

# CHAPTER I

## INTRODUCTION

### 1.1 Why Oxidation Reaction?

Oxidation reactions are of prime importance at an industrial level and correspond to a huge market, for example in the US in 1994, about 31% of the catalytic production of major organic chemicals corresponded to oxidation catalytic processes. The market corresponds to 20 billions US \$ in the USA and world wide such numbers have roughly to be multiplied by a factor of 2.5 [1-2]. Oxidation reactions are widely practiced in industry and are thoroughly studied in academic and industrial laboratories. Catalyzed oxidation reactions are today one of the most dynamic and fruitful field in catalysis. Major achievements were attained in oxidation catalysis. They resulted in the development of many new selective oxidation processes; for example, oxidation of ethylene to acetaldehyde, oxidation of butylenes to maleic anhydride, oxidation of methanol to formaldehyde, etc [3-4]. These processes have deeply affected the structure of the global chemical industry. Environmental protection also relies mainly on oxidation reactions. Remarkable results obtained in this field contribute to promote the social image of chemistry which gradually changes from being the enemy of nature to becoming its friend and savior.

As a novel catalytic material, titanium silicalite-1 (TS-1) has attracted much attention last decade, because of its unique catalytic properties for the selective oxidations of organic compounds, such as aromatic hydroxylation, epoxidation of alkenes, ammoximation of cyclohexanone and oxidation of alkanes and alcohols by hydrogen peroxide as an oxidant. Among of them, the hydroxylation of phenol is one of the most important and promising chemical processes. The main industrial products from phenol include phenol resins, caprolactam, bisphenol A, adipic acid,

alkylphenols, and miscellaneous other products [5]. Catechol, hydroquinone and *p*-benzoquinone are the derivatives of high value. They are widely used as photographic chemicals, antioxidants, and polymerization inhibitors and are also used in pesticides, flavoring agents, and medicine. Catechol is also used as an organic sensitizer in a photoelectrochemical cell. It is most desirable that the dihydroxybenzenes could be produced by the direct hydroxylation of phenol with the environmentally benign oxidant, hydrogen peroxide ( $H_2O_2$ ). *p*-Benzoquinone can be widely used in medicine, herbicides, chemical reagents, dyes and tanning agents. It is used in cosmetic industries primarily because of its ability to transform certain nitrogen-containing compounds into a variety of colored substances. For medical purposes, *p*-benzoquinone is used in pharmaceutical industry for production of cortisone. cortisone is a steroid hormone. Also, it is used as a tanning agent for leather industries and also used in photographic chemicals as well. TS-1 is a heterogeneous catalyst like ZSM-5 zeolite, but the structure contains framework titanium atoms instead of aluminium atoms tetrahedrally connected to  $SiO_2$ , linkaged.

TS-1 was first discovered by Tarasmasso in 1983 [6]. Therefore, TS-1 is quite expensive because the typical synthesis requires the preparation of TPAOH solutions. The key to synthesize cheaper TS-1 is the use of the inexpensive homologous template TPABr. Tuel [7] reported the synthesis of TS-1 by using TPABr as the template and various types of amine as the base in replacement of TPAOH. Utilization of TPABr provides much larger TS-1 crystals than using TPAOH [8]. In the hydroxylation of phenol with hydrogen peroxide the product distribution is also influenced by particles size. Smaller particles are more active than larger particles. Too produce small particle, it would be of great interest to synthesize TS-1 with substituting TPAOH partly by reduced cost TPABr.

Recently, A novel zeolite-like material with MWW topology, Ti-MWW, was by combining hydrothermal synthesis and subsequent acid treatment [9]. It is hoped this material can expand the potential applications of titanosilicates because the MWW structure having a unique crystalline structure. It expected to serve as such a candidate for preparing Ti-containing catalysts that are both highly stable and accessible. Besides two-dimensional sinusoidal channels of 10-membered rings, its large supercages have a pocket in shape at the crystal exterior. The unique pore system of intracrystalline supercages and abundant pockets covering the thin hexagonal crystals has already proved to serve as an open reaction space more than

TS-1. However, Ti-MWW catalyst for phenol oxidation process was not been reported.

This project aims to study optimal condition for synthesis of TS-1 and Ti-MWW catalysts and their activities in the phenol oxidation reaction with  $H_2O_2$  as an oxidizing agent.

## 1.2 Objectives

1.2.1 To search for the optimum synthetic conditions for TS-1 and Ti-MWW

1.2.2 To synthesize and characterize TS-1 and Ti-MWW with Si/Ti ratios in gel of 40.

1.2.3 To study their activities in the oxidation of phenol.

## 1.3 Related Work

### 1.3.1 The TS-1 Catalyst.

Taramasso *et al.* [6] invented a new catalyst material constituted by silicon and titanium oxide. The material was given the name titanosilicalite-1 or TS-1, and corresponds to the following empirical formula  $xTiO_2 \cdot (1-x)SiO_2$ . TS-1 is usually synthesized by using tetrabutyl orthotitanate (TBOT) as  $TiO_2$  source, tetraethyl orthosilicate (TEOS) as  $SiO_2$  source and tetrapropylammoniumhydroxide (TPAOH) as template. The reaction took place in an aqueous phase at a temperature of  $130^\circ C$  to  $200^\circ C$ , and the solid product obtained was calcined in air at  $550^\circ C$ . A major problem often encountered during the synthesis of TS-1 molecular sieve is the precipitation of oxides of titanium outside the lattice framework, leading to inactive samples for oxidation reactions. The maximum amount of  $Ti^{IV}$  that can be accommodated in framework positions in TS-1 has been the subject of debate. Even though a good fit of the experimental data confirm the maximum value of  $x = Ti/(Ti + Si)$ , equal to 0.025 (corresponding to  $Si/Ti = 39$ ), several attempts [6] to synthesize TS-1 with Ti contents up to  $x = 0.09$  (*i.e.*,  $Si/Ti = 10$ ) were reported. Thangaraj *et al.* [10] reported the synthesis of TS-1 incorporating larger amounts of  $Ti^{IV}$  into the framework (*i.e.*,  $Si/Ti = 10$ ) by conventional hydrothermal synthesis. The crystallization was carried out for 1–5 days under static conditions.

Serrano *et al.* [11] synthesized TS-1 by wetness impregnation of amorphous and prepared SiO<sub>2</sub>-TiO<sub>2</sub> solids by the sol-gel method. The preparation of the raw SiO<sub>2</sub>-TiO<sub>2</sub> solids was carried out by different two step processes in order to achieve the formation of Si-O-Ti bonds prior to the zeolite synthesis. The properties of the TS-1 samples obtained strongly depend on the method used in preparation of the starting amorphous co-gel. The size of the crystallite ranges between 0.4 and 0.5 μm depending on the method used to prepare the raw Si-O<sub>2</sub>-TiO<sub>2</sub> co-gel.

Davis and Liu [12] found that the isolation of tetrahedrally coordinated Ti atoms in silica correlated with the activity and selectivity of alkane epoxidation reaction, which suggests that those atoms were the active sites for oxidation. The method of synthesis, which affected the degree of homogeneity of component mixing, played a crucial role in determining the surface character of final catalytic materials.

Grieneisen *et al.* [13] synthesized titanium silicate-1 (TS-1) from two different methods in fluoride medium. The key step of the synthesis was the preparation of a sol or gel containing Si-O-Ti bonds prior to fluoride addition. The mixed alkoxide method utilized TPAOH+HF and the wetness-impregnation used TPABr+NH<sub>4</sub>F. The mixture after addition of fluoride was transferred to Teflon-lined autoclave at 170°C for 5 days. The DR-UV result of mixed alkoxide method showed that the samples at Si/Ti ratio 42 showed only the wetness-impregnation method, the sample with Si/Ti ratio 90 exhibited only a strong band at 220 nm. The size of the crystals depended on the synthesis variables. In the presence of seeds, small crystallite (< 2μm) were obtained. The corresponding samples exhibited high activity and selectivity for phenol hydroxylation by H<sub>2</sub>O<sub>2</sub> similar to TS-1 prepared in the presence of tetrapropylammonium hydroxide.

Khomane *et al.* [14] synthesized TS-1 in the presence of small amount of TPAOH using Tween 20, as nonionic surfactant. The mixture was crystallized at 140°C for 18 h under autogeneous pressure at the Si/Ti ratio 33. The result from DR-UV showed a charge transfer band at 220 nm, which is a characteristic of isolated framework of Ti<sup>4+</sup>. The sample prepared without the use of surfactant, on the other hand showed a band at 330 nm, which suggested the presence of extra-framework of TiO<sub>2</sub>.

Lee *et al.* [15] investigated the effect of synthesis mixture composition on the physical characteristics of titanosilicate (TS-1). Tetraethyl orthosilicate and

tetraethyl orthotitanate were used as precursors and TPAOH as template. The reduction in specific surface areas observed for samples produced using the templating agent with relatively higher alkali metal content was postulated due to blocked zeolite pores and channels as a result of the formation extra-framework crystallites.

Ramakrishna *et al.* [16] improved process for the synthesis of titanium rich titanium silicate-1 (TS-1) by microwave heating. Tetraethyl orthosilicate (TEOS) and titanium tetrabutoxide (Ti (OBu)<sub>4</sub>, TBOT) were used as the source of silicon and titanium, respectively. The synthesis time required in the present sample was 30 min for the TS-1 (Si/Ti = 33) in contrast to the conventional hydrothermal synthesis that required 3-7 days. DR-UV spectra show a broad band around 200-280 nm attributed to tetrahedral and octahedral coordinated Ti to oxygen. The activities of catalysts for phenol hydroxylation reaction are comparable to the catalysts prepared by the conventional methods.

Tuel [7] reported on the synthesis of TS-1 using TPABr as the templating agent and a diamine, hexanediamine (C<sub>6</sub>DN), as the only base. C<sub>6</sub>DN was chosen because of its pK value (pK = 11.85), thus providing gels with a relatively high alkalinity. A major difference between TS-1 obtained following the present recipe and those obtained with TPAOH solutions was the very unusual habit of the crystals. Indeed, for low titanium contents, crystals were in the form of large elongated coffins (>3μm). Samples obtained by the present synthesis route and having relatively low titanium contents were to be active as catalysts in the hydroxylation of phenol. Although the activity was slightly lower than that of a standard TS-1, the para/ortho ratio at the end of the reaction was significantly higher. That was attributed to the difference in external surface areas between the two samples.

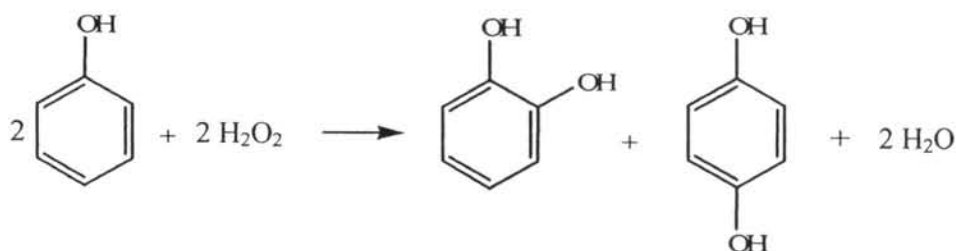
Xia and Gao [17] discovered a new procedure for the synthesis of pure titanium silicate-1 (TS-1). The crystallization kinetics of TS-1 mixed using quaternary ammonium halides (TEACl and TBACl) as template was studied. TEOS and TBOT were used as a source of silica and titanium and the crystallization was carried out statically at 160°C for 6-10 days. The influence of various synthetic parameters, like temperature, time, Si/Ti, (TEA and TBA)/Si, and NH<sub>3</sub>/Si, on the crystallization kinetics of TS-1 was investigated. The results showed that increasing the temperature of crystallization, Si/Ti ratio, (TEA and TBA)/Si, and NH<sub>3</sub>/Si ratio led to the increase in the crystallization rate and decrease in the mean crystal size. The dilution of the sol

mixture with water decreased the rate of crystallization and increased the average crystal size. The crystalline products were characterized and using X-ray diffraction (XRD), IR, UV-Vis, scanning electron microscopy (SEM) and chemical analysis methods. The hydroxylation of phenol with  $\text{H}_2\text{O}_2$  was employed as a test reaction for ascertaining the incorporation of Ti in the lattice of TS-1

The effect of organic amine to the formation of TS-1 [18] was studied with various types of amine which are *n*-butylamine, TEAOH, TBAOH, 1,6-hexanediamine, ethylenediamine, diethylamine and triethanolamine. To decrease the cost, TPABr was used as template instead of TPAOH. TBOT was used as the titanium source with the Si/Ti ratio of 33. They found that the organic amine cannot act as template in the presence of  $\text{TPA}^+$ . It can only regulate the basicity of the gel. The order of the template effect of different templates is as follows:  $\text{TPA}^+ > \text{TBA}^+ > \text{TEA}^+ > > \text{organic amine}$ . UV-Vis spectra of all prepared titanosilicalites show two absorption peaks: one at 220 nm, which was attributed to tetra-coordinated titanium, another at 270-280 nm, which is attributed to  $\text{Ti}^{4+}$  ions in an octahedral coordination with two water molecules in the coordination sphere or small hydrated oligomeric  $\text{TiO}_x$  species. TS-1 samples had larger crystal size (usually 2-3  $\mu\text{m}$  from SEM) than conventional TS-1. Van der Pol *et al.* [11] reported that when TS-1 particle size was larger than 0.3  $\mu\text{m}$ , diffusion limitation governed the hydroxylation rate of phenol with  $\text{H}_2\text{O}_2$ . While in epoxidation of propylene with  $\text{H}_2\text{O}_2$ , TS-1 samples with 2-3  $\mu\text{m}$  crystal size still remain high activity. The reason was perposed that the dynamic diameter of propylene (0.5 nm) is smaller than that of TS-1 (0.55-0.6 nm), so the diffusion limitation was not the controlling step during the epoxidation of propylene with hydrogen peroxide. Catalysts exhibited good performance in epoxidation of propylene was able to be obtained using TPABr as template and ammonia, *n*-butylamine, diethylamine, hexanediamine or TBAOH as base [19]. The synthesis of TS-1 by using TPABr as the template and *n*-butylamine as base was reported, and the catalytic properties were investigated in detail over the synthesized TS-1. The results showed that TS-1 of MFI structure had high crystallinity and large crystal size, and with two kinds of titanium species. The crystals appeared in the shape of elongated prisms of about  $6\mu\text{m} \times 2\mu\text{m} \times 1\mu\text{m}$ . However, it exhibited high activity in the epoxidation of propylene. Stirring vigorously and increasing the reaction time decreased the effect of crystal size on the catalytic properties. Methanol was formed to be a preferable solvent, and the addition of adequate amount of water

to the medium did not influence the reaction activity. The proper pH value was important for the epoxidation of propylene [20]. The synthesized TS-1 did not deactivate after use for 20 times. In the fixed-bed reactor, the catalyst remained high activity and selectivity when using ammonium water as neutralizer.

Van der Pol *et al.* [8] synthesized titanosilicalite-1 samples of different particle size. In the hydroxylation of phenol with hydrogen peroxide large differences in activity are found between different TS-1 samples. Smaller particles were more active than larger particles. From calculations of the Weisz modulus it can be concluded that large zeolite particles were not fully utilized because of pore diffusion limitations. The product distribution is also influenced by particle size. These authors excluded a major influence of external surface activity. On the other hand, Tuel *et al.* [21] concluded that the product ratio of hydroquinone to catechol was mainly controlled by the external surface activity. Hydroquinone and catechol were thought to be the preferred reaction products in the micropores of TS-1 and on the external surface titanium sites, respectively. Phenol was oxidized to give catechol hydroquinone and *p*-benzoquinone in almost equal yield and with high selectivity. The reaction is schematically represented as follows:



After initial discovery of the catalytic activity of TS-1 for this reaction [22-23], other titanium containing zeolites such as TS-2 have been found to be active catalysts; indeed, this reaction has become a standard for measurement of the activity and selectivity of different titanium-containing zeolites. Suitable solvents are H<sub>2</sub>O methanol mixtures or H<sub>2</sub>O-acetone mixtures. The best results, 94% selectivity based on the phenol and 84% based on H<sub>2</sub>O<sub>2</sub> at 30% conversion of the phenol, can be obtained only when all the reaction conditions are optimized. The temperature must be controlled within few degrees of 363 K, the addition of H<sub>2</sub>O<sub>2</sub> must be gradual, and

the catalyst must be a pure phase. The results are strongly influenced by the dimensions of the catalyst crystallites, the range 0.2-0.3  $\mu\text{m}$  giving the best performance, as discussed above. In a number of papers it has been reported that benzoquinones were formed as major products in the oxidation of phenol, especially at low conversions of  $\text{H}_2\text{O}_2$  but that they were not present in the final reaction mixture when all the  $\text{H}_2\text{O}_2$  had been consumed (24-27). However, it has recently been shown that an error in the analytical method was responsible for these results [28].

The oxidation of phenol with  $\text{H}_2\text{O}_2$  catalyzed by TS-1 obtained by secondary synthesis by reacting  $\text{TiCl}_4$  with preformed ZSM-5 has led to conflicting results. In one case, the catalytic activity was found to be identical to that of TS-1 [29-30]; in another, low activity and formation of tarry products were reported and ascribed to the residual activity of the starting material and/or the presence of extra-framework  $\text{TiO}_2$  [31]. The oxidation of phenol has also been investigated with  $\text{TiO}_2$  deposited on silicalite as the catalyst [32]. The performances of the TS-1 and TS-2 catalysts for this reaction were shown to be identical when the titanium contents and crystallite dimensions were equal [33]. Because the oxidation of phenol is sensitive to the purity of the titanium silicate catalyst, it has been used to evaluate the purity of the catalytic materials. A standard material called EURO TS-1 has recently been prepared and evaluated in several laboratories [34].

The high selectivity by which dihydroxybenzenes can be obtained from phenol and  $\text{H}_2\text{O}_2$  when titanium silicates are used as catalysts has led to the development of a new process and the construction of a plant capable of producing 10,000 tons of catechol and hydroquinone per year. This plant, built by Enichem in Ravenna, Italy, includes a catalyst production and regeneration unit. Having started operations in 1986 [35], this facility is working with excellent technical and economical results. The advantages of the new process relative to previous technologies include low  $\text{H}_2\text{O}_2$  decomposition and high phenol conversions, with the formation of <10% high-boiling by products. These characteristics minimize the power requirements and make the process economics competitive.

Yokoi *et al.* [36] investigated effect of time on phenol hydroxylation over the TS-1/ $\text{H}_2\text{O}_2$  system. TS-1 was hydrothermally synthesized and treated with acid to remove extraframework Ti species and residual alkali cations. The Si/Ti atomic ratio determined by ICP was 33 for the acid-treated TS-1. The UV spectra of acid-treated TS-1 showed mainly the isolated framework titanium of tetrahedral coordination. The



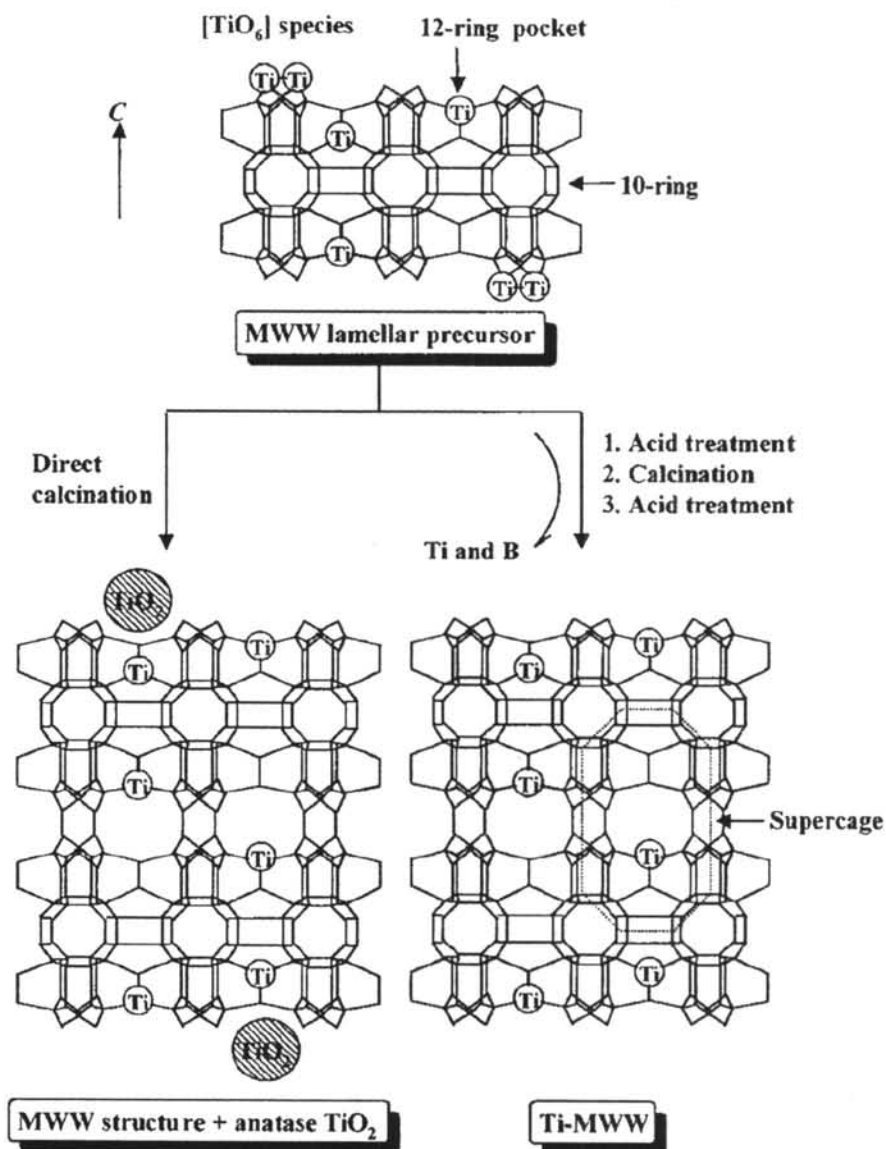
products of the hydroxylation of phenol over TS-1/H<sub>2</sub>O<sub>2</sub> system were catechol, hydroquinone and *p*-benzoquinone. For a typical run, 50 mg TS-1, 5 mmol phenol, 2.5 mmol H<sub>2</sub>O<sub>2</sub> as oxidant and 5 ml H<sub>2</sub>O as solvent were stirred vigorously at 333 K. The results showed that increasing the reaction time led to the increase in the conversion and decrease in the para/ortho ratio. The competitive oxidation of phenol with benzene was carried out under the same conditions with the exception of partly replacing phenol with the competitive substrate. The *p*-selectivity increased with increasing percentage of benzene in the substrates. It was suggested that the coexistence of benzene with phenol within the medium pores of TS-1 would impose enhanced restriction for the transition state of phenol hydroxylation to result in higher *p*-selectivity.

Wilkenhöner *et al.* [37] was investigated investigated to understand the role of the zeolite structure, the crystal size, the external surface of the zeolite, and the nature of the solvent on the product selectivity on phenol hydroxylation. Reaction was usually carried out at 60°C with magnetic stirring in a 24-ml glass batch reactor equipped with a Teflon sample port. After dissolution of 1.3 g of phenol in 5ml of the solvent, 0.13 g of TS-1 was added. To start the reaction 4.6 mmol of H<sub>2</sub>O<sub>2</sub> of a 30 wt% aqueous solution was added in a single portion. The conversion of phenol in the presence of hydrogen peroxide was determined by the pore geometry, the external surface titanium sites, the crystal size of the titanium containing molecular sieve, and the nature of the solvent. Smaller pore dimensions (TS-1 vs Al-free Ti-beta) led to a decreased conversion and an enhanced selectivity for hydroquinone. Comparing Al-free Ti-Beta and TS-1 samples with similar pore lengths, the activity as well as the ratio of catechol to hydroquinone was significantly higher for Al-free Ti-Beta, showing diffusional constraints for the conversion of phenol and geometric constraints for the formation of catechol. The phenol hydroxylation was strongly diffusion limited and small crystals should be applied. With small crystals the external surface sites contribute significantly to the total rate of reaction and its selectivity. Especially in water as solvent, a significant part of phenol conversion was due to external surface activity. While in the pores of TS-1, hydroquinone was clearly the preferred product, the major product formed on the external surface was solvent dependent: catechol was preferred in acetone, hydroquinone in protic solvents. In protic solvents, the coordination of solvent molecules to the titanium peroxo site led

to a geometric constraint in the TS-1 pores, inducing “transition-state shape selectivity” with the para isomer preferentially formed.

### 1.3.2 The Ti-MWW Catalyst.

Wu *et al.* [6] has been successfully prepared a novel MWW-type titanosilicate containing the tetrahedral Ti species in the framework by combining a conventional hydrothermal synthesis and an acid treatment. The lamellar precursor containing Ti can be synthesized with Piperidine or hexamethyleneimine as a structure directing agent in alkali-free conditions, but boric acid is necessary as a structure supporting agent. The formation process lamellar precursor is described graphically in Figure 1.1, where for clarity, Si, B, O, and organic species are omitted, but with an emphasis on Ti sites. Ti species incorporated occupy both the tetrahedral framework sites within the sheets and octahedral sites on the terminal surface of the sheets. A direct calcination on the precursor caused crystallization between the sheets to form the three-dimensional MWW structure and simultaneously a condensation of octahedral Ti species to form an anatase phase, which was hardly removed by acid treatment. However, by treating directly the lamellar precursor with an acid solution, the octahedral Ti species were removed readily together with a large amount of B, while the tetrahedral Ti species remained to a high level. Subsequent calcination led to the total formation of the MWW structure with tetrahedral Ti species probably existing within the supercages, the exterior pockets, and the channels of the 10-ring. Ti-MWW catalysts have been studied for the oxidation of alkenes (cyclohexene and 1-hexene) using hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) as an oxidant [38]. Ti-MWW shows superior activity independent of the nature of oxidant when compared to the other Ti-containing catalysts both of microporous TS-1 and Ti-MOR and of mesoporous Ti-MCM-41 in the oxidation of cyclohexene. Compared to large-pore Ti-Beta, Ti-MWW is less active than in the oxidation of cyclohexene using H<sub>2</sub>O<sub>2</sub>, but it shows comparable activity in the case of TBHP. Ti-MWW is very stable in both the structure and the states of Ti species in the actual cycle of reaction regeneration. The framework B species remaining within the Ti-MWW catalysts seem to have little influence on the intrinsic activity of framework Ti species.



**Figure 1.1** The formation of lamellar precursor between the sheets to form the three-dimensional MWW structure.

The catalytic properties of Ti-MWW in the epoxidation of allyl alcohol (AAL) with hydrogen peroxide to glycidol (GLY) have been studied in detail by a comparison with those of TS-1 and pure silica Ti-Beta [39]. Ti-MWW catalyzed the AAL epoxidation more actively and selectively than TS-1 and Ti-Beta in the presence of H<sub>2</sub>O or MeCN, and exhibited a conversion of 95% for AAL and a selectivity of

99% for GLY when the AAL epoxidation was carried out at 333 K for 30 min and at 12 wt% of catalyst to substrate. It is conceivable that the unique tortuosity makes the sinusoidal 10-MR channels of Ti-MWW more suitable for molecular diffusion, and also allows the Ti sites to be more accessible to the carbon-carbon double bonds of substrate molecules than those in the tunnel-like channels of TS-1. Ti-MWW was more hydrophilic than TS-1, but much more hydrophobic than Ti-Beta. The hydrophilicity of Ti-MWW was presumed to derive mainly from the defect sites due to the incomplete dehydroxylation between the layers and partially as a result of deboronation. The sinusoidal 10-MR channels serving as the reaction space for the AAL epoxidation were considered to be hydrophobic, thus rendering the Ti-MWW catalyst applicable to the substrates and solvents, both of a polar nature.

Catalytic properties of Ti-MWW in the epoxidation of *cis/trans*-alkenes (hex-2-enes, hept-2-enes, hept-3-enes and oct-2-enes) were investigated in detail by comparing with TS-1 and Ti-Beta [40]. The effects of reaction conditions, alkenes, and oxidants on the product selectivity, and the characterizations such as liquid adsorption and determination of active sites by selective poisoning have been carried out extensively to clarify the mechanism of the *trans*-selectivity of Ti-MWW. Ti-MWW exhibits a singularity never been observed on conventional titanosilicates, that it selectively epoxidizes the *trans*-isomer to give a selectivity of ca. 80% for corresponding *trans*-epoxide from an alkene mixture with a *cis/trans* ratio of 50:50. The uniqueness of Ti-MWW strongly attracts our attention to the importance of "steric fitting" between the substrate molecules and the Ti species when investigating into the shape selectivity. Besides the well-known shape selectivity for reactants, products and transition-states the unusual results observed on novel Ti-MWW for the stereoisomers of alkenes bring out a new concept of the shape selectivity in the constrained space in heterogeneous catalysts.