

CHAPTER I

INTRODUCTION



1.1 Introduction

Zeolite catalysts offer a broad range of possibilities for carrying out reactions with high selectivity in organic synthesis. Thus, the catalytic properties of titanium-silicalite (TS-1) are of great scientific and technological importance [Notari, (1990)].

Titanium-substituted silicalite-1 (TS-1) with MFI structure was first revealed by Taramasso and co-workers in 1983. It is a zeolite catalyst like ZSM-5 structure containing framework titanium atoms instead of aluminium atoms. As a novel catalysis material, TS-1 plays a role as a catalyst in chemical industries because it has several unique catalytic properties especially in several oxidation reaction processes. For example, the selective oxidation reactions of a large family of organic substrates under mild conditions (liquid phase, low temperature and pressure) using hydrogen peroxide as the oxidant, such as aromatic hydroxylation, epoxidation of alkenes, hydroxylation of phenol, ammoximation of cyclohexanone, oxidation of alkanes and alcohols, usually use TS-1 as a catalyst. Moreover, good thermal stability, non-corrosive nature, the absence of waste and disposal problem which are properties of MFI structure also make TS-1 favor in chemical industries because it brings more convenient for applying in a continuous processes and high thermal. Therefore, TS-1 is of great practical interest to develop a more efficient, easily separable, reusable, and environment friendly catalyst for the oxidation process.

Even though zeolite TS-1 has been the subject of numerous studies in past years, there is still a great controversy about: (a) preparation methods; (b) the highest titanium loading that can be incorporated into the framework; (c) the existence or not of different Ti^{4+} environments with different coordination in the framework; (d) the role played by extra-framework titanium in the catalytic properties; and (e) the loading various types metal into catalyst framework (TS-1) such as Al, Fe, Au, Sn, Nb, Cr, Cu, V, and Co can change catalyst properties to proper for some reactions. However, the second transition elements are not so easy to be incorporated in the MFI

framework, and the amount of incorporated element had a very limited level. It is also known that in general, the catalytic properties depend on reaction conditions, catalyst compositions, metal dispersion, and types of inorganic supports used. Thus, changes the catalyst compositions and/or even though the compositions of supports used may lead to significantly enhance the catalytic properties as well. Therefore, second metal was introduced to TS-1 framework to improve TS-1 properties to proper for some reactions as we see in former researches (See Table 1.1).

In addition, many inorganic supports such as SiO_2 , Al_2O_3 , TiO_2 and zeolites have been extensively studied for supported Co catalysts for years. For example, cobalt has been largely studied in modifying silicalite (MCM-41) catalysts. The preparation of MCM-41 supported Co-Mo catalysts for hydrodesulfurization of petroleum residuals by using impregnation method [Song and Reddy, (1999)]. The catalytic behaviors of mixed TiO_2 - SiO_2 -supported cobalt(Co) Fischer-Tropsch (FT) catalysts via carbon monoxide (CO) hydrogenation reaction and the effect of the different crystalline phase composition of titania supported Co catalysts (Co/TiO_2) were studied [Jongsomjit et al.,(2005)]. Then, the modifying method to doped Co in titania was prepared by a cogellation method [Jongsomjit et al., (2005)]. Therefore, cobalt is an interesting metal ion considered as a key component for modifying the catalytic properties and catalytic behavior (acid site, activity, selectivity). In recent year, however, the research about cobalt incorporated into TS-1 framework to change the catalytic properties and the effect of amount of cobalt on Co-TS-1 properties have rarely to be explored. The previous researches had not yet investigated about the factor that affected the preparation of Co-TS-1 catalysts such as the types of salt, pH of the solution and the different conditions in preparing catalysts.

This research, therefore, has been set up to investigate the improvement of incorporations Co atom directly into the TS-1 framework during the formation of TS-1 crystalline (both of titanium atoms and second metals are loaded directly into the framework simultaneously with SiO_2 framework forming). It is interested to investigate factors affecting the preparing of Co-TS-1 catalysts such as whether the metal in TS-1 framework come from gel or decant solution and which one control the morphology of TS-1 in the hydrothermal method. Because of the various amount of Co incorporate into the TS-1 will affect the physical properties, chemical properties

and catalytic behavior. Therefore, this study, concerns about the source and type of metal that can be incorporated into the framework. Then, the prepared TS-1 with Co loading in different conditions will be characterized using different analytical technique to investigate Co-TS-1 properties.

In the recent years, most of the test reactions used to explore TS-1 and metal modified TS-1 properties were usually oxidation in liquid phase as demonstrated in Table 1.1. However, several problems such as the existence of more than one phase occur from mixing between two or more reactants with different polarity and separation of catalyst can occur in liquid phase operation. To avoid the above mentioned problems, oxidation in gas phase is therefore selected to be the test reaction used to explored Co-TS-1 properties and find the optimum condition of catalyst.

The main objective of this research is to investigate factors that affect to the addition of Co into the MFI structure during the synthesis of TS-1 by hydrothermal method and the catalytic properties of the modified catalysts.

This research has been scoped as follows:

1. Prepare Co-TS-1 catalysts by using hydrothermal method. The synthesizing parameters that are studied
 - a. The cobalt incorporation in either the gel solution or the decant solution cans control the TS-1 morphology.
 - b. The various types of salts such as cobalt (II) nitrate hexahydrate, cobalt (II) chloride hexahydrate and cobalt (II) acetate tetrahydrate.
2. Characterization of Co-TS-1 catalyst samples using various techniques as following
 - a. Determine the bulk composition of Si, Ti and Co by X-ray fluorescence spectroscopy (XRF).

- b. Determine the structure and crystallinity of catalyst by X-ray diffraction (XRD).
 - c. Determine the functional group in the catalysts by Fourier-transform infrared spectroscopy (FT-IR).
 - d. Determine the morphology catalyst by Scanning electron microscopy (SEM).
 - e. Determine the surface area and pore volume of catalyst by BET.
 - f. Determine the strong acid and weak acid sites of the catalyst by temperature programmed desorption (TPD).
3. Catalytic activity testing using an appropriated test reaction such as gas phase oxidation of 2-propanol.

This present thesis is organized as follows:

Chapter I presents the background and scopes of the research.

Chapter II presents the theory of this research, studies about the introduction of TS-1, catalyst properties, parameters affecting the synthesis of TS-1 catalysts and the oxidation reaction and its possible mechanism

Chapter III presents literatures relate to TS-1 catalysts, modified TS-1 for various reactions in the past and comments on previous work.

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

Chapter V presents the experimental results of the characterization of Co-TS-1 catalysts, and the 2-propanol oxidation reactions over these catalysts, including an expanded discussion.

Chapter VI contains the overall conclusion emerging from this research and some recommendations for future work.

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, calibration curves from area to mole of alcohols, alkenes, ketones and the others, and data of the experiments which had emerged from this research are included in appendices at the end of this thesis.

Table 1.1 Former researches of effect of 2nd metal loaded into TS-1 catalyst.

Author (year)	2nd metal	Synthesized method	Effect of 2nd metal	Reaction Phase	Advantage
Pirutko <i>et al.</i> (2001)	Fe	Incorporation	Form Zeolite matrix (α -sites) in high concentration.	Liquid	Catalyze the oxidation of benzene to phenol with high activity and selectivity.
Wang <i>et al.</i> (2003)	Ag	Deposition- precipitation	Good performance for propylene epoxidation.	Gas	Increase the propylene conversion and the selectivity of propylene oxide.
Rafael <i>et al.</i> (2004)	Al	Impregnation	Higher polar solvents that effect on activity and selectivity.	Liquid	The best catalytic performance regarding both the activity and selectivity towards valuable products (octaldehyde and octenols).
Li <i>et al.</i> (2004)	Cu	Ion-exchange and Impregnation	Main active component in the catalyst.	Gas	Purify the exhaust from lean burn engine.

Author (year)	2nd metal	Synthesized method	Effect of 2nd metal	Reaction Phase	Advantage
Taylor <i>et al.</i> (2005)	Au	Deposition- precipitation	Higher amount of active sites of catalyst.	Gas	Improve the epoxidation of propylene.
Xinbin <i>et al.</i> (2005)	Sn	Impregnation	Higher amount of weak acid site of catalyst.	Liquid	Increase selectivity of diphenyl- oxalate from transesterification of dimethyloxalate with phenol.
Prasetyoko <i>et al.</i> (2005)	Nb	Impregnation	Higher amount of Brønsted acid sites.	Liquid	Increase selectivity of 1,2-octanediol from 1-octene epoxidation.
Zhao <i>et al.</i> (2006)	Cr	Impregnation	Higher activity in the oxidative dehydrogenation.	Gas	Increase ethylene selectivity in dehydrogenation of ethane.