	3505.6	1.31
SZ33(3)-Ti	0.002	-	0.047	3527.9	2.07
SZ33(1)-HCl-Ti	0.002	-	0.009	3485.0	0.14
SZ33(2)-ATO	0.010	-	0.001	3469.2	0.26
SZ33(2)-THF	0.005	-	0.002	3470.5	0.30
TS-1		-	0.019		

(*) sample was contacted for 20 minutes rather than 1 hour with $TiCl_4$

Table 5.2 Elemental analyses and d-spacings (302) plane of the zeolite Beta samples.

Sample	Ti / Si (gel)	Ti / Si (product)	d-spacing
Si-Beta	-	-	3.9345
Ti-Beta(1)	0.015	0.0182	3.9362
Ti-Beta(2)	0.030	0.0238	3.9372

Table 5.3 Reaction data from titanium-containing molecular sieves.

Sample	Ti / Si	<---------1-Hexene--------->			<--------Cyclohexene------>			<--------Cyclooctene-------->		
		Conv.^{a}	Selec.^{b}	Effic.^{c}	Conv.^{a}	Selec.^{b}	Effic.^{c}	Conv.^{a}	Selec.^{b}	Effic.^{c}
TS-1	0.019	11.9	97	98	2.4	36	100	2.0	100	98
SZ33(1)-Ti	0.039	4.0	12	74	21.4	0	96	13.7	95	84
SZ33(2)-Ti	0.044	5.1	44	49	23.3	2	89	24.2	99	86
SZ33(3)-Ti	0.047	5.7	27	49	23.3	2	89	24.2	99	86
SZ33(2)-Ti(*)	0.014	0.7	16	73	19.4	0	100	15.4	97	97
SZ33(1)-HCl-Ti	0.009	0.4	100	77	11.4	1	98	10.1	100	94
SZ33(2)-ATO	0.001	0	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SZ33(2)-THF	0.002	0	-	-	n.d.	n.d.	n.d.	1.0	100	100
Ti-Beta (1)	0.018	2.9	37	39	27.0	2	85	33.3	100	100
Ti-Beta (2)	0.024	4.2	31	37	29.3	0	90	32.9	100	97

a. Conv. = % conversion of the respective alkene
b. Selec. = % selectivity to the epoxide product
c. Effic. = total moles of hydrogen peroxide reacted divide by moles of oxygenated product
n.d. : not determined

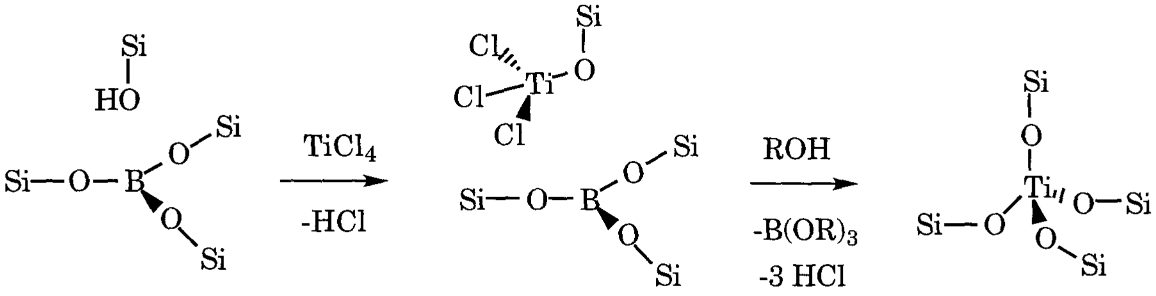

Figure 5.1 Mechanism of titanium insertion by secondary synthesis proposed by Rigutto et al.

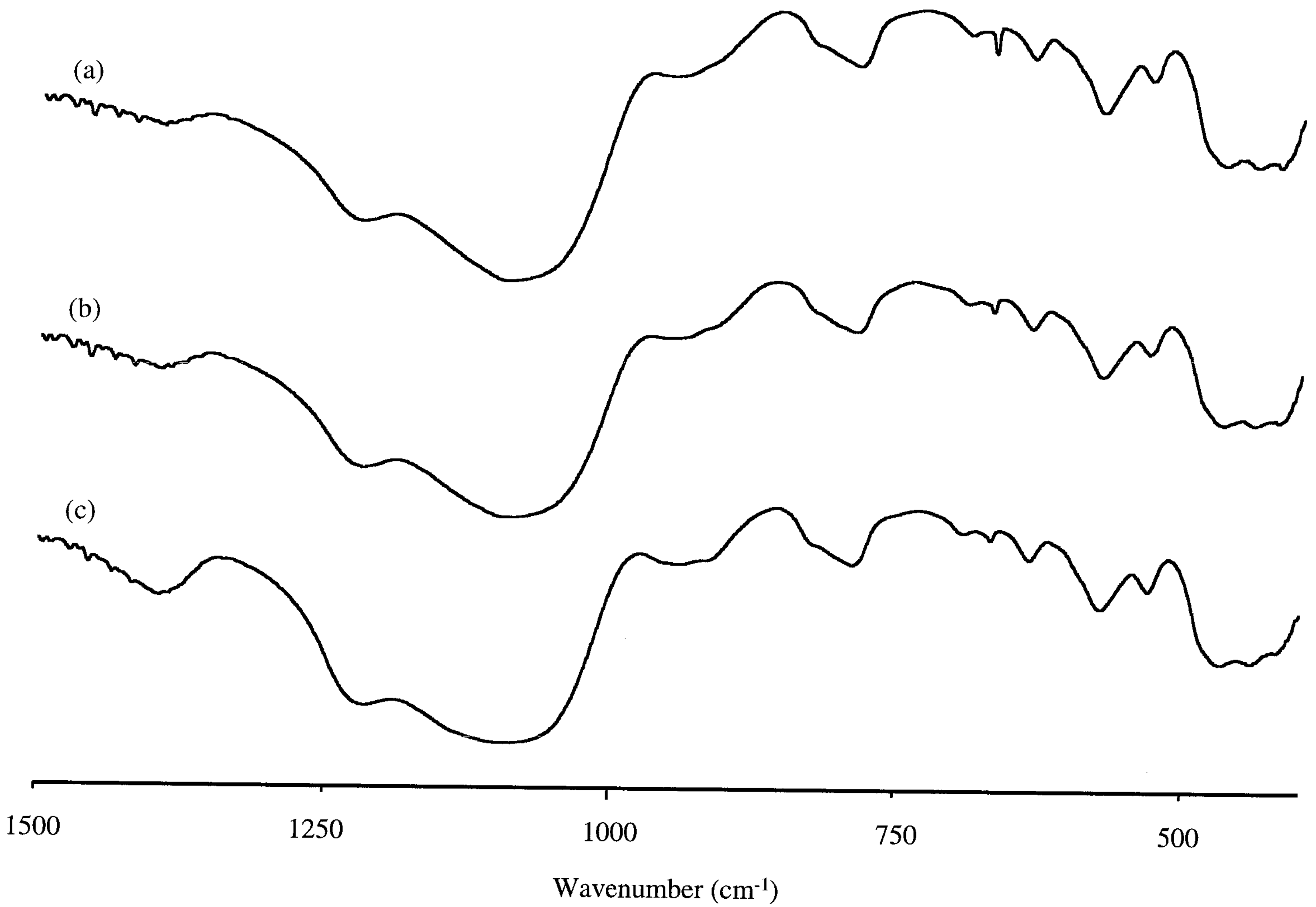

Figure 5.2 FTIR spectra of calcined SZ33(1) (a), SZ33(2) (b), and SZ33(3) (c).

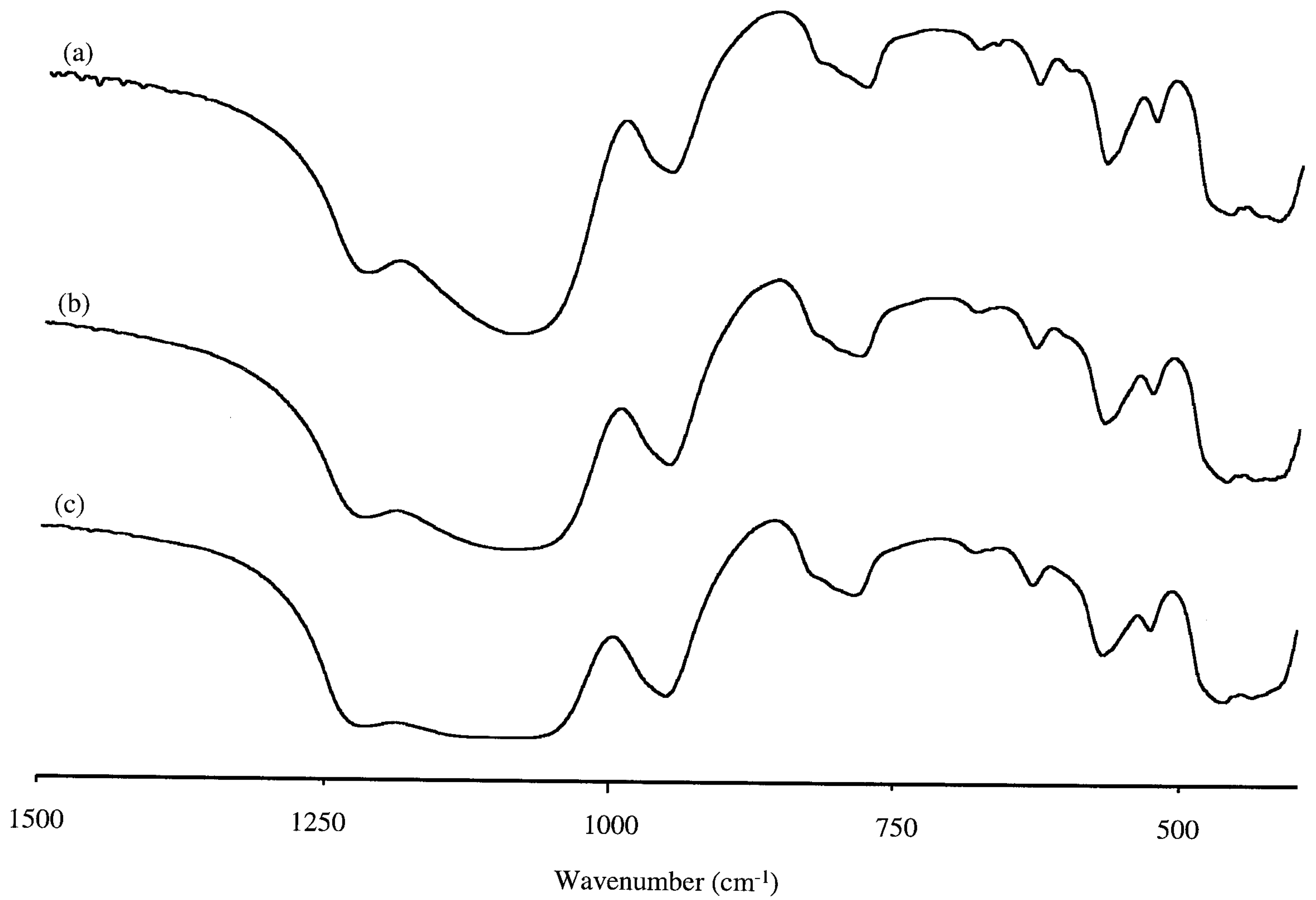

Figure 5.3 FTIR spectra of SZ33(1)-Ti (a), SZ33(2)-Ti (b), and SZ33(3)-Ti (c).

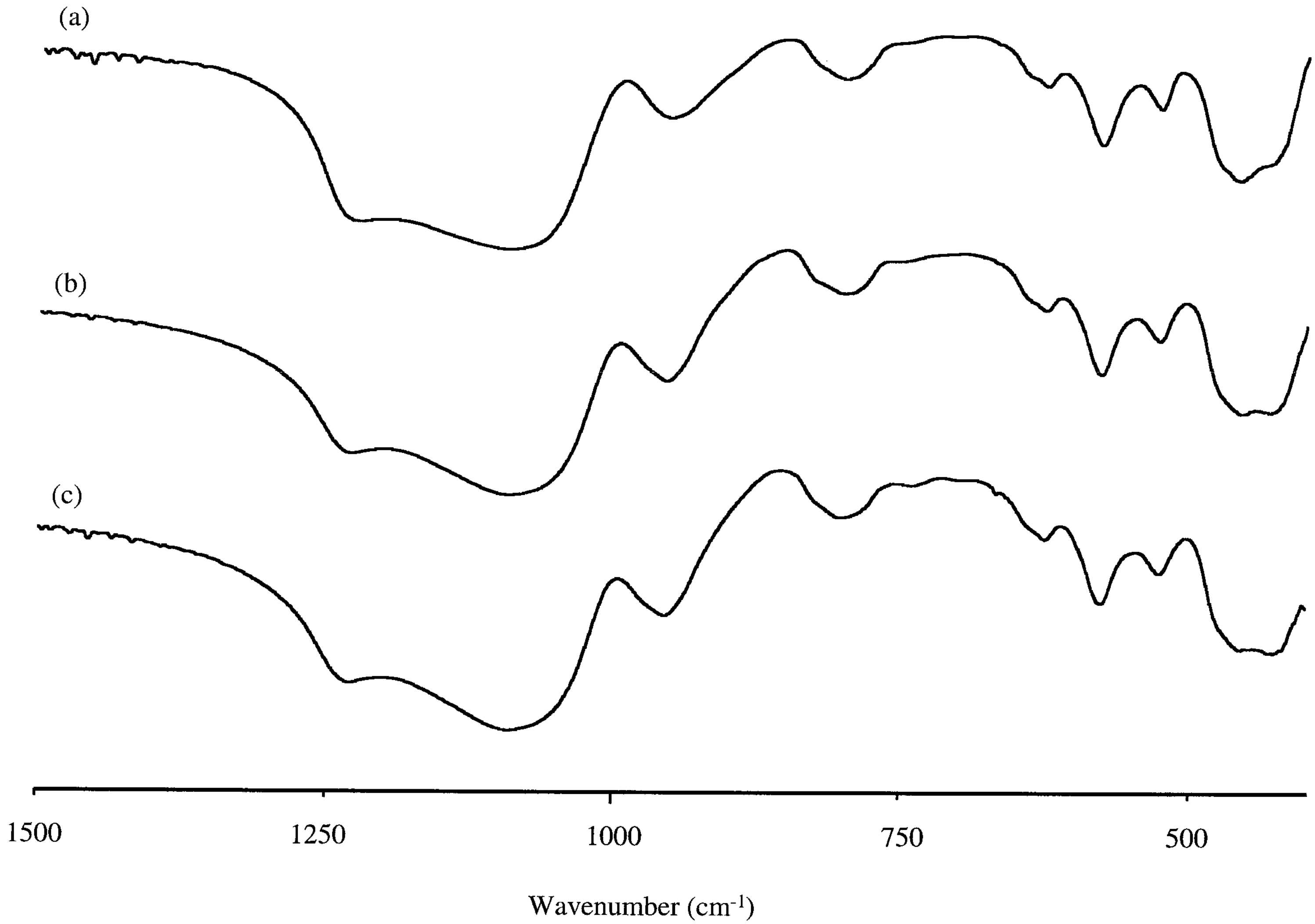

Figure 5.4 FTIR spectra of calcined Si-Beta (a), Ti-Beta(1) (b), and Ti-Beta(2) (c).

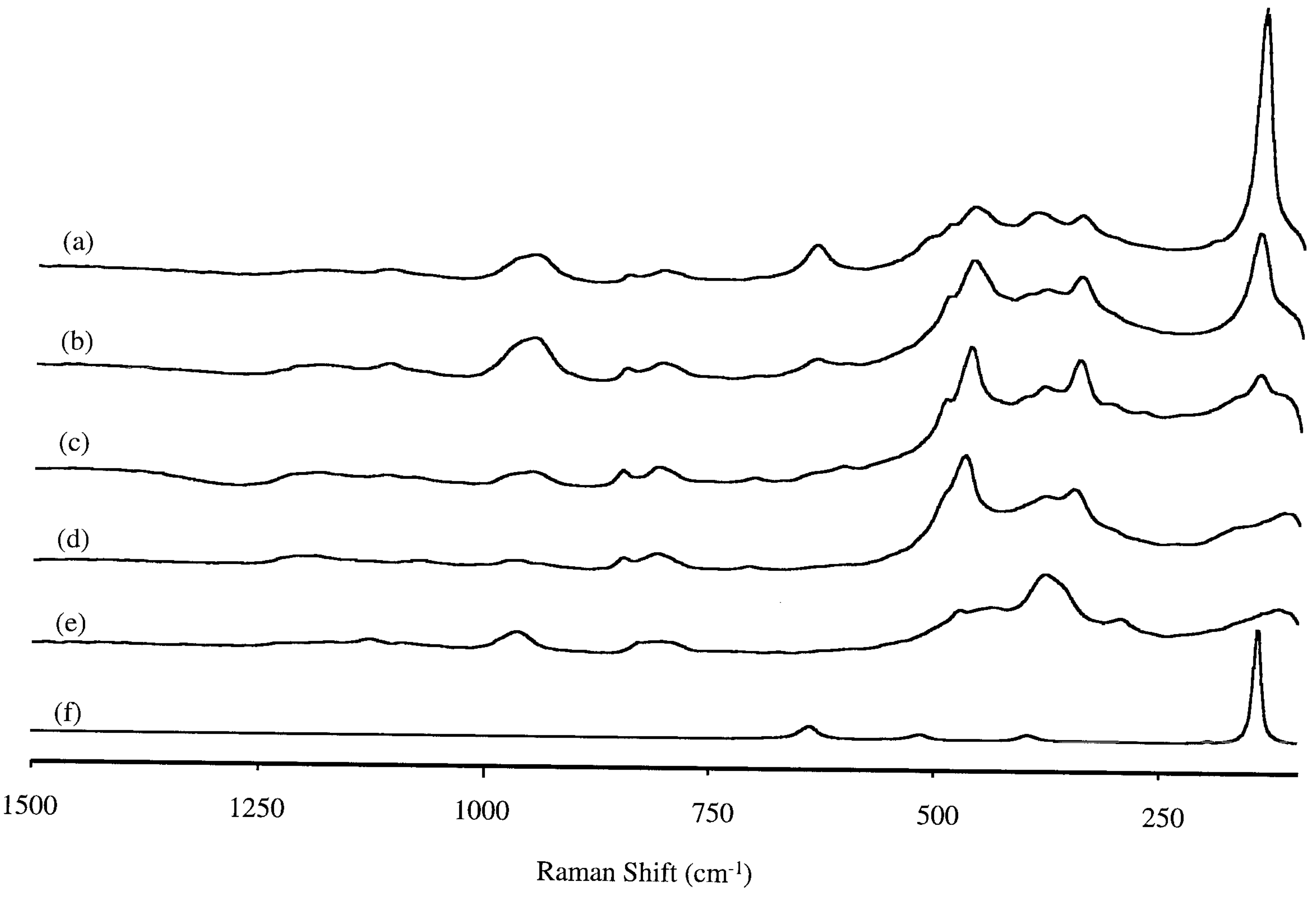

Figure 5.5 FT-Raman spectra of calcined SZ33(3)-Ti (a), SZ33(2)-Ti (b), SZ33(2)-Ti(*) (c), SZ33(2) (d), TS-1 (e), and anatase (f).

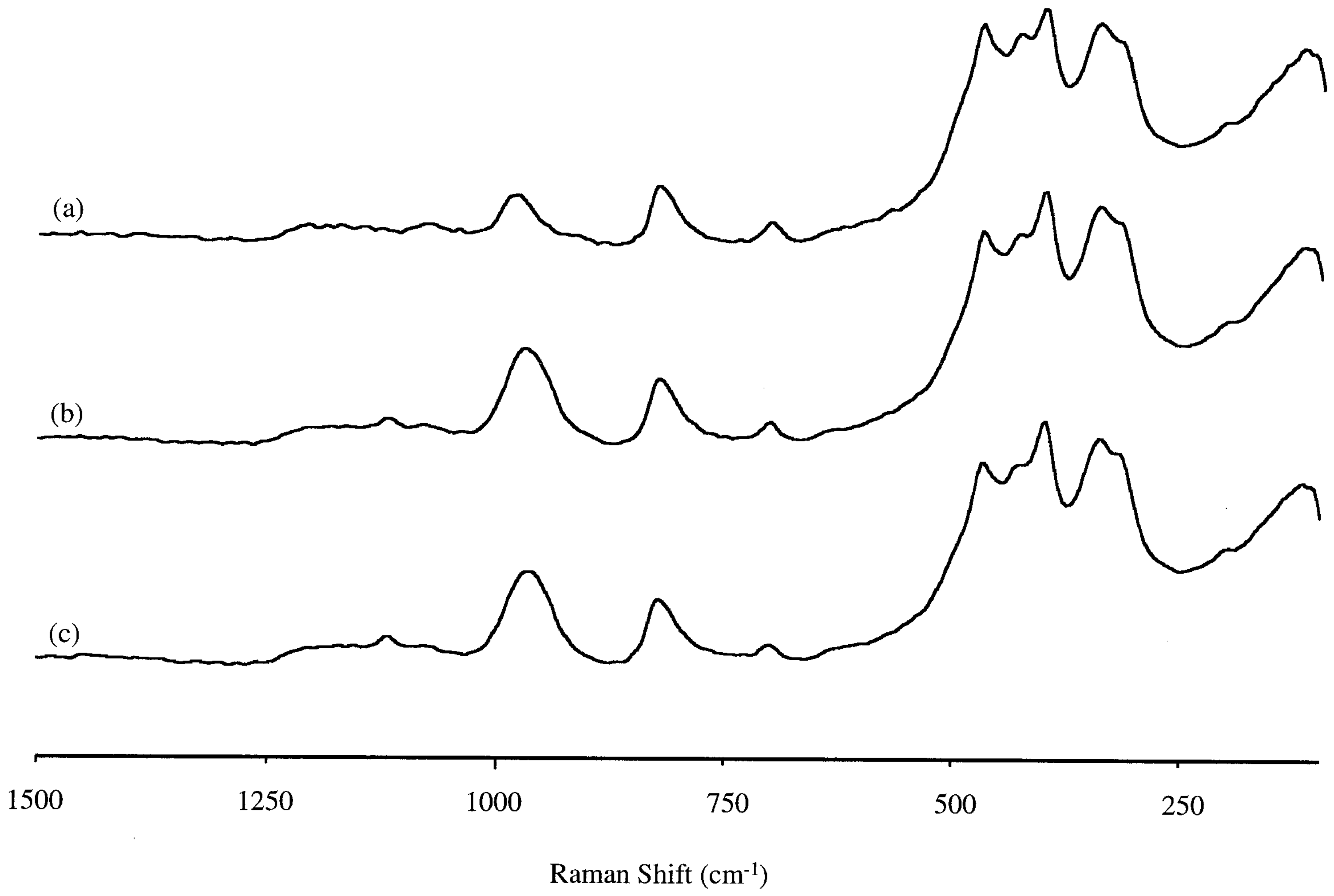

Figure 5.6 FT-Raman spectra of calcined Si-Beta (a), Ti-Beta(1) (b), and Ti-Beta(2) (c).

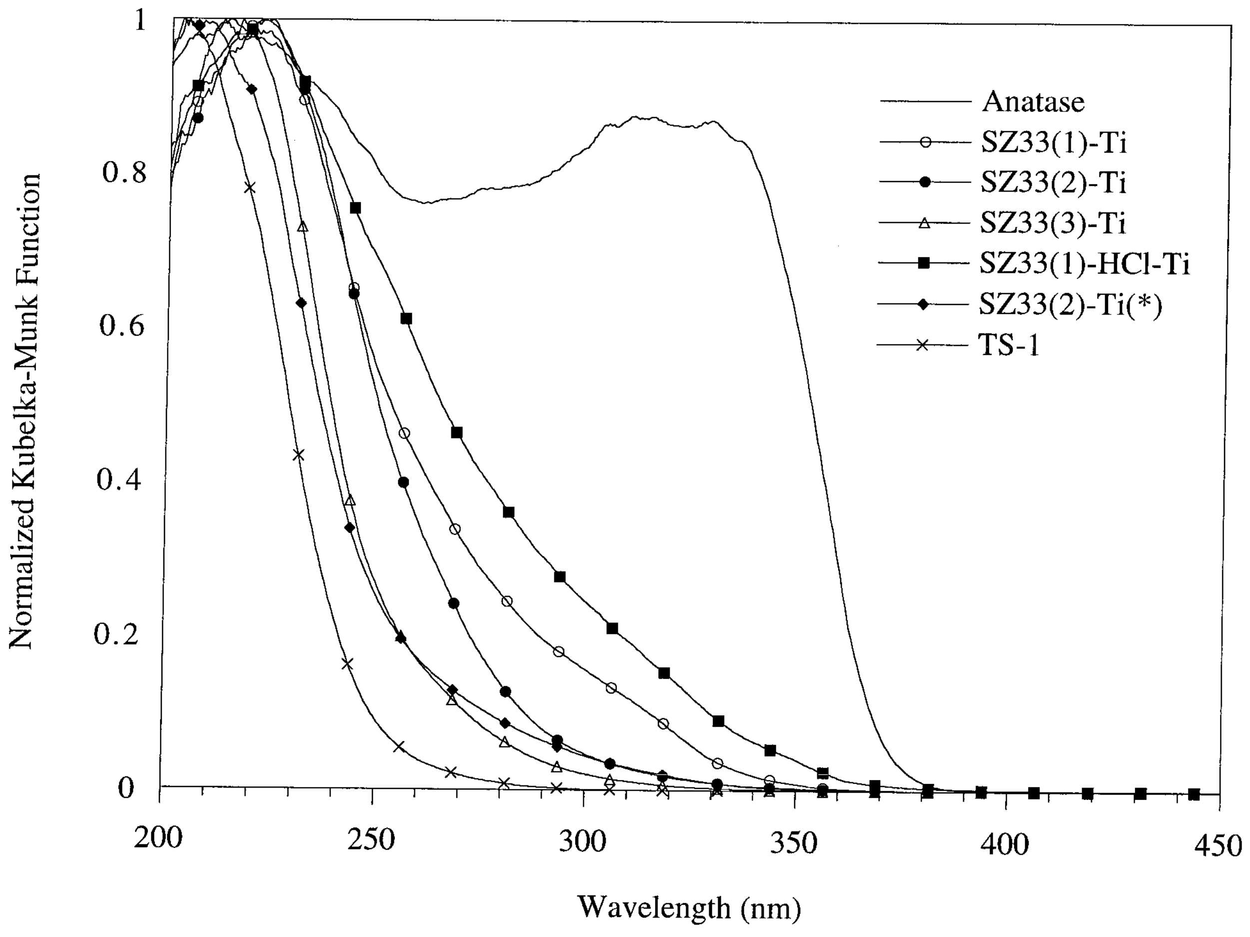

Figure 5.7 DR-UV spectra of various titanium-containing SSZ-33 materials

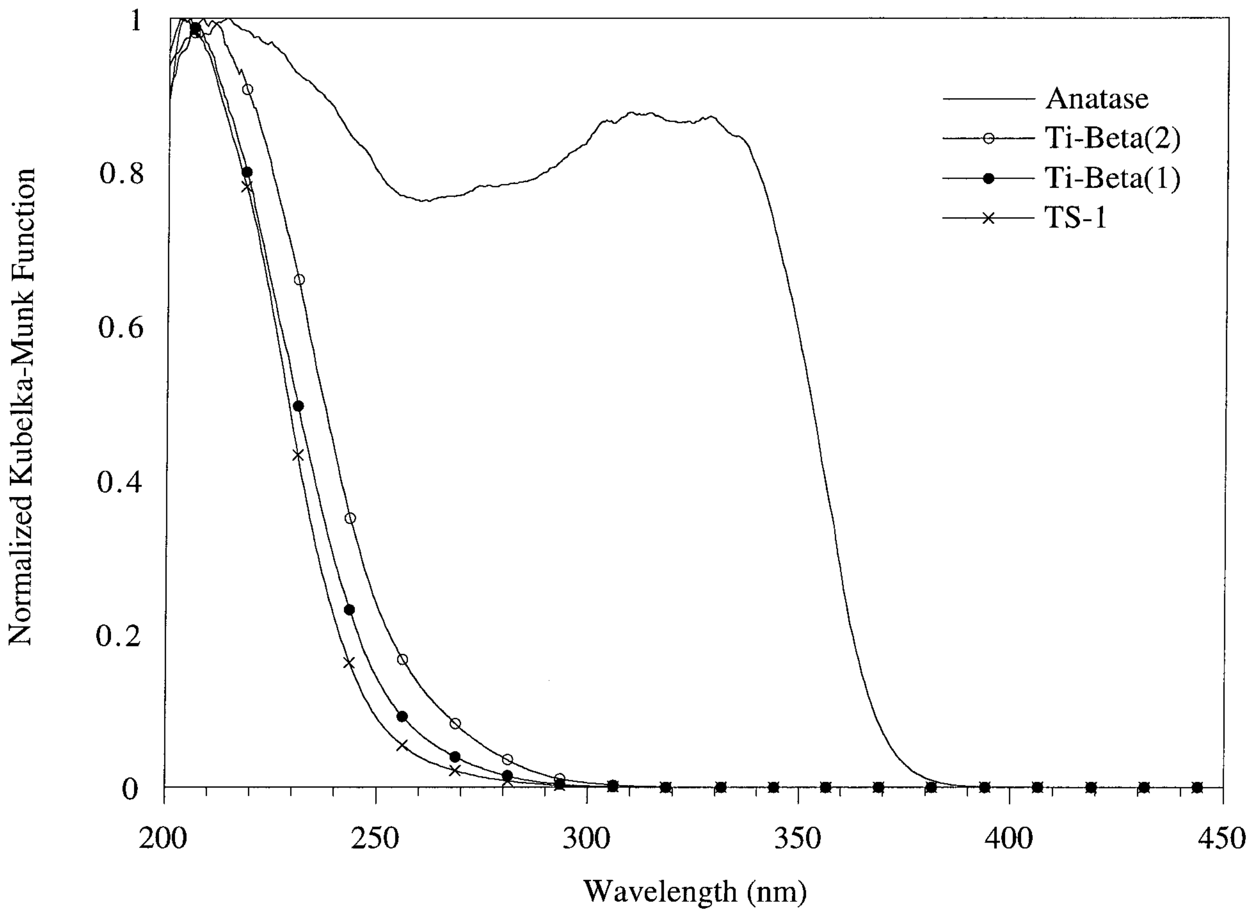

Figure 5.8 DR-UV spectra of TS-1, Ti-Beta(1), Ti-Beta(2), and anatase

CHAPTER SIX

Conclusions

The overview of emerging catalytic trends in the production of fine chemicals indicates that molecular sieve technology can help alleviate problems associated with selected catalytic systems. Some of the areas where zeolites have the greatest chance to impact reaction schemes are in non-traditional roles. The acidic nature of zeolites has been exploited for over thirty years. However, base catalysis with molecular sieves has recently been shown to be feasible for at least one intermediate used in the manufacture of fungicides. Production of certain valuable chemicals may also be achieved by taking advantage of the shape selective nature of these microporous solids. The size restrictions within the pores of a zeolite often favor the production of less bulky products, e.g., *meta* directed products of aromatic compounds. The ultimate challenge in shape-selectivity is the catalytic synthesis of a single enantiomer. The anchoring of chiral ligands to a zeolite support has shown promise in this regard. The crystallization of a chiral zeolite would also be a major step towards asymmetric heterogeneous catalysis, and this goal is being vigorously pursued. Another area of novel research is in the field of metal substituted zeolites. Titanium-containing molecular sieves have had an enormous impact on partial oxidation catalysis in the thirteen years since their discovery.

In an effort to learn more about these Ti-Si composite catalysts, 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 the oxidant at temperatures below 100 °C. Although some of the physicochemical properties of these samples are similar, significant differences are found amongst the catalysts prepared in different manners. 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 the oxidant. In a hydrophobic environment, such as a high-silica molecular sieve, water is most likely screened out of the pores in favor of the more abundant organic species. This prevents the typical problem of water strongly binding to titanium sites, rendering them inactive. Octahedral titanium in ETS-10 and titanium species in the TiO_2-SiO_2 co-precipitate are not catalytically active for the oxidation of alkanes, alkenes, and phenol using aqueous H_2O_2 as the oxidant. The higher coordination in ETS-10 most likely results in drastic steric hindrances around the metal center thereby blocking access of the reactants.

The addition of aluminum during the synthesis of TS-1 reduces its activity for n-octane oxidation. The aluminum is more easily incorporated into the framework, effectively leaving less sites for the titanium to reside. The presence of sodium in the synthesis gel of TS-1 completely eliminates the catalytic activity for alkane oxidation. The sodium present during synthesis of TS-1 causes TiO_2 to precipitate. This titanium phase is insoluble in the reactive gel and is not available for insertion into framework positions. However, the presence of sodium in pre-formed TS-1 does not have a significant effect on its catalytic activity. Once the titanium has been incorporated into the crystalline network, sodium is not able to cause its transformation to TiO_2.

In a more extensive study on synthesis effects, the TS-1 sample prepared from TEOS and TEOT proved to be the most active. Raman spectroscopy shows this sample to contain no anatase (extra-framework TiO_2). As the amount of anatase was found to increase, the hydrogen peroxide efficiency decreased. When colloidal SiO_2 or fumed, amorphous SiO_2 was used as the silica source, some titanium precipitated as anatase. Anatase formed in the preparation of a SiO_2/TiO_2 co-precipitate was found in the sample prepared using the co-precipitate as both the Si and Ti source. TS-1 prepared at near neutral pH conditions was found to contain no titanium in framework positions. Framework titanium was found to be necessary for olefin epoxidation as well as alkane hydroxylation.

Other zeolitic structures have been claimed as being capable of incorporating Ti atoms into lattice positions. ZSM-48 and zeolite Beta were both synthesized in the presence of titanium and tested for partial oxidation activity. In these studies, aluminum was used in the synthesis gel for zeolite Beta (both with and without Ti). The synthesis of Ti-ZSM-48 produced a material that did not contain framework titanium, and was inactive for epoxidation and alkane hydroxylation. Anatase was observed by Raman spectroscopy and very little increase in unit cell volume was measured. The Ti-Al-Beta catalyst was also inactive in the tests for oxidation activity. However, both framework and extra-framework titanium were observed through spectroscopic means. The presence of framework titanium should have resulted in some activity; the hydrophilic nature of this structure may have allowed water to reside in the pores in concentrations high enough to allow strong binding with the framework titanium centers. With water bound to the active sites, the catalyst would then be inactive for partial oxidation reactions. Both diffuse reflectance UV and Raman spectroscopies proved to be excellent methods for determining the state of the titanium in the catalysts. However, the presence of framework aluminum in the zeolite Beta samples resulted in an IR and Raman peak at approximately 960 cm^{-1}. This masks the presence of a band associated with framework siting of titanium.

To investigate the possibility of producing a large-pore molecular sieve active for epoxidation of olefins too large to react within TS-1, post-synthetic treatments were employed to place titanium within samples of SSZ-33. By reacting the samples with $TiCl_4$ vapor at elevated temperatures, this goal was accomplished. Titanium atoms are speculated to displace boron atoms formerly in the framework. This boron is then allowed to react with methanol to form a volatile product. Cyclooctene was epoxidized with these Ti-SSZ-33 samples, while TS-1 proved relatively inactive at similar conditions. Using spectroscopic methods described above, titanium was found to have been sited in framework positions of the molecular sieve. Unfortunately, this treatment led to extra-framework TiO_2 (as anatase) in these samples as well. Using a new structure-directing agent developed by researchers at ARCO [1], a titanium-containing sample of zeolite Beta free of aluminum was synthesized and tested. It was also active in the epoxidation of olefins too large to react easily within TS-1. Both the Ti-Beta and Ti-SSZ-33 catalysts had lower activity than TS-1 for small olefins which have minimal steric restrictions in any of the structures tested.

Literature Cited

1 U.S. Patent appl. #08/329732 assigned to ARCO Chemical Technology, L.P.