



CHAPTER I

INTRODUCTION

The discovery of titanium silicalite-1 (TS-1) which is a zeolite of the pentasil family by Taramasso and co-worker in 1983 opened a new route for the catalysis and catalytic reaction. The new material has attracted a great deal of attention. Structurally, the titanium (Ti^{4+}) in TS-1 isomorphously replaces silicon (Si^{4+}) in a tetrahedral site of the MFI silicalite lattice. As such, it combines the advantages of the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicalite framework, while retains the spatial selectivity and specific local geometry of the active sites of molecular sieve structure.

As a novel catalytic material, TS-1 has attracted much attention since the 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. Schuster et al. (2001) reported that TS-1 was a very active catalyst for the gas phase oxidative dehydrogenation of propane. Wang et al. (2005) reported that TS-1 could catalyze the epoxidation of allyl chloride with molecular oxygen in the presence of 2-ethyl anthrahydroquinone under mild conditions. Furthermore, it has been reported that TS-1 possessed an excellent stability, and could be reused without significant loss of activity for the ammoximation of cyclohexanone in acetic acid (Sooknoi and Chitranuwatkul, 2005).

In recent years, the number of metals e.g. V, Al, Cr, Fe, Co and Ru were introduced as a second metal into the TS-1 matrix to improve some properties of the catalyst. Laufer and Hoelderich (2001) found that Pd/Pt/TS-1 catalyst could improve the selectivity of propylene oxide in the direct oxidation of propylene. Ma et al. (2005) studied the transesterification of dimethyl oxalate with phenol over stannum modified TS-1 and found that the Sn-modified TS-1 catalysts had fewer Lewis acid sites than the unmodified TS-1 but its catalytic activity was increased greatly by the interaction of Sn with $Ti-O-SiO_3$ weak Lewis acid centers. Gas-phase epoxidation of

propylene over small gold ensembles on TS-1 was investigated by Taylor et al. (2005). They found that low gold loadings resulted in an inherently small number of very active sites and forcing the gold loading to higher values resulted in poor activity and stability. Zhao and Wang (2006) synthesized series of chromium catalysts supported on TS-1 molecular sieves with different atomic ratios of silicon/titanium (n_{Si}/n_{Ti}) by impregnation method and found that Cr/TS-1 ($n_{Si}/n_{Ti} = 30$) catalyst effectively dehydrogenated ethane to ethylene in the presence of carbon dioxide.

Since vanadium is a key component of several selective catalysts for the oxidation reaction, therefore interest lies also in comparing the vanadium based catalyst with the other metals based catalysts. Martinez-Mendez et al. (2006) studied the catalytic properties of silica supported titanium, vanadium and niobium oxide nanoparticles towards the oxidation of different organic substrates (cyclohexane, cyclohexene, 1-hexene) using tertbutylhydroperoxide (TBHP) and molecular oxygen as the oxidizing agents and reported that vanadium oxide nanoparticles gave the highest oxidation activity for the three substrate studied. Furthermore, vanadium has been largely studied in modifying many zeolites including zeolite in pentasil family. Pirutko et al. (2001) synthesized the metal modified TS-1 catalysts and tested in the oxidation of benzene to phenol by N_2O . Vanadium was one of metal used for loading into TS-1 catalyst but they had not paid an attention to this synthesized V/TS-1 catalyst. Sunphloi (2005) studied the effect of amount of vanadium on TS-1 structure and its catalytic activity in gas phase oxidation of 2-propanol. Vanadium titanium silicalite-1 catalysts (V/TS-1) were synthesized using hydrothermal method by adding the amount of vanadium salt (VCl_3) in both gel solution and decant solution. The research found that the highest quantity of vanadium could be incorporated into the TS-1 before the collapse MFI structure is about 0.3% mole and the surface area of the prepared catalysts decreased inversely with the amount of vanadium incorporated into TS-1 and the vanadium added into catalyst could improve the dehydration reaction.

The influence of synthesis parameters of vanadium incorporated in zeolites was also investigated. Aldalgisa et al. (2006) prepared vanadium silicalite-1 samples at 170 °C from fluoride-containing gels. The amounts of vanadium and fluoride salts were varied in gels of initial composition $10SiO_2 : xVO_2 : 1.25TPABr : yMF : 330H_2O$

with the vanadium source = VOSO_4 , V_2O_5 , $\text{VO}(\text{acac})_2$ and $0.05 \leq x \leq 3.0$; $\text{M} = \text{NH}_4$, Na , K and $y = 1, 3, 5, 7, 10$ and $\text{TPABr} = \text{tetrapropylammonium bromide}$. They investigated the influence of synthesis parameters (Na/Si , MF/Si , Si/V , the vanadium source) and found that sodium and potassium cations showed different behaviors with respect to ammonium ions on the crystallization rates and crystal aspect ratios. Crystal morphologies were found to be strongly influenced by the nature of the fluoride salt added to the reaction mixture. The vanadium incorporation in zeolite crystals increased regularly with the initial transition metal and fluoride content in the reaction batch and the vanadium incorporation was similar for the various salts used. Parvulescu et al. (2003) studied the effect of the preparation conditions (direct hydrothermal synthesis or impregnation) on the structure, texture, morphology and acidity of vanadium incorporated mesoporous silicate catalysts and they found that vanadium modified mesoporous silicates with a well ordered hexagonal and cubic structure were synthesized by direct hydrothermal synthesis or impregnation. All of the synthesized V-MCM-41 catalysts had very low activity in the oxidation of alcohols and high activity and selectivity in the oxidation of styrene and benzene.

From the former researches, we can see that different synthesis parameters had some influence on the structure and catalytic activity of the metal modified molecular sieve catalyst. For preparing a metal modified TS-1, there are many different methods such as incorporation, impregnation, deposition-precipitation and ion exchange. The previous researches reported that different preparation methods gave different catalytic properties of the prepared catalysts. Li et al. (2004) synthesized Cu-TS-1/cordierite catalysts as catalysts for selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by ion-exchange and impregnation methods. They found that Cu-TS-1/cordierite prepared with two methods both exhibited similar high activities, but the ion-exchanged Cu-TS-1/cordierite had superior duration and anti-poison properties while the impregnated Cu-TS-1/cordierite not. Guo et al. (2004) studied the effect of preparation method on the catalytic properties of Ag/TS-1 in the gas phase epoxidation of propylene in a fixed bed, quartz reactor. The results showed that the catalysts prepared by both deposition-precipitation and impregnation methods exhibited catalytic activity and selectivity in the reaction. 0.48% propylene conversion with 57.88% selectivity to propylene oxide was obtained over Ag/TS-1

catalyst prepared by impregnation method. However, the deposition-precipitation method was optimum.

The incorporation is the easiest way to prepare the metal modified TS-1 catalyst because the mixture of the second metal and the reagents will be crystallized in only one step by the hydrothermal method. Two sets of solution are used to prepare the modified TS-1 in this method, the gel solution and the decant solution. Since it has been reported that vanadium was loaded into the TS-1 using incorporation method by adding the amount of vanadium salt in both gel solution and decant solution gave the highest limit of vanadium quantity that could be incorporated into the TS-1 before the collapse MFI structure (Sunphloi, 2005). The interesting problems had been raised; those are if vanadium was loaded into the TS-1 by adding the amount of vanadium salt in either gel solution or decant solution, would it give the same results as the previous research and what will happen if we use the different vanadium sources that have different oxidation states of vanadium.

Since, this research initially focused on the preparation of the vanadium titanium silicalite-1 (V/TS-1) catalyst using the incorporation technique to introduce vanadium from different vanadium sources (VCl_3 , $VO(acac)_2$, V_2O_5) into the TS-1 structure during the hydrothermal synthesis. Therefore, the objective of this research is to study the influences of synthesis methodology (method of vanadium salt addition i.e. incorporation method) by adding the amount of vanadium salt in either gel solution or decant solution. Catalyst characterization and catalytic behavior using the gas phase oxidation of 2-propanol as a test reaction will be considered afterwards.

The advantage of using the reaction in gas phase is to eliminate a problem about mixing of reactants with different polarity that tends to exist in liquid phase. Since, 2-propanol has only one reactive group, the OH group in the molecule assists in tracing the reaction pathway. This OH group may be dehydrated to produce C=C bond or oxidized to produce C=O bond. The oxidation product may be an aldehyde or a ketone depends on the location of the OH group. For 2-propanol, the ordinary product from the oxidation should be acetone and the product from the dehydration is propylene.

The specific scopes of this research are:

1. The V/TS-1 catalysts ($\text{Si/Ti} = 50$, $\text{Si/V} = 100$) are synthesized by hydrothermal method using titanium(IV)butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$), sodium silicate ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$), vanadium(III)chloride (VCl_3), vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) and Vanadium(V)oxide (V_2O_5) as the source of Ti, Si, V^{3+} , V^{4+} and V^{5+} respectively for preparation of the gel solution and the decant solution. Tetrapropylammonium bromide ($(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NBr}$) is used as the organic template.

2. The synthesis parameters investigated is the addition step of vanadium salt. The vanadium salt is added in either the gel solution or the decant solution or both. The effects of using different types of vanadium salt are investigated afterwards.

3. The synthesized catalysts are characterized by necessary methods, for example as X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Brunaur-Emmett-Teller (BET) surface area, pore volume and pore sized analysis, Scanning electron microscopy (SEM), Electron spin resonance (ESR) and Temperature programmed desorption (TPD).

4. The catalytic behavior of the synthesized catalysts are evaluated by using the gas phase oxidation of 2-propanol (8 vol% oxygen, 5 vol% 2-propanol, balanced with argon) as a test reaction. The catalytic reaction is carried out in a microreactor at a temperature range 100-500 °C, atmosphere pressure.

This present work is organized as follows:

The background and the scopes of the research are described in Chapter I.

The theory about the framework substitution, the properties of titanium silicalite-1, the hydrothermal method, the basic catalyst characterization methods and a criteria for test reaction selection including an expanded discussion of alcohol reactions (i.e. oxidation and dehydration) are illustrated in Chapter II.

The experimental procedure of this research consists of the standard TS-1 synthesis procedure, the previously used synthesis procedure of the V/TS-1 catalyst, the catalyst characterization and the catalytic reaction in gas phase oxidation of 2-propanol are presented in Chapter III.

Chapter IV shows the results of the catalyst characterization and the gas phase oxidation of 2-propanol over the synthesized catalysts including an expanded discussion.

Chapter V contains the overall conclusion emerging from this research and some recommendation of future work.

Finally, the example of the calculation of catalyst preparation and acid site, calibration curves from area to mole of 2-propanol, propylene, acetone and carbondioxide, and the experimental data which had emerged from this research are included in appendices at the end of this thesis.