

CHAPTER I

INTRODUCTION

Titanium silicalite-1 (TS-1) catalyst, one of the most important innovations in heterogeneous catalysis over the last decades, was revealed in 1983 by Taramasso and co-workers. The structure of TS-1 which is a zeolite of the pentasil family is MFI structure. TS-1 is a high performances composite material specially designed for industrial oxidation reactions because its satisfied activity on several oxidation reactions. TS-1 has good thermal stability and non-corrosive nature. Therefore, there are the varieties of useful reactions used TS-1 catalyst as shown in Table 1.1.

It is clear that during the past years, the development to improve properties of TS-1 catalyst to satisfy the requirement of some reactions has been impressive. According to literatures, there were attempts to improve performance of TS-1 catalyst as support of the second metal as shown in Table 1.2. The advantage of deposition-precipitation, impregnation and ion exchange method is able to choose the suitable molar ratio of Si/Ti. However, these techniques have also disadvantages because they must consist of two steps for catalyst preparation process that are synthesis of TS-1 catalyst and then loading the second metal.

The simplest way for modifying TS-1 catalyst is incorporation method. The incorporation method is the combination of addition the second metal salt during the formation of TS-1 crystal. For the incorporation method, two groups of solutions are utilized. One is gel solution and another is decant solution. The second metal salt can be added both in the gel solution and in the decant solution. It is very interesting to clarify whether adding the second metal salt in the gel solution would obtain the same result as introducing it in the decant solution. In this study, chromium is selected as the second metal because it can modify acid property and stabilize inside zeolite with ZSM-5 structure. According to several former researches shown in Table 1.3, there are some evidences confirmed that chromium can be loaded to ZSM-5 including MFI structure and can improve activity of catalyst. The synthesis of the chromium-titanium silicalite-1 catalyst using incorporation method has some problem

concerning about how to control silicon to chromium ratio [Poompichate (2005)]. Therefore, to solve this problem, synthesis methodology affecting chromium-titanium silicalite-1 catalyst is proposed to study the preparation procedure(s) and factor(s) affecting the chromium-titanium silicalite-1 catalyst synthesis such as kinds of chromium salt, solution for chromium salts to be added.

According to the mixing problem of reactants with different polarity that exists in liquid phase, the gas phase reaction was selected. Since 2-propanol has only one active functional group (-OH); therefore, it is easy to follow the reaction pathway. There are several reactions related to this functional group; for example, dehydration reaction, oxidation reaction. The products derived from the dehydration and oxidation of 2-propanol are propylene and acetone, respectively. Therefore, the catalytic behavior of the synthesized catalysts will be evaluated using the gas phase oxidation of 2-propanol.

This research has been scoped as follows:

- 1) Preparation of Cr-TS-1 catalysts by varying chromium salt [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and CrO_3] and solutions in the incorporation method.
- 2) Characterization of Cr-TS-1 catalysts by using various techniques.
- 3) Catalytic reactions in gas phase oxidation of 2-propanol at 100 - 500°C, atmospheric pressure to determine catalytic activity.

Table 1.1 Reactions used for testing TS-1 catalyst including modified TS-1 in former researches

Author (year)	Reaction	Oxidant	Reaction phase
van der Pol <i>et al.</i> (1993)	Alcohol oxidation	H ₂ O ₂	liquid
Gontier and Tuel (1994)	Aniline hydroxylation	H ₂ O ₂	liquid
Bhaumik and Tatsumi (1998)	Alcohols dihydroxylation	H ₂ O ₂	liquid
Hulea <i>et al.</i> (1998)	Cyclopentene oxidation	H ₂ O ₂	liquid
Schuster <i>et al.</i> (2000)	Propane oxidation	O ₂	gas
Atoguchi and Yao (2001)	Phenol hydroxylation	H ₂ O ₂	liquid
Jenzer <i>et al.</i> (2001)	Propylene epoxidation	O ₂	gas
Sooknoi and Limtrakul (2002)	Cyclohexane oxidation	H ₂ O ₂	liquid
Chairat (2004)	Alcohols oxidation	O ₂	gas
Guo <i>et al.</i> (2004)	Propylene epoxidation	O ₂	gas
Zhuang <i>et al.</i> (2004)	Styrene hydroxylation	H ₂ O ₂	liquid
Sooknoi and Chitranuwatkul (2005)	Cyclohexanone ammoximation	H ₂ O ₂	liquid
Wan <i>et al.</i> (2005)	Aniline hydroxylation	H ₂ O ₂	liquid
Wróblewska <i>et al.</i> (2005)	Methyl alcohol epoxidation	H ₂ O ₂	liquid
Shul'pin <i>et al.</i> (2006)	Alkane oxidation	H ₂ O ₂	liquid
Wu <i>et al.</i> (2006)	Cyclopentene epoxidation	H ₂ O ₂	liquid

Table 1.2 Former researches of effect of 2nd metal loaded into TS-1 catalyst

Author (year)	2 nd metal	Synthesized method	Result
Pirutko <i>et al.</i> (2001)	Fe	Incorporation	Catalyze the oxidation of benzene to phenol with high activity and selectivity.
Taylor <i>et al.</i> (2005)	Au	Deposition-precipitation	Improve the epoxidation of propylene.
Xinbin <i>et al.</i> (2005)	Sn	Impregnation	Increase selectivity of diphenyl-oxalate from transesterification of dimethyl-oxalate with phenol.
Prasetyok <i>et al.</i> (2005)	Nb	Impregnation	Increase selectivity of 1,2-octanediol from 1-octene oxidation.

Table 1.3 Former researches of ZSM-5 catalyst containing Cr in framework

Author (year)	Cr source	Catalyst framework	Synthesized method
Kucherov <i>et al.</i> (1995)	Cr ₂ (SO ₄) ₃	Cr-SiO ₂	incorporation
Giannetto <i>et al.</i> (1997)	Cr(NO ₃) ₃ .9H ₂ O	Cr-Al-SiO ₂	impregnation
Pirutko <i>et al.</i> (2001)	Cr ₂ (SO ₄) ₃	Cr-TS-1	incorporation
Arujo <i>et al.</i> (2002)	Cr(NO ₃) ₃ .9H ₂ O	Pt-Cr-SiO ₂	ion-exchange
Penkova and Hadjiivanov (2003)	Cr(NO ₃) ₃ .9H ₂ O	Cr-ZSM-5	ion-exchange
Gaspar <i>et al.</i> (2005)	CrO ₃	Cr-SiO ₂	impregnation
Poompichate (2005)	Cr(NO ₃) ₃ .9H ₂ O	Cr-TS-1	incorporation
Lounis <i>et al.</i> (2006)	Cr(NO ₃) ₃	Cr-ZSM-5	ion-exchange
Zhao and Wang (2006)	Cr(NO ₃) ₃	Cr-TS-1	impregnation

This present work is organized as follows:

Chapter I describes the background and scopes of the research.

Chapter II presents related theory.

Chapter III consists of procedures of catalyst preparation, catalyst characterization and catalytic reaction in gas phase oxidation of 2-propanol.

Chapter IV shows the experimental results of the characterization of TS-1 catalysts and the oxidation reactions over these catalysts, including an expanded discussion.

Chapter V contains the overall conclusions emerging from this research and some recommendations for future work.

Finally, Appendices of this thesis contain the sample of calculation of catalyst preparation, g value and acid site, calibration curves from area to mole of alcohols, alkenes, ketones and the others, and data of the experiments.