

CHAPTER I

INTRODUCTION

1.1 Background

Ti-containing zeolite with the MFI structure, TS-1, has become one of increasing interests due to a variety of important applications. In particular, this zeolite can function either as a catalyst by itself or as a catalyst support. The presence of Ti atoms occupying framework positions in the zeolite lattice is responsible for the remarkable catalytic properties for a broad range of oxidations with hydrogen peroxide, such as the epoxidation of olefins, the oxidation of saturated hydrocarbons, and the oxidation of alcohol. The titanium in silicalite framework sites is proposed to form a five-membered cyclic structure, combining a titanium hydrogeneous moiety (Ti-OOH) and a protic molecular at the Ti sites, which has been suggested as the active species for epoxidation of lower olefins with hydrogen peroxide. The activation of H₂O₂ on the titanyl group by formation of titanium peroxy complexes has also been proposed for the ammoximation reaction mechanism. Structurally, the titanium in TS-1 isomorphously replaces silicon in a tetrahedral site of the MFI silicalite lattice. As such, it combines the advantages of the high coordination, ability of Ti⁴⁺ ions with the hydrophobicity of the silicalite framework, while retaining the spatial selectivity and specific local geometry of the active sites of the molecular sieve structure.

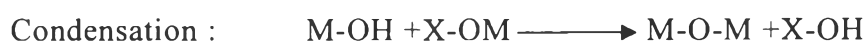
Although some researchers have observed that increasing the titanium content of TS-1 enhances its catalytic activity, there is a limit to the possible extent of incorporation of titanium into the tetrahedral framework. Theoretically, the larger size of its ionic radius precludes titanium incorporation in the lattice of the silicalite structure, however, in practice tetravalent titanium is usually present in an octahedral coordination. The synthesis of material containing isolated tetrahedral Ti is rather difficult giving its strong tendency to polymerize in aqueous systems-especially at the

high pH conditions normally encountered in TS-1 synthesis, often resulting in the formation of separating, stable titanium dioxides phases.

The maximum mole fraction of titanium incorporated in TS-1 framework reported in the original patent was 0.025, which corresponds to approximately 2.5 Ti per unit cell. Criticism of research reporting high levels of titanium incorporation generally centres on the extent and detail of characterization of the titanium species, suggesting that much of the material is actually present as extra framework Ti. There is significant difficulty preventing TiO_2 from precipitating during crystallization when the synthesis solution contains over 2 weight percent titanium. The presence of extra framework titanium dioxide significantly lowers the catalytic activity of the material because of its high activity for the decomposition of hydrogen peroxide to water and oxygen as well as the possibility of the TiO_2 blocking access of reacting molecules to the internal active framework Ti^{4+} sites. Therefore, the location of the titanium ions in framework or extra-framework positions and their coordination in the molecular sieves are interesting not only from a structural point of view, but also in connection with the mechanism of the catalytic transformations (Lee and Porter, 2002).

1.2 Zeolite Synthesis

Most zeolites used come from either nature or synthesis. Synthetic zeolites are obtained via the sol-gel process which amorphous gel is produced from an interaction between titanium glycolate and silicate or silica sol. The sol-gel process undergoes two main steps, hydrolysis and condensation reactions. ($x = \text{H or R}$)



The rate trends in acid and base catalyzed process for successive hydrolysis of the four alkoxy groups around metal can be described in term of electronic effects. Alkyl groups are more electron donation group than

hydroxy group. Thus, for the positively charged transition state of the acid-catalyzed reaction, which more alkoxy groups are replaced by hydroxy groups, the transition state becomes less stabilized and the reaction rate decreases. Conversely, for the negatively charge transition state of the base-catalyzed reaction, more OH groups mean more stabilization of the transition state and faster reaction. Similar arguments obviously show that the reverse esterification reaction rate is more likely in acidic conditions, where esterification stabilizes the transition state, than in basic conditions.

To obtain any crystalline phase, further hydrothermal treatment is needed. It can be processed by either conventional or microwave heating. In both systems, the amorphous gel undergoes continual dissolution and reconstruction, and crystalline phase grows (Barrer, 1983 and Szostak, 1989) under hydro-pressure. However, the nucleation rate in both cases is different. For conventional heating, transferring heat from the generation source to media or materials deals with heat transfer coefficient of each material, causing convection current of heat or non homogeneous heat distribution. As a result, the nucleation rate is very fast at the area of high temperature and very low at low temperature region (Sathupunya *et al.*, 2002).

The application of microwave to chemical synthesis has received considerable attention during recent times. Microwave irradiation induces rapid rotation of the polarized dipoles of the dielectric materials. Because of uniform adsorption of microwave energy throughout the entire volume of reaction mixture, rapid heating can be also achieved. Microwave irradiation, in-conjunction with the use of supported reagents, provides high yield protocols in organic synthesis with enhanced reaction rates and better selectivity. For the synthesis of microporous molecular sieves, the advantage is utilized to get homogeneous nucleation and substantial reduction in crystallization time periods compared to the conventional method (Ramakrishna *et al.*, 2002).

In this work, the influence of synthesis parameters, which are Si/Ti, Na⁺/Si, TPA/Si, OH⁻/Si, reaction temperature, reaction time and aging time on the crystallization kinetics of TS-1 were studied by microwave technique.

From previous work, control of hydrolysis and condensation is the key to synthesis of mesoporous and microporous materials through sol-gel processing. The moisture-stable and inexpensive titanium glycolate and silatrane (Piboonchaisit *et al.*, 1999), synthesized by the OOPS method (Phonthammachai *et al.*, 2003), were used as precursors.

1.3 Objective

The objective of this research work is to study the influence of Si/Ti, Na⁺/Si, TPA/Si, OH⁻/Si, reaction temperature, aging time, and reaction time to the crystallization of TS-1.