

CHAPTER II LITERATURE REVIEW

2.1 Synthesis of TS-1 Zeolite

TS-1 has become one of increasing interests due to a variety of important applications. The presence of Ti atoms occupying framework position in the zeolite lattice is responsible for the remarkably catalytic properties for a broad range of oxidations with hydrogen peroxide. The most relevant oxidation reactions catalyzed by TS-1 are summarized in figure 2.1.

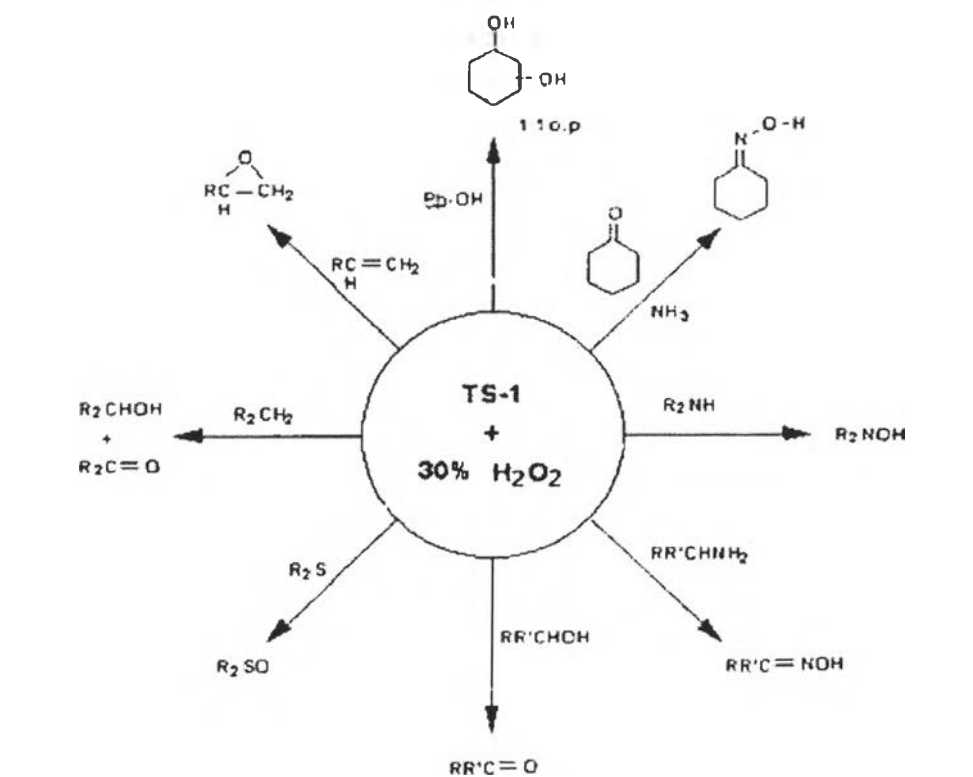


Figure 2.1: Schematic representation of the most relevant oxidation reaction catalyzed by TS-1.

In the years since Taramasso and co-workers first synthesized the zeolite titanium silicalite (TS-1), this material has attracted a great deal of

attention from many scientists to improve the method and precursor for higher level of titanium incorporation in TS-1 framework.

Serrano *et al.* (1995) synthesized TS-1 by wetness impregnation of amorphous and prepared SiO₂-TiO₂ solids by the sol-gel method. The preparation of the raw SiO₂-TiO₂ 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 to prepare the starting amorphous co-gel. The size of the crystallites ranges between 0.4 and 5 μm depending on the method used to prepare the raw SiO₂-TiO₂ co-gel.

Xia and Gao (1997) discovered a new procedure for the synthesis of pure titanium silicate-1 (TS-1). The influence of various synthetic parameters, like temperature, time, Si/Ti, (TEA+TBA)/Si, and NH₃/Si, on the crystallization kinetics of TS-1 was investigated. The results showed that increasing the temperature of crystallization, Si/Ti ratio, (TEA+TBA)/Si, and NH₃/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 using X-ray diffraction (XRD), IR, UV-Vis, scanning electron microscopy (SEM) and chemical analysis methods. The hydroxylation of phenol with H₂O₂ was employed as a test reaction for ascertaining the incorporation of Ti in the lattice of TS-1.

Davis and Liu (1998) 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 the final catalytic materials.

Grieneisen *et al.* (2000) 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. Characterization of the samples confirmed that the titanium species

were essentially located in framework position. The size of the crystals depends on the synthesis variables. The corresponding samples exhibited high activity and selectivity for phenol hydroxylation by H_2O_2 , similar to TS-1 prepared in the presence of tetrapropylammonium hydroxide.

Marro *et al.* (2000) studied the orthorhombic to monoclinic phase transition in high titanium loaded Ti-silicalite sample (2.6 wt% in TiO_2) using x-ray diffraction. They observed the transition temperature between the orthorhombic phase of $3 \times 1 \times 3$ and $3 \times 1 \times 3$ reflections. Refinement of the former data gave weak evidence, which about half of the total Ti content was located in the condition with 0.19 and 0.11 of titanium fraction. The result did not show any tendency to be hosted in the condition with -0.01 and -0.04 of titanium fraction, and that the remaining Ti atoms seemed to spread among the remaining eight T sites.

Newalkar *et al.* (2000) successfully prepared titanium substituted mesoporous SBA-15 molecular sieve at 373 K, using direct synthesis under microwave hydrothermal conditions within about 2 h. They found that isomorphous substitution of titanium in the silica framework of SBA-15 samples with Si/Ti ratios of 20, 30, and 40 occurred. The higher titanium loading led to the formation of extraframework titanium species. These results showed that microwave assisted synthesis was an ideal approach to prepare Ti substituted SBA-15, which is expected to be useful as a selective oxidation catalyst for reaction involving large molecules.

Bordiga *et al.* (2001) studied how the use of an UV laser ($\lambda = 244 \text{ nm}$) as exciting source of Raman spectra to enhance the 1125 cm^{-1} mode of TS-1, leaving the 960 cm^{-1} was unaffected. Quantum chemical calculations had unambiguously assigned the IR, Raman and Resonance Raman features of TS-1, on the basis of the symmetry of the vibrational modes related to the 1125 and 960 cm^{-1} component. On the structural ground, composition between neutron diffraction data performed on TS-1 and on Ti-free silicate allowed them to infer the insertion mechanism of Ti into the MFI lattice during synthesis.

Yeon and Frei (2001) found that irradiation at 266 nm of Ti silicalite (TS-1) molecular sieve loaded with CO and CH₃OH gas at 173 k gave methyl formate as the main product. CO was a photo-reduced ansient Ti³⁺ to HCO radical in the primary redox step. This finding opened up the possibility for the synthesis of carbon monoxide in transition metal materials by photo-activation of framework metal centers.

Kunii *et al.* (2002) prepared aluminophosphate molecular sieves (AlPO₄'s) by microwave heating without using organic template reagents. Aluminophosphate hydrous gels were prepared using three different kinds of aluminum sources, amorphous aluminum hydroxide, gibbsite, and boehmite. From the results, the microwave heating enhanced the crystallization of aluminophosphate gels, and gels were successfully obtained as single phase in a relatively short reaction time. The microwave can rise the temperature of the reactant to a desired range quickly in a few minutes and the heat is supposedly induced by the fiction of molecular rotation enhanced by microwave irradiation, thus, it is possible to heat the reactants selectively and homogeneously from the inside.

Lee *et al.* (2002) investigated the effect of synthesis mixture composition on the physical characteristics of titanium silicate (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.* (2002) improved process for the synthesis of titanium rich titanium silicate-1 (TS-1) by microwave heating. Tetraethyl orthosilicate (TEOS) and titanium tetrabutoxide (Ti (OBu)₄, TBOT) were used as the sources 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 with the conventional hydrothermal synthesis that required 3-7 days.