การเตรียมตัวเร่งปฏิกิริยาโคบอลต์-ไทเทเนียม ซิลิกาไลต์ 1

นางสาวนิธิพร แสงเงิน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2548

ISBN 974-17-6472-3

PREPARATION OF COBALT TITANIUM SILICALITE 1 CATALYST

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2005

ISBN 974-17-6472-3

Thesis Title	PREPARATION OF COBALT-TITANIUM SILICALITE-1
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Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tharathon Mongkhonsi, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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นิธิพร แสงเงิน : การเตรียมตัวเร่งปฏิกิริยาโคบอลต์-ไทเทเนียม ซิลาคาไลต์ 1
(PREPARATION OF COBALT-TITANIUM SILICALITE 1 CATALYST)
อ. ที่ปรึกษา : รศ.ดร.ธราธร มงคลศรี, 94 หน้า. ISBN 974-17-6472-3

ไทเทเนียมซิลิกาไลต์-1 (TS-1) ถูกสังเคราะห์โดยวิธีไฮโดรเทอร์มอลและเติมด้วยโคบอลต์ที่ปริมาณต่าง ๆ กัน ตัวเร่งปฏิกิริยาได้รับการวิเคราะห์ด้วยเครื่องมือหลายชนิดได้แก่ XRF, BET, XRD, FT-IR, SEM, XPS และ NH_3-TPD เพื่อศึกษาผลของโคบอลต์ที่มีต่อโครงสร้างและการก่อรูปร่างของผลึกไทเทเนียมซิลิกาไลต์-1 จากนั้นได้นำตัวเร่งปฏิกิริยามาศึกษาคุณสมบัติในการเร่งปฏิกิริยาออกซิเดชันของสารประกอบ 2-โพรพานอลในวัฏภาคแก๊ส ผลการศึกษาแสดงให้เห็นว่าปริมาณสูงสุดของโคบอลต์ที่สามารถเติมลงไป โดยที่ยังไม่มีผลกระทบต่อการเกิดโครงสร้างคือประมาณร้อยละ 0.38 โดยโมล การวิเคราะห์ด้วยเทคนิค XPS แสดงให้เห็นว่าโคบอลต์มีเติมเข้าไปมีเลขออกซิเดชันค่าเป็น +2 การเติมโคบอล์ตยังไปเพิ่มสัดส่วนตำแหน่งที่เป็นกรดอ่อนบนพื้นผิวของตัวเร่งปฏิกิริยา โดยไปลดสัดส่วนของตำแหน่งบนพื้นผิวที่เป็นกรดแก่ลง จากคุณสมบัติดังกล่าวพบว่าการเกิดปฏิกิริยาดีไฮเดรชันของ 2-โพรพานอล บนตัวเร่งปฏิกิริยาโคบอลต์ไทเทเนียมซิลิกาไลต์สูงขึ้น โดยปริมาณโคบอลต์ที่มากขึ้นทำให้ค่าการเลือกเกิดของโพรพิลีนมีแนวโน้มสูงขึ้นและดีกว่าตัวเร่งปฏิกิริยาที่ไม่เติมโคบอลต์

ภาควิชา.............วิศวกรรมเคมี........ ลายมือชื่อนิสิต.....นิธิพร แสงเงิน.........
สาขาวิชา...........วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา.............................
ปีการศึกษา..........2548....................

##4770330321: MAJOR CHEMICAL ENGINEERING

KEY WORD: COBALT-TITANIUM SILICALITE 1

NITIPORN SANGNGAEN: PREPARATION OF COBALT-TITANIUM SILICALITE 1 CATALYST. THESIS ADVISOR: ASSOC. PROF. THARATHON MONGKHONSI, Ph.D. 94 pp. ISBN: 974-17-6472-3

Titanium silicalite incorporated with various content of cobalt was synthesized by the hydrothermal method. The synthesized catalyst (Co-TS-1) were characterized by various techniques XRF, BET, XRD, FT-IR, SEM, XPS and NH_3-TPD, to study the effects of cobalt on the formation of titanium silicalite crystal. The oxidation properties of Co-TS-1 catalysts were investigated by using the gas phase oxidation reaction of 2-propanol as the test reaction. The study reveals that the maximum amount of cobalt which can be incorporated into the TS-1 structure without any interference to the main TS-1 structure is about 0.38 mol%. The analysis by XPS reveals that the oxidation state of cobalt cation in the TS-1 framework is +2. In addition, the incorporation of cobalt increases the amount of the weak acid site while the amount of the strong acid site decreases. The Co-TS-1 catalysts exhibit higher catalytic activity for the dehydration reaction than the unmodified TS-1 was also found that the selectivity toward propylene of Co-TS-1 is also higher than that of the unmodified TS-1.

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Field of study….Chemical Engineering… Advisor's signature…………………...

Academic year…………2005…………...

ACKNOWLEDGEMENTS

The author would like to express her greatest gratitude and appreciation to her advisor, Associate Professor Tharathon Mongkhonsi for his invaluable guidance, providing value suggestions and his kind supervision throughout this study. In addition, she is also grateful to Associate Professor ML. Supakanok Thongyai, as the chairman, Dr. Suphot Phatanasri and Dr. Amornchai Arpornwichanop, who have been member of thesis committee.

Many thanks for kind suggestions and useful help to Mr. Pichit Tidtaweerat, Mr. Watcharapong Khaodee, Mr. Eakawut Poompichate, Miss Darunee Sookhom, Miss Rattanawalee Sunphloi, Mr Piyawat Supphasrirongjaroen, Mrs. Pramrutai Kruachot, Miss Pareeyanun Kamonsawat. Mr. Jutkarun Phongpatthanapanich and many friends in the petrochemical laboratory who always provide the encouragement and cooperation along the thesis study.

Finally, she would like to dedicate the achievement of this work to her parents, who have always been the source of her support and encouragement.

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CHAPTER I

INTRODUCTION

Titanium Silicalite (TS-1) was first synthesized by Taramasso et al. in 1983. TS-1 is distinguished from their pure silica congeners by the substitution of small amount of Ti for Si in the crystal lattice. Titanium silicalite molecular sieves are TS-1 with MFI type structure which is in the pantasil family of zeolite. Unit linked through edges to form chain and those chains are connected to form corrugated sheets. These sheets link to form a three dimentional framework (see appendix A). TS-1 based on processes (phenol hydroxilation, cyclohexanone ammoximation, and propylene epoxidation [Boccuti et al. (1989)]) have a very eco-friendly potential and its used z in industrial reactors and offer many advantages because of their non-corrosive nature, the absence of waste and disposal problem is easy in continuous processes and high thermal.

TS-1 have been developed by Enichem [Notari et al. (1993)]. TS-1 is now used for the production of two industrial chemicals:catechol and hydroquinone. They have been produced since 1986 by the hydroxylation of phenol with H_2O_2 [Notari et al. 1991]. In the conversion of cyclohexanone into cyclohexanone oxime in the presence of ammonia and H_2O_2, TS-1 offers a substantial reduction in coproduct formation [Roffia et al. 1990, Thangarai et al. (1991)]. TS-1 is also a particularly active catalyst for the epoxidation of low-molecular-weight linear alkenes [Notari et al. (1993), Notari et al. (1991)]. Hence, TS-1 and related material appear very suitable for developing clean hemolytic or heterolytic processes. In the last several years, considerable attention has been given on the modification of TS-1 catalyst for improving its performance by incorporating various types of metal in the TS-1. 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. Table 1.1 shows recent investigations concerning the modified TS-1 catalyst on various reactions and the synthesized of Co-silicalite (MCM-41) are shown in Table 1.2.

In the present study researches related to, the incorporation of Co in microporous TS-1, with MFI structure. The catalytic activity of Co-TS-1 was evaluated by the oxidation reaction of 2–propanol in gas phase which have not a problem about separation between product and catalyst while the liquid phase can cause problem about mixing between two or more reactant exists in difference phase and no have researcher that study in this case. 2- Propanol can be converted into alkenes by dehydrogenation reaction or ketone by the oxidation reaction The reaction is performed between 100-500 ºC and atmospheric pressure.

This research has been scoped as follows:

1) Preparation of Co-TS-1 by hydrothermal method.
2) Characterization of Co-TS-1 catalysts using various techniques following
    - Determine the bulk composition of Si, Ti and Co by X-ray fluorescence spectroscopy (XRF).
    - Determine the structure and crystallinity of catalyst by X-ray diffraction (XRD).
    - Determine the functional group in the catalysts by Fourier-transform infrared spectroscope (FT-IR).
    - Determine the morphology catalyst by Scanning Electron microscopy (SEM).
    - Determine the chemical valence states of metals in catalyst by X-ray photoelectron spectroscopy (XPS).
    - Determine the surface area and pore volume of catalyst by BET.
    - Determine the strong acid and weak acid sites of the catalyst by temperature programmed desorption (TPD).
3) Catalytic reaction (2- propanol) in gas phase oxidation between 100-500 °C and ambient pressure.

This present work is organized as follows :

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

Chapter II presents criteria for catalyst performance evaluation method such as the basic catalyst characterization methods employed and criteria for test reaction selection.

Chapter III consists of catalyst preparation, catalyst characterization and catalyst tested with 2-propanol oxidation in gas phase.

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

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

Finally, the sample of calculation of catalyst preparation, 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 Research study concerning the modified TS-1 catalyst on various reactions.

Year	Worker	Catalyst	Phase		Reaction	Object
			React.	Oxid.		
1999	Laufer et al.	Pd-TS-1	Liq.	Liq.	Epoxidation of propylene	The objective of this work assessed the loss of epoxidation capacity of the TS-1 catalyst and the decomposition of H_2O_2 by the Pd loading which the catalyst was prepared by impregnation method.
2001	Jenzer et al.	Pd-Pt/TS-1	Liq.	Liq.	Epoxidation of propylene	This work studied the epoxidation of propylene and natured side reaction in a continuous fixed bed reactor under high pressures conditions, which the catalyst chosen corresponds to the best performing material and the feed stream composition was set to mimic the initial composition in their batch experiments.
2001	Caixia et al.	Au/TS-1	Liq.	Liq.	Epoxidation of propylene	This work have been used as a carrier of Au/TS-1 catalyst for the direct vapor-phase epoxidation of propylene in the copresence of H_2 and O_2 the catalyst was prepared by a decomposition-precipitation method.

Year	Worker	Catalyst	Phase		Reaction	Object
			React.	Oxid.		
2004	Guo et al.	Ag-TS-1	gas	Liq.	Epoxidation of propylene	In this paper, researcheres studied the effect of preparation method of Ag-TS-1 catalyst, such as deposition-precipitation and impregnation and ion-exchange methods. And precipitators, such as Na_2CO_3, K_2CO_3 and Cs_2CO_3,on the propylene epoxidation in the gas phase.
2004	Pirutko et al.	Al, V, Cr, Fe,Co, Ru on TS-1	Liq.	Liq.	Oxidation of benzene	This work studied the potential for producing active catalysts using the titanosilicalite. TS-1 as a matrix with iron or some other metal introduced at the stage of hydrothermal synthesis, which other matals are shown to be inert for oxidation of benzene to phenol.
2004	Rafael et al.	Al-TS-1	Liq.	Liq.	Rearrangement of 1,2-epoxyoctane	This work studied influence of the solvent nature in the catalytic activity and product distribution for the liquid-phase rearrangement of long straight-chain epoxide over Al-containing zeolite and mesostructured materials, the result obtained in the rearrangement, chosen as a model molecular, over catalysts mesoporous material are discussed in regard to the role of different solvents conventionally used in these isomerization processes.

Table 1.2 Research study concerning the Co-MCM-41 catalyst

Year	Worker	Object
1996	Jentys et al.	This work reported the synthesis and characterization of mesoporic material containing highly dispersed cobalt that were prepared by direct addition of $CoCl_2$ to the synthesis gel. The pore volume and the surface area of this material were slightly smaller compared to MCM-41 indicating that indeed Co is placed inside the pores.
1998	Schieber et al.	In this paper, researcher reported a comparison of Pt Rh and Co supported on siliceous MCM-41 for the catalytic reduction of NO_x with propene. Co/MCM-41 was found to have a low level of activity for such reaction.
1998	Jentys et al.	This work investigated the structure properties of Co/MCM-41 with pore diameters between 2.9 and 3.6 nm prepared by direct synthesis and impregnation. For both preparation method, the size of the metal particles decreased that direct synthesis method led to significantly smaller metal clusters compared to the impregnation method.
1999	Song et al.	This work studied MCM-41 supported Co-Mo catalysts for hydrodesulfurization of petroleum residuals. High metal loaded Co-Mo/MCM-41 catalysts prepared by impregnation shown higher hydrogenation and hydrocracking activities than conventional Co-Mo/Al_2O_3.

Year	Worker	Object
2000	Kim et al.	In this case, Investigation of metallic cobalt supported on mesoporous silica MCM-41 for the Pauson-Khand reaction (cycloaddition of alkenes and carbon monoxide to cyclopentanones).
2000	Suvanto et al.	This research reported the preparation of Co/MCM-41 samples by deposited $Co_2(CO)_8$ from the gas phase onto the MCM-41 surface in a fluidized bed reactor. Two different kinds of preparation methods were used, direct deposition in order to achieve the monolayer coverage of $Co_2(CO)_8$ with one deposition treatment and the pulse deposition method to further increase the metal loading on the support.
2001	Yin et al.	This report have synthesized hexagonal mesoporous silica and used it as a support of 15% Co catalysts. hexagonal mesoporous silica is different from MCM-41 in part by its thicker framework wall and smaller domain size with shorter channels. High CO conversion and high yield of hydrocarbons were obtained at high pressure. They have concluded that hexagonal mesoporous silica matrials facilitate the reactant to access the active sites, permit better transport of higher hydrocarbon products, and diminish secondary reactions, such as cracking and isomerization of long chain hydrocarbons.
2002	Panpranot et al.	This work reported that CoRu/MCM-41 prepared from Co and Ru nitrate resulted in a higher FTS activity compared to CoRu/SiO2 catalysts prepared with the same precursors. However, cobalt was found to concentrate more toward the external surface area than in the interior of MCM-41.

Year	Worker	Object
2003	Panpanot et al.	To study, the effect of H_2 partial pressure on surface reaction parameter during CO hydrogenation on Ru-Promoted silica-supported Co catalysts. They found that the increase in rate with increasing hydrogen partial pressure resulted due to the increase in methane surface intermediates and, more importantly, the increase in hydrogen surface concentration.
2003	Turaga et al.	This work investigated the activity of a mesoporous molecular sieve MCM-41 supported Co-Mo catalyst in comparison to a commercial γ-alumina (Al_2O_3)-supported Co-Mo catalyst for the desulfurization of a light cycle oil with a sulfer content of 2.19 wt%. The MCM-41 supported catalyst demonstrates considertly higher activity for the deep hydrodesulfurization of the refractory dibenzothiophenic sulfer compounds.
2004	Karadikar et al.	This work synthesized copper and cobalt complexs immobilized on the walls of MCM-41 modified with aminopropyl groups. FT-IR and UV-vis spectra show evidence of adduct formation of the amino group through the axial coordination with the metal which enhance the catalytic. The molecular dispersion of the complex with sufficient void space and hydrophobic surface are appropriate for activation of hydrocarbons as evidence by higher TON on immobilization.

CHAPTER II

CATALYST CHARACTERIZATION AND PERFORMANCE EVALUATION

To understand a catalyst, one normally has to know characters and performance of the investigated catalyst. Many characterization and performance evaluation techniques exist but which one should be used depends on several factors, such as necessarity, availability etc.

This chapter lists analytical techniques use for catalyst characterization in section 2.1. Section 2.2 discusses criteria for selecting a test reaction for catalyst performance evaluation.

2.1 characterization method

In this study, the basic characterization methods used to characterize physical and chemical properties of the investigated catalyst are listed in Table 2.1.

Table 2.1 Characterization methods and their purposes in this study.

Method	**Measurement**
X-ray Fluorescence spectroscopy (XRF)	Composition of element.
Atomic absorption spectroscopy (AAS)	Composition of element.
X-ray diffraction (XRD)	Information about the structure, composition, and state of polycrystalline materials.
N_2 physisorption (BET)	BET surface area, pore volume and average pore diameter.
Scanning electroscopy (SEM)	Catalyst granule morphology and element distribution.
X-ray photoelectron spectroscopy (XPS)	The chemical valence states of metals.
Energy dispersive x-ray spectroscopy (EDX)	The elemental concentration distribution on the catalyst granules.
Temperature programmed reduction (TPR)	The reducibility of catalyst.
Temperature programmed desorption of Ammonium (NH_3-TPD)	Acidity of catalyst.
Fourier transform infrared spectrometry (FT-IR)	Function group on the catalyst surface.
CO-pulse chemisorption	The catalyst dispersion.
Thermalgravity Analysis (TGA)	The weight loss pattern and reducibility.
Ultraviolet-visible (UV-Visible)	Oxidation stage.

.

In the present study we used XRD, SEM, XPS, FT-IR, NH_3-TPD, XRF, for characterize the TS-1 and Co-TS-1 catalyst after that testing catalyst with reaction which determine selection condition and parameter in performance reaction use criteria for test reaction as shown in section 2.2.

2.2 Criteria for test reaction selection

Performance (e.g. Activity, selectivity) of a catalyst can be evaluated by subjecting the total catalyst under reaction conditions. The key of the test is to select a suitable test reaction. The criteria for selecting a proper test reaction is discussed below.

1. The reactant must not too inert or too reactive. If the reactant is too inert the test catalyst may behave as an inactive catalyst and the reactant is too reactive. The performance comparison between different catalysts will be difficult.

2. The reactant should have only one active functional group. This will help in determination the reaction pathway.

3. The homogeneous reaction of the reactant should be kept as minimum as possible in order to prevent the interference of the desirable reaction on result interpretation.

4. The reactant should not cause catalyst deactivation such as poisoning, coking.

From criteria above, we selected 2-propanol as a reactant because it have one function group for active in reaction that is -OH group which OH group can be converted in dehydration reaction into alkene and oxidized in oxidation reaction into ketone and aldehyde which we can be investigated the direction of reaction. Therefore this work should study oxidation reaction of 2-propanol.

CHAPTER III

EXPERIMENTS

The experimental systems and procedures used in this work are divided into three parts:

1. The preparation of catalysts.
2. The characterization of catalysts.
3. The catalytic activity measurements.

The details of the experiments are described as the following.

The scope of this study

The reaction conditions are chosen as follows:

Catalyst : Titanium silicalite -1 (TS-1), Cobalt-Titanium silicalite-1 (Co-TS-1)
Reactant : 2-Propanol pure
Feed composition : 2-Propanol 5 vol%, Oxygen 8 vol%, Argon balance
Flow rate of reactant : 100 ml/min
Reaction temperature : 100-500 °C
Space velocity : 60,000 $g^{-1}h^{-1}$

3.1 Preparation of TS-1 and Co-TS-1 catalysts

3.1.1 Chemicals

The details of chemicals used in the preparation procedure of TS-1 are shown in Table 3.1.

Table 3.1 The chemicals used in this experiment.

Chemical	Grade	Supplier
Cobalt (II) nitrate Hexahydrate	Analytical	Aldrich
Titanium (IV) butoxide 97%	-	Aldrich
Tetra-n-propyl ammonium bromide 98%	-	Aldrich
Sodium silicate solution	Extra Pure	Merck
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich

The preparation procedure of Co-TS-1 by rapid crystallization method was shown in Table 3.2. This method could advantageously and rapidly prepare the uniform and the uniform and fine zeolite crystals with the following improvements: (i) the preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals, (ii) the precipitated gel was milled before the hydrothermal treatment, which was essential to obtain the fine crystals, and (iii) the temperature under the hydrothermal treatment was programmed to minimize the time which was necessary for the crystallization. The detail preparation of Co-TS-1 was described below.

3.1.2 Preparation of Decantation Solution and Gel Solution

The source of metals for preparation of decantation and gel solution were $Ti[O(CH_2)_3CH_3]_4$ for Ti and $Co(NO_3)_2.6H_2O$ for Co, respectively TPABr (tetra-n-Propyl Ammonium Bromide ($CH_3CH_2CH_2$)4NBr) was used as organic template. The atomic ratio of silicon/titanium was set at 50. The preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals. The detailed procedure were as follows: Firstly, a gel mixture was prepared.

Table 3.2 Reagents used for the preparation of TS-1 and Co-TS-1 :Si/Ti = 50 (Appendix B).

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]_4$	2.2085	g
TPABr	5.72	g	TPABr	5.72	g
NaCl	11.95	g	NaCl	11.95	g
De-ionized water	60	ml	De-ionized water	60	ml
H_2SO_4(conc.)	3.4	ml	H_2SO_4(conc.)	3.4	ml
$Co(NO_3)_2.6H_2O$	x	g	$Co(NO_3)_2.6H_2O$	x	g
Solution B1			Solution B2		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	g			
H_2SO_4 (conc.)	1.55	g			

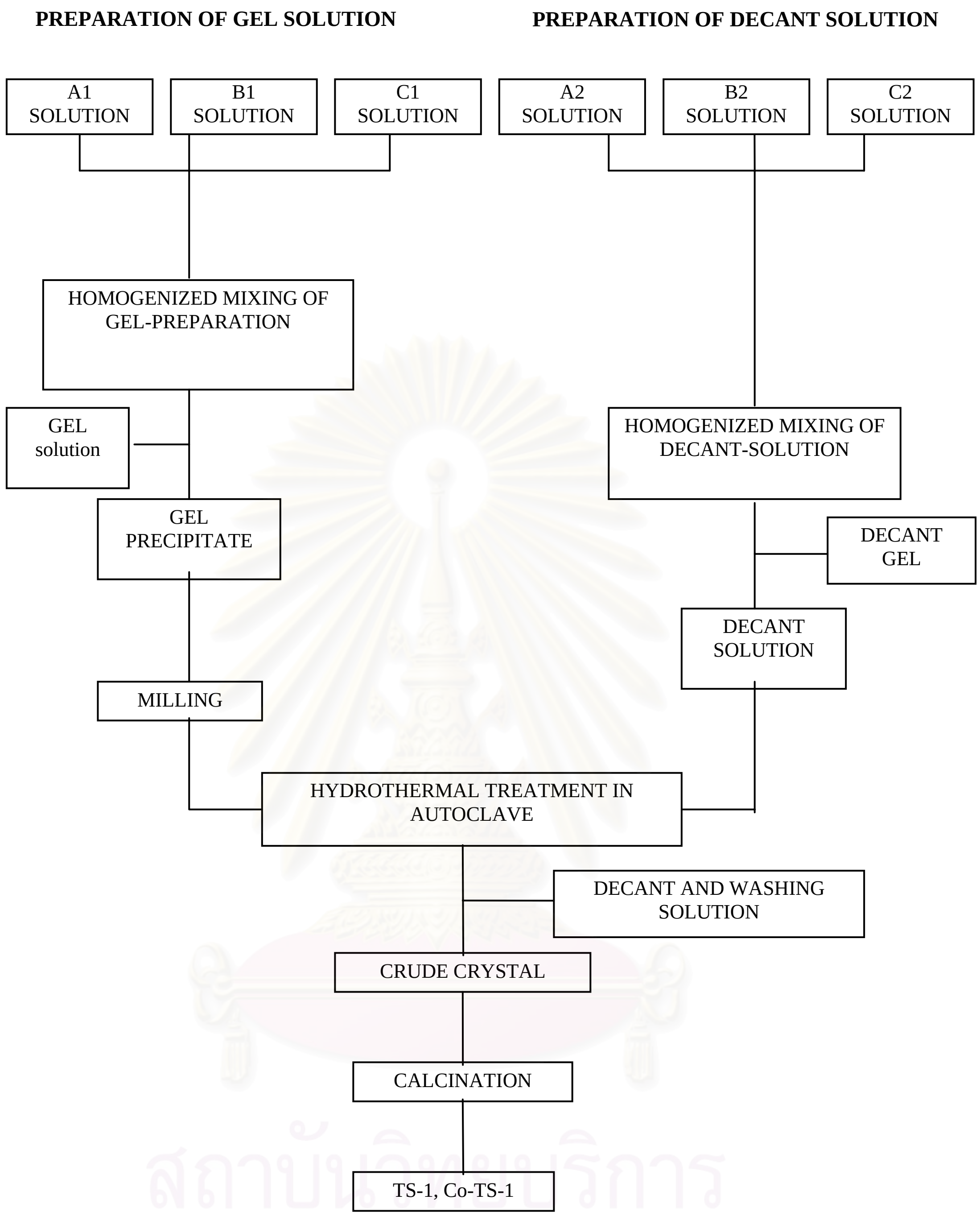


Figure 3.1 The preparation procedure of TS-1 and Co-TS-1 by rapid crystallization method.

by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the mixed solution was maintained within 9-11, since it was expected that this pH value was suitable for precipitation. The gel mixture was milled for totally 45 min. The milling procedure were as follows : milled 15 min centrifuge (to remove the liquid out) milled 15 min centrifuge milled 15 min. Milling the gel mixture before the hydrothermal treatment was essential to obtain and fine crystals. Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2 with the same method of the preparation of gel mixture. The supernatant liquid fro A-2, B-2 and C-2 was mixed together with the milled gel mixture. However, before mixing. The pH of the solution was adjusted to be between 9-11 with H_2SO_4(conc.) or 1M NaOH solution.

3.1.3 Crystallization

The mixture of the precipitate and the supernatant of decant solution were mixed together in a glass vessel in an autoclave. The atmosphere in the autoclave was replaced by nitrogen and pressurized up to 3 kg/cm^3 gauge then, the autoclave was heated from room temperature to 160 ^{o}C in 90 min and then up to 210 $^{\circ}$C with a constant heating rate 12 ^{o}C/hr, followed by cooling down the hot mixture to room temperature overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization . The produced crystals were washed with de-ionized water about 8 time by using the centrifugal separator (about 15 min for each time) to remove Cl^{-1} out of the crystals, and dried in an oven at 110 $^{\circ}$C for at least 3 hr.

3.1.4 Calcination

The dry crystals were calcined in an air steam at 550 $^{\circ}$C for 7 hr by heating them from room temperature to 550 $^{\circ}$C in 60 min. This step was to burn off the organic template and to leave the cavities and channels in the crystals. Then, the calcined were cooled to room temperature in a dessicator. After this step the catalysts formed were called Co-TS-1.

3.2 The characterization of TS-1 and Co-TS-1 catalysts

3.2.1 Surface area measurement

The specific surface area were determined from the BET adsorption isotherm of nitrogen measured by an automatic apparatus ASAP 2020 consturected by Micrometrics, U.S.A at Petrochemical Engineering Laboratary,Chulalongkorn University.

3.2.2 X-ray Fluorescence spectroscopy (XRF)

The composition analysis of elements in the bulk of the catalyst was performanced by X-ray Fluorescence spectroscopy using Bruker SRS 3400.

3.2.3 X-ray diffraction (XRD)

XRD pattern of the prepared of the catalysts were performed by using SIEMENS XRD D5000 diffractometer using CuKα radiation with Ni filter in the 2θ range of 4-60^{o} with a step size of $2\theta = 0.02^{o}$ and number of scan = 10. The sample is placed into XRD plate before placing on the measured position of XRD diffractometer at Petrochemical Engineering Laboratary, Chulalongkorn University.

3.2.4 Morphology

The shape and size of the crystals of prepared catalyst were observe by using JEOL JSM-35 CF The SEM was operated using the back scattering electron (BSE) mode at 10 kV. scanning Electron Microscope (SEM) at center of department of chemical engineering, Faculty of engineering, chulalongkorn university.

3.2.5 Fourier transform Infrared (FT-IR)

The function group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Infrared spectra were recorded between 400 and 2000 cm^{-1} on a microcomputer at Petrochemical Engineering Laboratary, Chulalongkorn University.

3.2.2 X-Ray photoelectron Spectra (XPS)

The chemical valence states of metals in the catalysts were measured by XPS technique using an AMICUS instrument using the C 1s peak at 285 eV as reference at Petrochemical Engineering Laboratary, Chulalongkorn University.

3.2.7 Ammonia Temperature Programmed Desorption (NH_3-TPD)

The strong acid and weak acid sites of the catalyst were determined by measuring the amount of adsorbed ammonia on the surface using Micromeritrics Chemisorb 2750 at Petrochemical Engineering Laboratary, Chulalongkorn University.

3.3 The catalytic activity measurements

3.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 3.2. The system consists of a saturator, a microreactor, an automatic temperature controller, an electrical furnace and a gas controlling system. The liquid phase reactant was filled in the saturator. N_2 or Ar is passed through the evaporator to evaporate the reactant and carried to the microreactor.

The microreactor is made from a stainless steel tube. Three sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

The gas supplying system consists of cylinders of ultra high purity nitrogen or argon and air, each equipped with pressure regulators (0-120 psig), on-off valves and needle valves for adjusting the flow rate of these gases.

The composition of oxygenate compounds in the feed and product streams were measured by a Shimadzu GC8A gas chromatograph equipped with flame ionization detector.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and carbon monoxide and a Porapak-Q column to separate CO_2 and water were operated in parallel. The operating conditions are shown in the Table 3.3.

Table 3.3 Operating conditions for gas chromatograph.

Gas chromatograph	Shimadzu GC8A	Shimadzu GC8A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	3% SP-1500
Carrier gas	He (99.999%)	N_2 (99.999%)
Carrier gas flow	25 ml/min	25 ml/min
Column temperature		
- Initial	100	70
- Final	100	120
Detector temperature	130	120
Injector temperature	130	120
Heating rate	-	4^0C/min
Analyzed gas	CO, CO_2,H_2O	Oxygenates

3.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

2. The total flow rate was 100 ml/min. Flow rate of 2-propanol, nitrogen or argon and air were adjusted to the required values. The gas mixtures for oxidation reaction were 5 vol% alcohols, 8 vol% oxygen and balance with nitrogen (or argon in case of no O_2 in feed gas).

3. The reaction temperature was between 100-500 ^{o}C. The effluent gases were analyzed by using the FID and TCD gas chromatographs. The chromatograph data were changed into mole of propylene, ethanol, 2-propanol, isopropyl ether, acetone CO and CO_2 by calibration curves in Appendix D.

The result of catalytic test was calculated in the term of

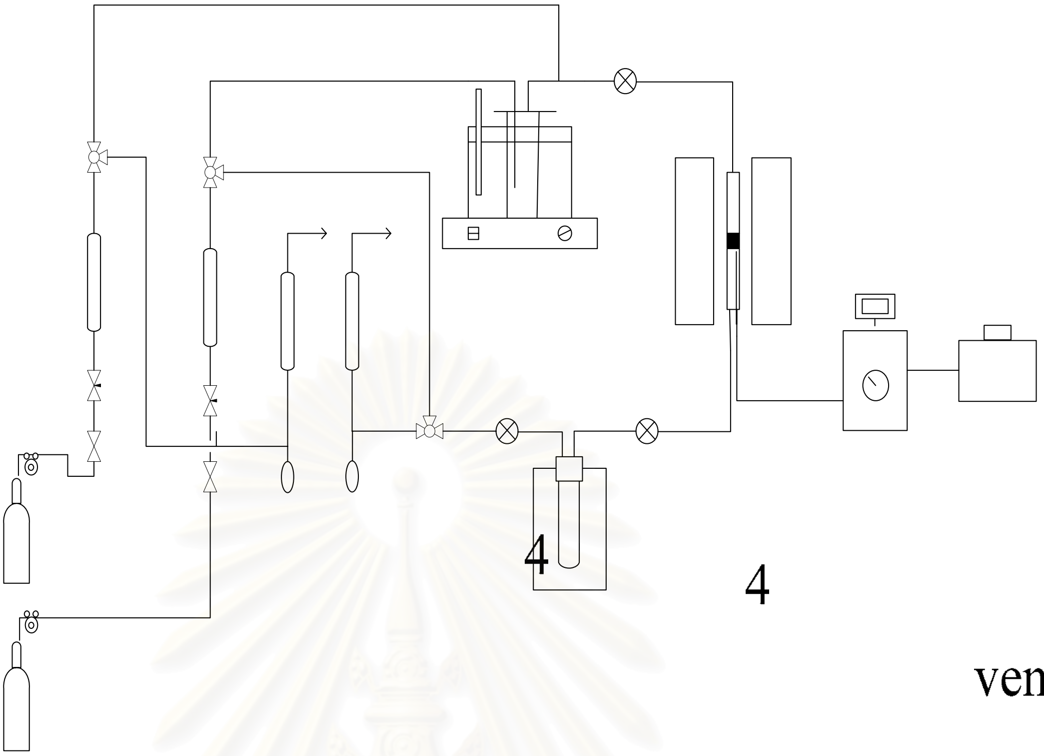
$$\%\ \text{A conversion (C)} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

$$\%\ \text{Selectivity (S) to B} = \frac{\text{mole of B formed}}{\text{mole of A converted}} \times \frac{\text{no. of C atom of B}}{\text{no. of C atom of A}} \times 100$$

$$\%\ \text{Yield (Y) to B} = \frac{\%\ \text{A conversion} \times \%\ \text{selectivity to B}}{100\%}$$

Where, A is reactant

B is product



1. Air vessel
2. N_2/Ar vessel
3. Mass Flow controller
4. Three-way-valve
5. Gate valve
6. Needle valve
7. Rotary meter
8. Rubber cock
9. Sampling point
10. Condenser
11. Saturator
12. Furnace
13. Reactor
14. Catalyst bed
15. Temperature controller
16. Digital temperature indicator
17. Variable voltage transformer
18. Thermocouple/Thermometer
19. Pressure regulator
20. Water bath
21. Heating and Stirring controller

Figure 3.2 Flow diagram of oxidation reaction system.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, results and discussion are divided into two parts. The first one is the results of characterization of TS-1 and Co-Ts-1 samples using different analytical techniques, such as XRF, BET, XRD, FT-IR, SEM and XPS. The second part is the results of catalytic activity study of 2-propanol oxidation reactions.

4.1 Bulk and surface structures of Co-TS-1

This section presents bulk and surface structure of the catalysts. The catalysts are all prepared by hydrothermal method containing the desired amount of metal which bulk composition and surface structure of TS-1 and Co-TS-1 were characterized by various analysis techniques such as XRF, XRD, BET, FT-IR, SEM, XPS.

4.1.1 Determination of metal content of catalyst

The chemical compositions of the synthesized catalysts were determined using XRF. The results are given in Table 4.1. In this study, cobalt incorporated into the catalyst sample were approximately 0.097, 0.103, 0.217, and 0.382 mol%, respectively.

Table 4.1 The metal composition of TS-1 and Co-TS-1 catalysts.

Sample	%Co	%Si	%Ti	Si/Co	Si/Ti
TS-1	0	32.15	0.442	∞	72.8
Co-TS-1	0.097	31.9	0.52	328.51	61.5
Co-TS-1	0.103	32.14	0.46	311.07	69.79
Co-TS-1	0.217	31.88	0.35	146.39	89.96
Co-TS-1	0.382	32.24	0.175	84.5	184.61

4.1.2 BET surface areas

BET surface area, pore volume and pore size of TS-1 and Co-TS-1 catalysts, were determined by the adsorption and condensation of N_2 at liquid N_2 boiling point temperature (-196°C) using static vacuum procedure. This technique is called “BET” method according to the inventor’s name (Bruanauer, Emmett, and Teller). The obtained results are summarized in Table 4.2. The catalysts after cobalt incorporation have BET surface areas, pore volume and pore size in the range of 320- 350 m^2/g, 0.20-0.24 ml/g, 22-30 Å respectively which are around the values of TS-1 before cobalt incorporating.

Table 4.2 Surface area, pore volume and average pore size of catalysts.

Catalyst	**BET surface (m^2/g)**	**Pore volume (ml/g)**	**Average Pore Size (Å)**
TS-1	323	0.208	23.7632
Co-TS-1 (0.097)	317.36	0.238	29.5102
Co-TS-1 (0.103)	322.00	0.211	26.6422
Co-TS-1 (0.217)	336.00	0.222	26.4862
Co-TS-1 (0.382)	350.62	0.208	23.7632

4.1.3 X-ray Diffraction (XRD)

The crystal structures of the synthesized catalysts were identified by using X-ray diffraction technique. Figure 4.1 illustrates the XRD spectra of TS-1 and Co-TS-1 catalysts.

The XRD patterns of the synthesized TS-1 and series of Co-TS-1, with amount of cobalt various between 0.097, 0.103, 0.217, 0.382 mol.% , indicates that a small amount of cobalt incorporated into the MFI framework does not significantly affects the main structure of MFI. The patterns obtained are the pattern typical for a crystalline zeolite having a MFI structure. The XRD results demonstrate that the catalyst contained a well defined single-phase XRD pattern and is consistent to those already reported in literatures [Taramasso et al. (1983)]. All the XRD patterns show six main characteristic peaks at 2θ as 8, 8.8, 14.8, 23.1, 24, and 29.5 degree, marked with dark circle. The incorporation of Ti^{4+} into the framework is indicated by the conversion of the monoclinic structure of silicalite-1, an orthorhombic structure, evidenced by the disappearance of peak splitting at $2\theta = 24^{\circ}$ and $2\theta = 29.5^{\circ}$ [Taramasso et al. (1983)]. Because of the low Ti content in the support materials (Ti< 3 wt%), addition TiO_2 crystalline phases, i.e., anatase ($2\theta = 25.5°$) and rutile ($2\theta = 48.2°$) [Yap et al. (2004)], does not appear in the XRD patterns. Since the catalysts prepared by the hydrothermal method have the same XRD patterns. It can be concluded that the addition of cobalt incorporating of the catalysts does not modify the main structure. Thus the XRD patterns are not changed.

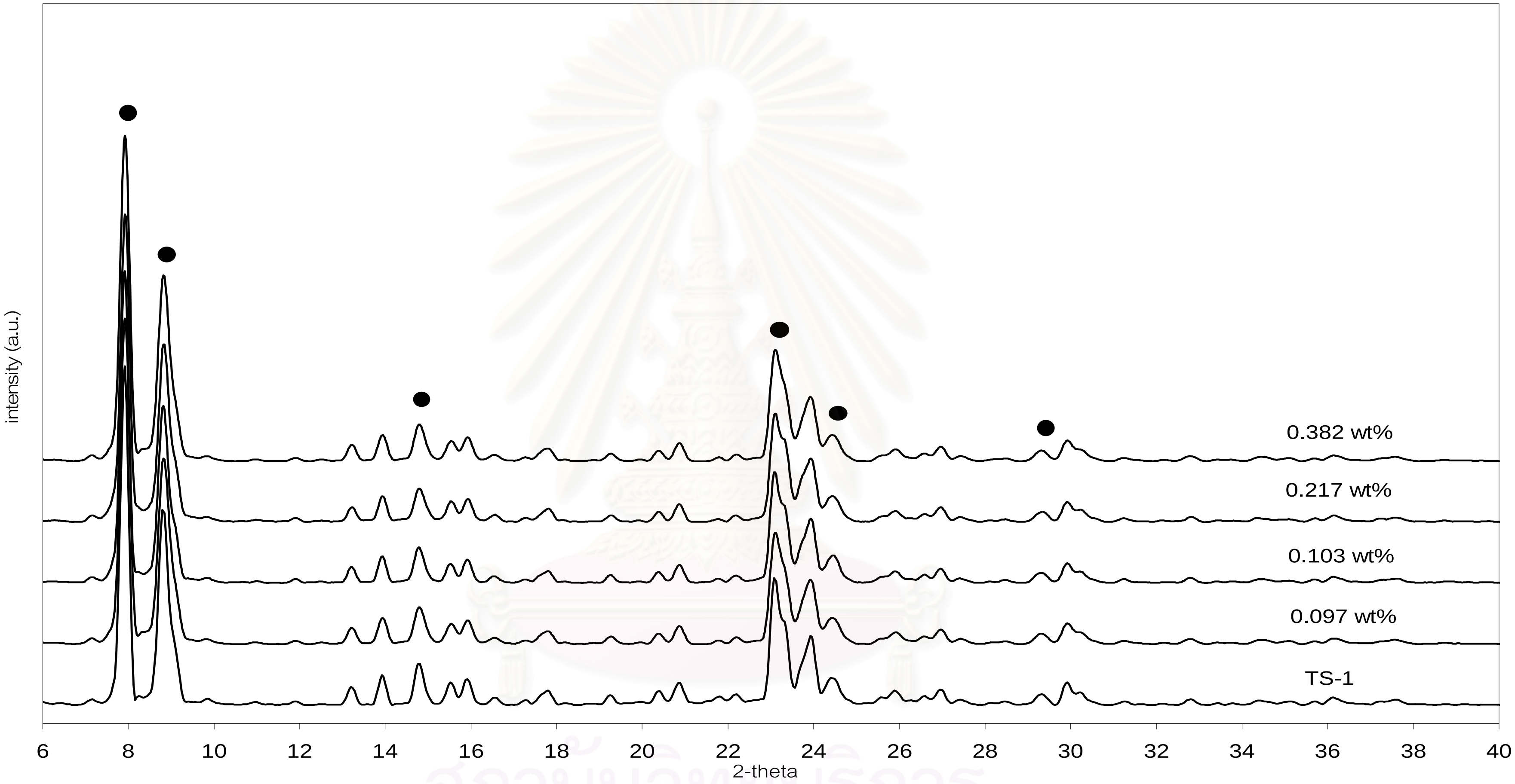


Figure 4.1 X-ray diffraction pattern of the prepared TS-1 and Co-TS-1 catalysts.

4.1.4 Fourier Transform Infrared Spectrometer (FT-IR)

A comparative IR spectrometric study was performed to obtain information concerning the existence of the framework titanium. The spectra obtained is exhibited in Figure 4.3. It is well known that the vibration of TS-1 is characterized by an absorption band in the 900–975 cm^{-1} region [Taramasso et al. (1983)]. It has been suggested that the presence of a 960–975 cm^{-1} band is a necessary, but not sufficient, condition for the catalytic activity of TS-1 [Huybrechts et al. (1991)]. In addition, the defective orthorhombic silicalites, with fully hydroxylated nanocavities generated by the extraction of a few adjacent (SiO_4) units, also have an extra-broad IR absorption band at ca. 970 cm^{-1} [Perego et al. (1986)] as illustrated in Figure 4.3. These IR spectra indicate that the amounts of cobalt incorporated into TS-1 are much less to be able to be distinguished by the changes in IR bands.

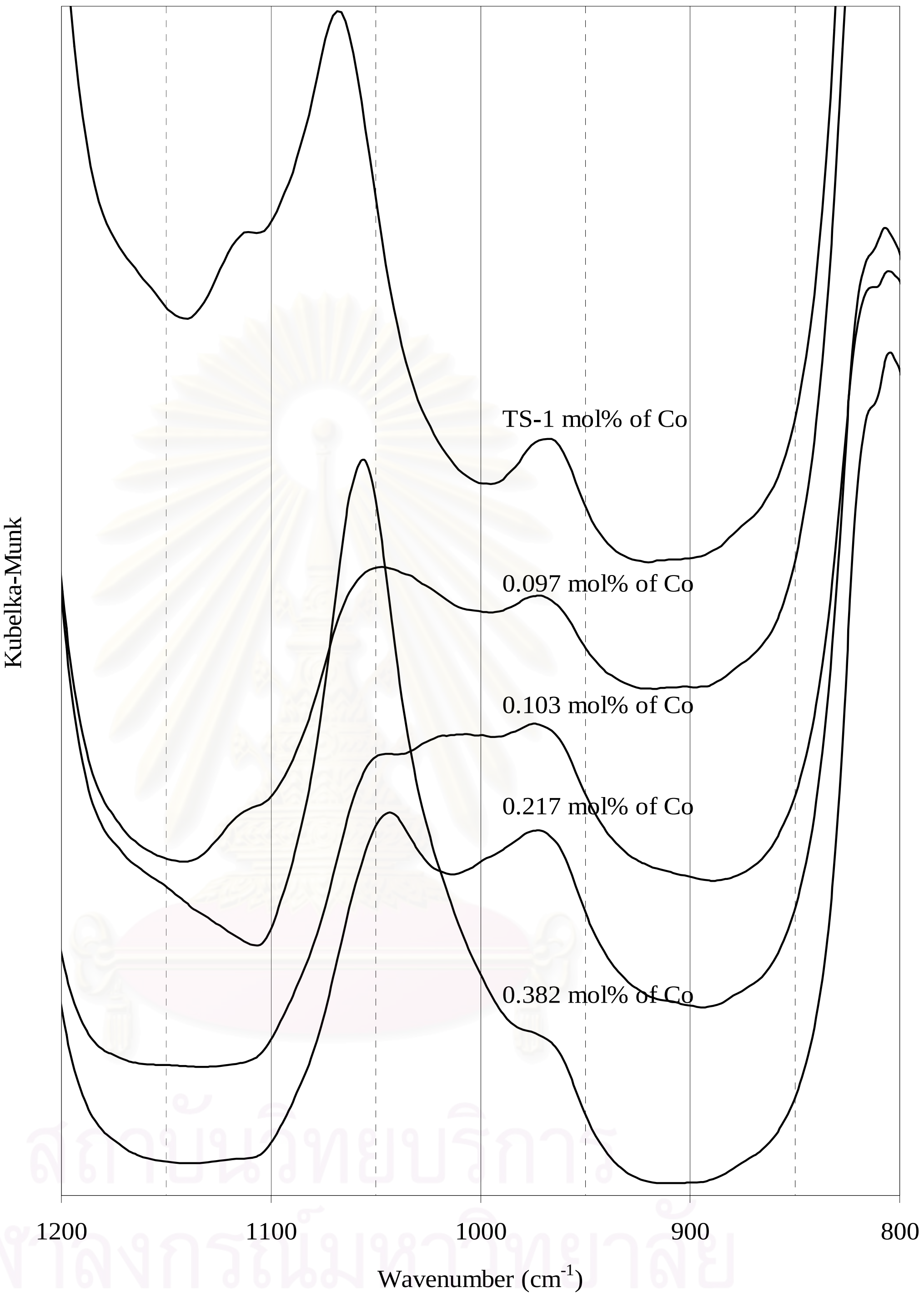


Figure 4.2 IR spectra of the synthesized TS-1 and Co-TS-1 catalysts.

4.1.5 Morphology

Scanning electron microscopy (SEM) photographs of the prepared catalysts are shown in Figures 4.3-4.7. As shown, the shapes of all the catalysts are roughly crystallized orthorhombic shape which are composed of many small regular plates. It is observed that cobalt incorporated does not greatly alter the shape of the crystals. The size of TS-1 showed a uniform crystallite shape and sizes of about 5 µm.

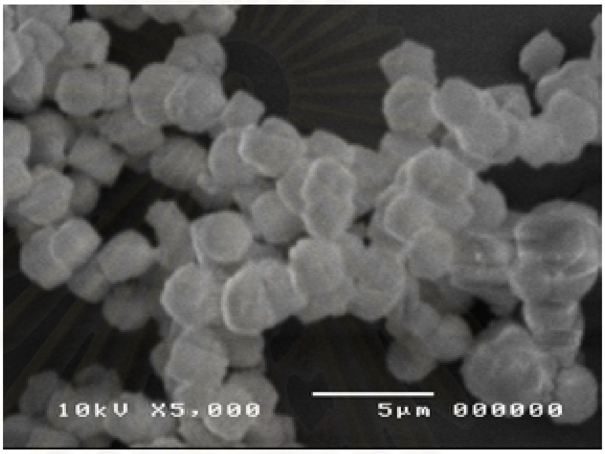


Figure 4.3 SEM photo of TS-1

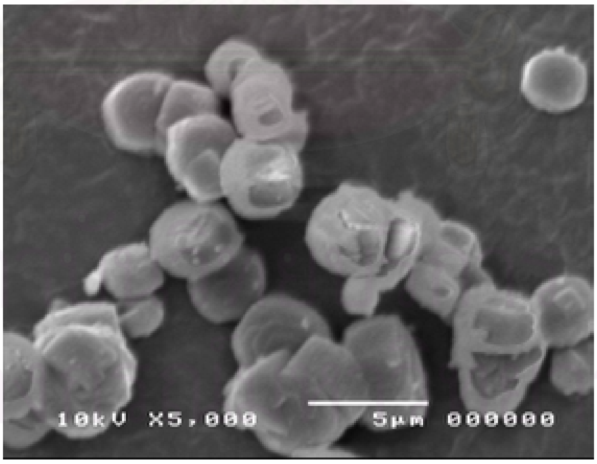


Figure 4.4 SEM photo of Co/TS-1 (0.097 mol % of Co).

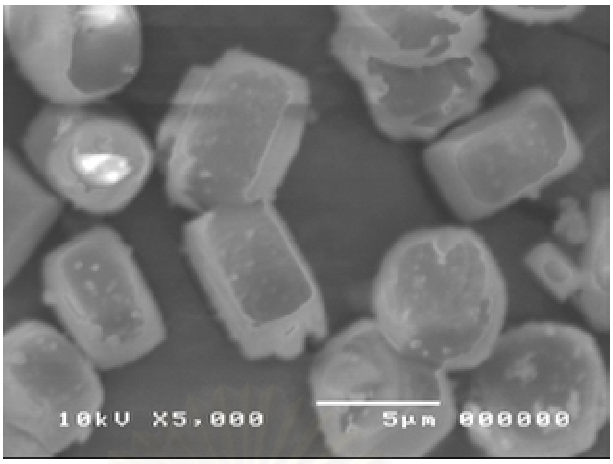


Figure 4.5 SEM photo of Co/TS-1 (0.103 mol % of Co).

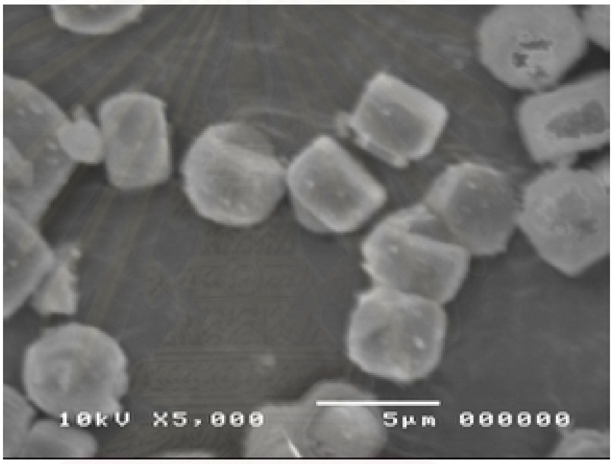


Figure 4.6 SEM photo of Co/TS-1 (0.217 mol% of Co).

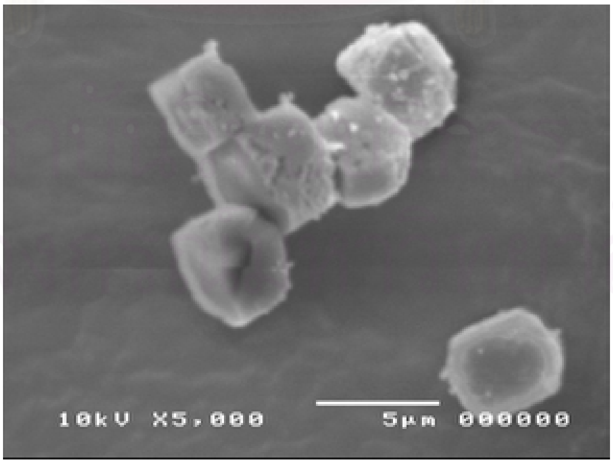


Figure 4.7 SEM photo of Co/TS-1 (0.382 mol% of Co).

4.1.6 X-ray photoelectron spectroscopy (XPS).

To obtain information on the chemical state of the surface cobalt species, all the catalysts have been examined by XPS technique. The correction of binding energy was performed by using the C 1s peak of carbon at 285 eV as reference. The oxidation states of Co can be determined from the binding of Co $2p_{3/2}$ and Co $2p_{1/2}$ photo-electron.

The peak positions of Co-TS-1 samples investigated in the present study are shown in Table 4.3. The results in Table 4.3 confirm the presence of paramagnetic Co^{2+}. The main peak of Co $2p_{3/2}$ appears at binding energy around 782-783 eV with a satellite peak around 786-788 eV. This suggests that the oxidation state of Co observed here is 2+.

Table 4.3 Measured Co $2p_{3/2}$ photoelectron peak position of catalysts

sample	satellite peak Co $2p_{3/2}$ BE.(eV)	main peak Co $2p_{3/2}$ BE.(eV)
Co-TS-1(0.097)	788.64	783.32
Co-TS-1(0.103)	788.99	783.56
Co-TS-1(0.217)	786.96	782.43
Co-TS-1(0.382)	787.18	782.55

Two groups of researchers [Mclntyre et al. (1975), Ernst et al. (1999) in Barakat et al. (2005)] have reported that the distance between the two photoelectron peaks of cobalt, Co $2p_{3/2}$ and Co $2p_{1/2}$, is about 15 eV. The Co $2p_{3/2}$ peak occurs at binding energy 778 eV [Shan et al. (1991), Chastain et al. (1995) in Barakat et al. (2005)]. Since no such peak can be observed in all the obtained XPS spectra, there is no existence of any Co^0 on the catalyst surface. The reported peak position for this satellite peak in paramagnetic Co^{2+} is 786.3 eV. [Nahm et al. (2001) in Barakat et al. (2005)]. The measured peak positions of our samples, as shown in Table 4.3, confirm the presence paramagnetic Co^{2+}. The peak due to the presence of Co_2O_3 or mixed-valent Co_3O_4 reported occurs at 779.9 [Haber et al. (1977) in Barakat et al. (2005)] and 779.3 eV [Chastain et al. (1995) in Barakat et al. (2005)], respectively. It should be noted here that the discrepancy among the reported binding energy values arise from using difference reference a binding energy of C 1s. In the paper mentioned above, it is likely that the value of the binding energy of C 1s peak is about 3 eV less than the present work.

From the characterization results of XRF, BET, XRD, FT-IR, SEM and XPS some effects of Co compound on the formation of TS-1 can be seen. The presence of $Co(NO_3)_2.6H_2O$ up to 10% by mol does not affect the formation of the TS-1, as can be seen from the XRD pattern and BET surface area. The amount of $Co(NO_3)_2.6H_2O$ used in the preparation of the catalyst with the highest Co content (0.382 mol%), though, is about 15 times higher than the amount of $Co(NO_3)_2.6H_2O$ used in the synthesis of the catalyst with the lowest Co content (Co-TS-1 0.097 mol%), the amount of Co cations can be incorporated is only about 4 times different (the amount of $Ti[O(CH_2)_3CH_3]_4$ used in each synthesis was fixed). The amount of Co can be incorporated into the TS-1 framework does not linearly increase as the amount of $Co(NO_3)_2.6H_2O$ used during the synthesis is increase, but is likely up to a level. In conclusion, the XPS analysis suggests that the oxidation number of cobalt atom on the TS-1 surface is +2.

4.2 A comparative study of TS-1 and Co-TS-1 catalysts in 2-propanol oxidation reaction.

This section presents the effect of cobalt, the acidity (strength and amount), oxidation state of Co and catalytic properties of Co-TS-1. The oxidation states of Co cation in the catalysts are reported in section 4.2.1. The surface acidity, measured by ammonium temperature programmed desorption (NH_3-TPD), is reported in section 4.2.1. The catalytic activity, evaluated from the oxidation of 2-propanol, is discussed in section 4.2.2.

4.2.1 Ammonium Temperature Programmed Desorption (NH_3-TPD).

NH_3-TPD was used to determine the strength and amount of the acid site of the catalysts. The results are shown in Table 4.4 and Figure 4.8. Deconvolution details of each NH_3-TPD profile are shown in Figures 4.10-4.14. Each NH_3-TPD profile can be deconvoluted into two main peaks. The first peak, will be named here “the weak acid site”, appears around 140-150 °C. The second peak, will be named here “the strong acid site”, appears around 230-240 °C.

Table 4.4 NH_3 -TPD data of TS-1 and Co-TS-1 with different amount Co.

Catalyst	Weak Acid site		Strong Acid site	
	Max Temp. (° C)	Acid site (μmol/g)	Max Temp. (°C)	Acid site (μmol/g)
TS-1	139	130	232	102
Co-TS-1 (0.097)	142	179	236	64
Co-TS-1 (0.103)	149	163	229	33
Co-TS-1 (0.217)	146	190	235	53
Co-TS-1 (0.382)	145	208	240	64

Since the locations of the peaks of both the weak acid and the strong acid site are about the same. The discrepancy is the area under the peaks, i.e. the amount of acid site. These results indicate that the added Co has significant effect on the amount of surface acidity of TS-1. The effect on the strength of the surface acidity can not be evaluated from the NH_3-TPD profiles. When the catalyst was incorporated with Co, the amount of the weak acid site on the surface increases while the amount of the strong acid site decreases.

The product of the reaction of 2-propanol on an acidic site depends on the strength of the acidic site. The oxidation reaction need the acidic site with the strength more than that is required for the dehydration reaction. The increase in the amount of the weak acid site and the decrease in the amount of the strong acid site, the result of the incorporation of cobalt into the TS-1 framework, suggest that the reaction of 2-propanol over Co-TS-1 should produce more propylene and less acetone than the reaction over the unmodified TS-1. This effect will become clear in the next section, section 4.2.2.

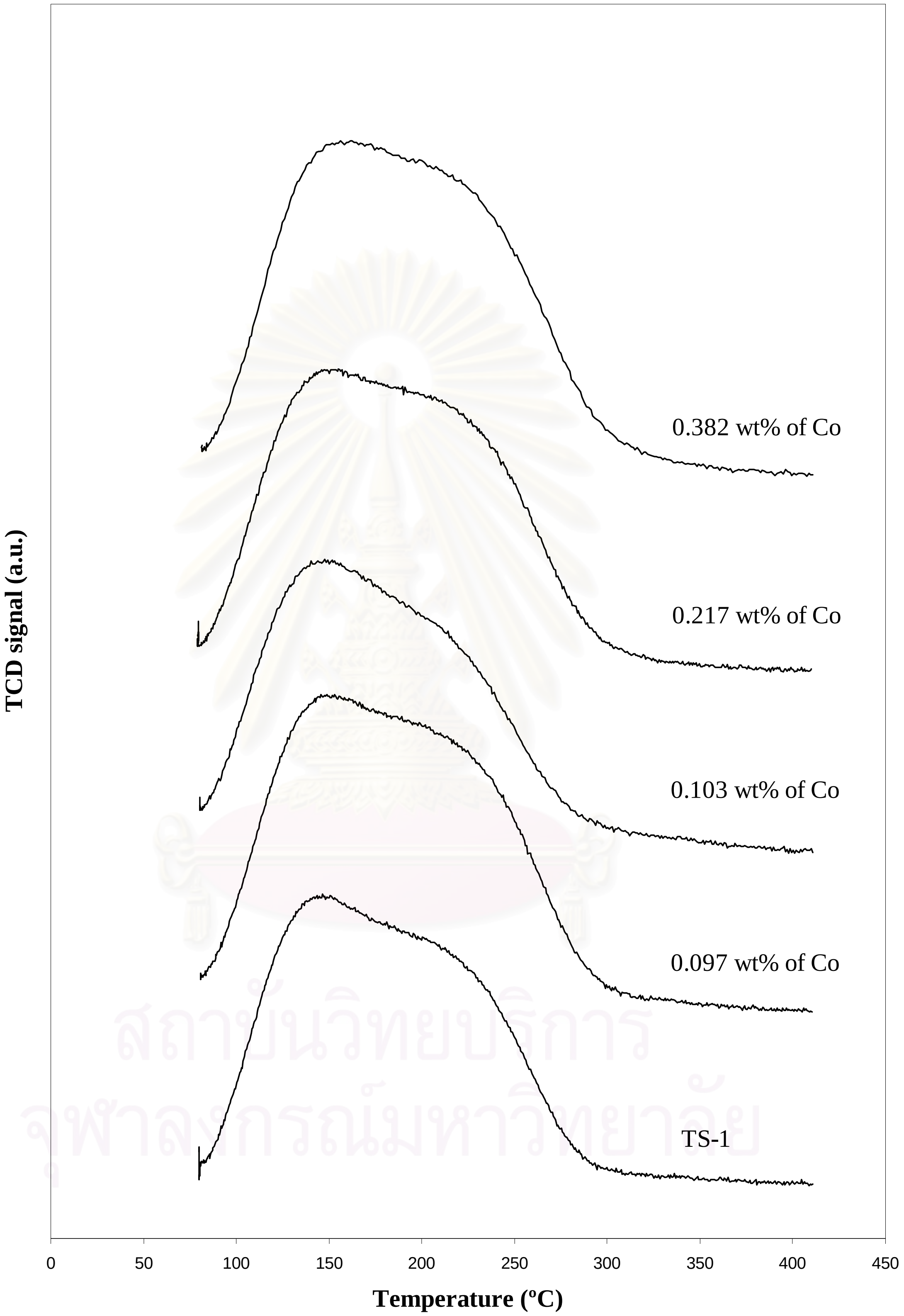
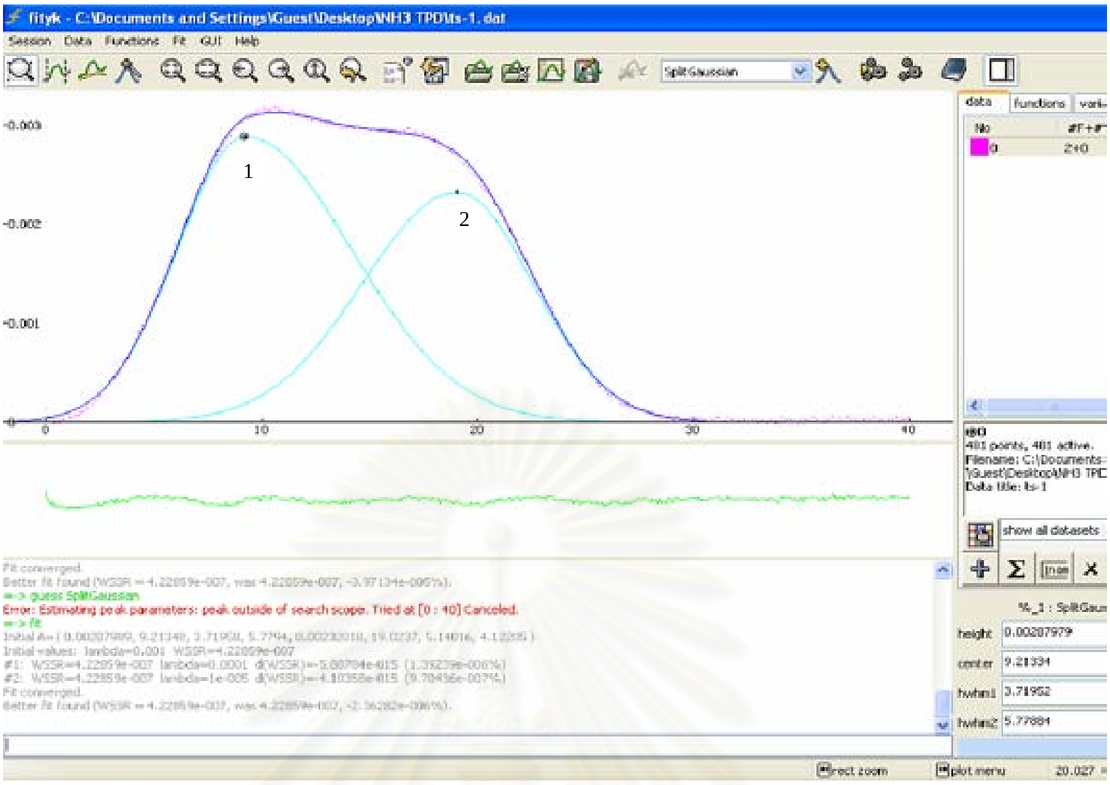


Figure 4.8 TPD profile of desorbed NH_3 from the catalysts.



```
Fit converged.
Better fit found (WSSR = 4.22859e-007, was 4.22859e-007, -3.97134e-006%).
=-> guess SplitGaussian
Error: Estimating peak parameters: peak outside of search scope. Tried at [0 : 40] Canceled.
=-> fit
Initial A=( 0.00287989, 9.21349, 3.71958, 5.7794, 0.00232018, 19.0237, 5.14016, 4.12205 )
Initial values:  lambda=0.001  WSSR=4.22859e-007
#1:  WSSR=4.22859e-007  lambda=0.0001  d(WSSR)=-5.00704e-015  (1.18239e-006%)
#2:  WSSR=4.22859e-007  lambda=1e-005  d(WSSR)=-4.10358e-015  (9.70436e-007%)
Fit converged.
Better fit found (WSSR = 4.22859e-007, was 4.22859e-007, -2.36282e-006%).
```

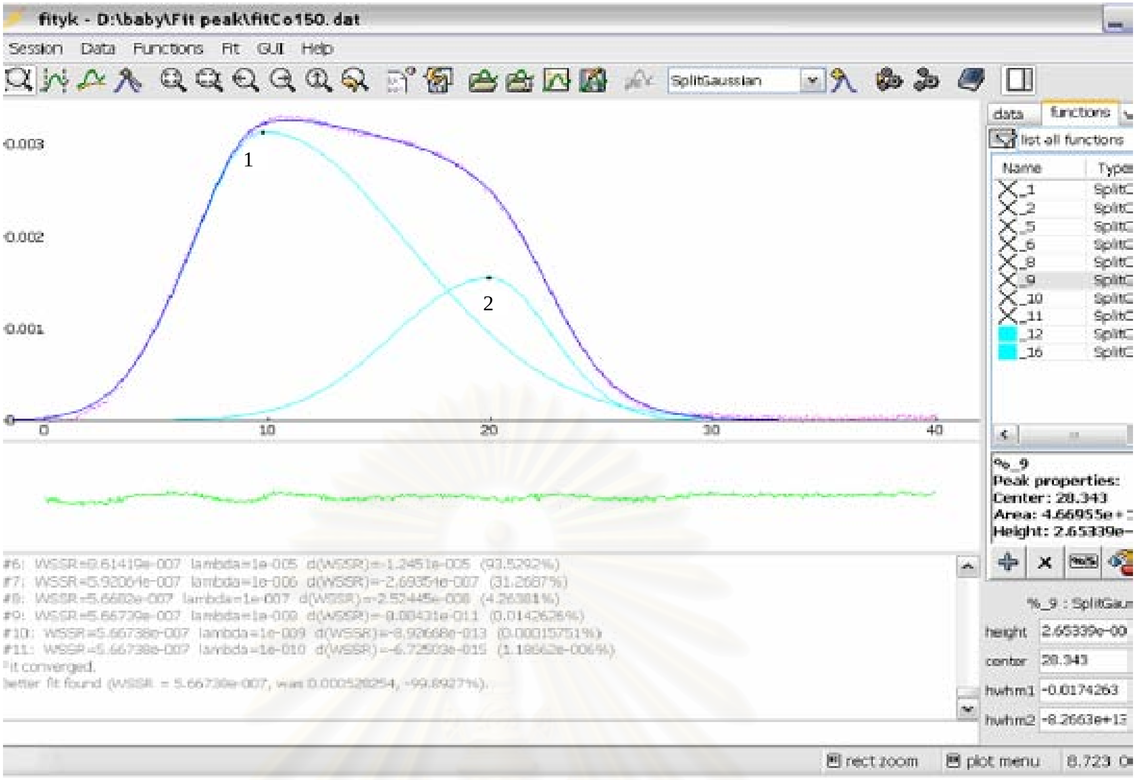
@0
401 points, 401 active.
Filename: C:\Documents
\Guest\Desktop\NH3 TPD
Data title: ts-1

%_1 : SplitGau
height 0.00287979
center 9.21334
hwhm1 3.71952
hwhm2 5.77884

Figure 4.9 Peak deconvolution of TS-1.

Data fit peak

Peak properties		**1**	**2**
Center	time (min)	9.21334	19.0234
	temp (°C)	139	232
Area		0.0582333	0.0457568
Height		0.00287979	0.00232038



```
#6:  WSSR=9.61419e-007  lambda=1e-005  d(WSSR)=-1.2451e-005  (93.5292%)
#7:  WSSR=5.92064e-007  lambda=1e-006  d(WSSR)=-2.69354e-007  (31.2687%)
#8:  WSSR=5.6682e-007  lambda=1e-007  d(WSSR)=-2.52445e-008  (4.26381%)
#9:  WSSR=5.66739e-007  lambda=1e-008  d(WSSR)=-8.08431e-011  (0.0142626%)
#10:  WSSR=5.66738e-007  lambda=1e-009  d(WSSR)=-8.92668e-013  (0.000157751%)
#11:  WSSR=5.66738e-007  lambda=1e-010  d(WSSR)=-6.72503e-015  (1.18662e-006%)
it converged.
etter fit found (WSSR = 5.66738e-007, was 0.000528254, -99.8927%).
```

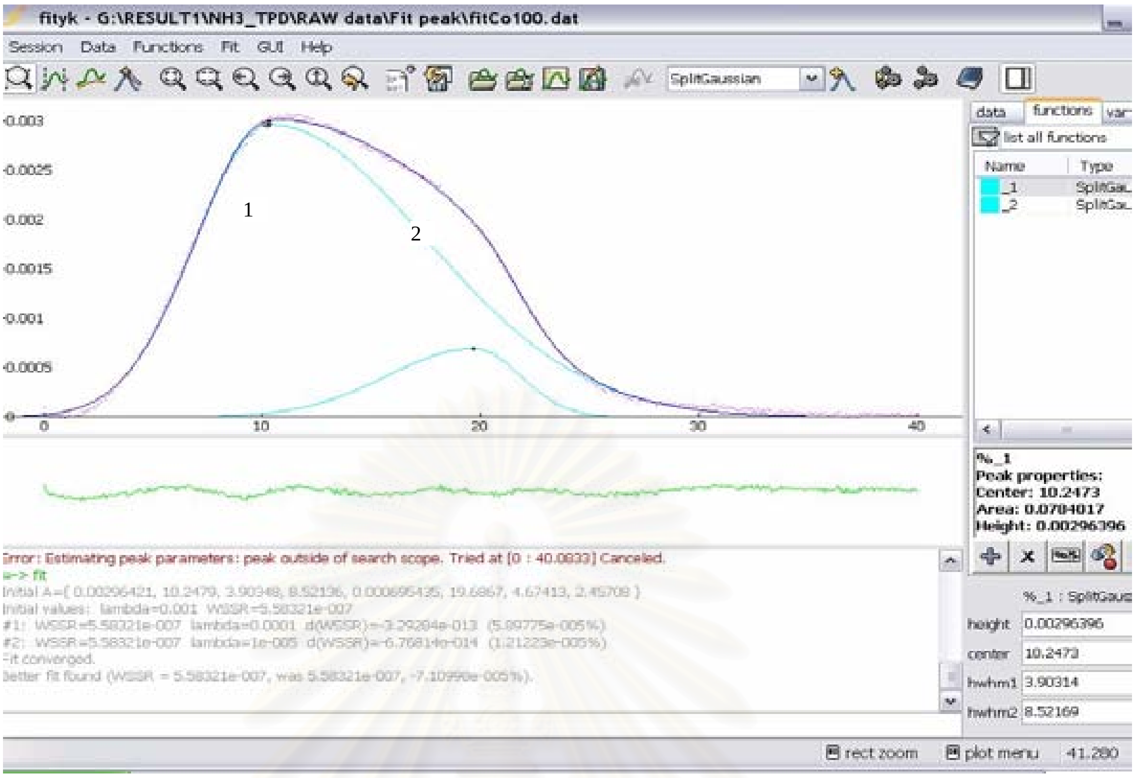
```
%_9
Peak properties:
Center: 20.343
Area: 4.66955e+
Height: 2.65339e-
```

```
%_9 : SplitGau
height  2.65339e-00
center  20.343
hwhm1   -0.0174263
hwhm2   -8.2663e+13
```

Figure 4.10 Peak deconvolution of Co-TS-1 0.097 mol% of Co.

Data fit peak

Peak properties	**1**	**2**
Center time (min)	9.79292	19.9395
temp (°C)	142	236
Area	0.0768117	0.027523
Height	0.00313584	0.00155392



Name	Type
_1	SplitGa
_2	SplitGa

```
rror: Estimating peak parameters: peak outside of search scope. Tried at [0 : 40.0833] Canceled.
=-> fit
nitial A=( 0.00296421, 10.2479, 3.90348, 8.52136, 0.000695435, 19.6867, 4.67413, 2.45708 )
nitial values:  lambda=0.001  WSSR=5.58321e-007
#1:  WSSR=5.58321e-007  lambda=0.0001  d(WSSR)=-3.29204e-013  (5.89775e-005%)
#2:  WSSR=5.58321e-007  lambda=1e-005  d(WSSR)=-6.76814e-014  (1.21223e-005%)
it converged.
etter fit found (WSSR = 5.58321e-007, was 5.58321e-007, -7.10990e-005%).
```

%_1
Peak properties:
Center: 10.2473
Area: 0.0784017
Height: 0.00296396

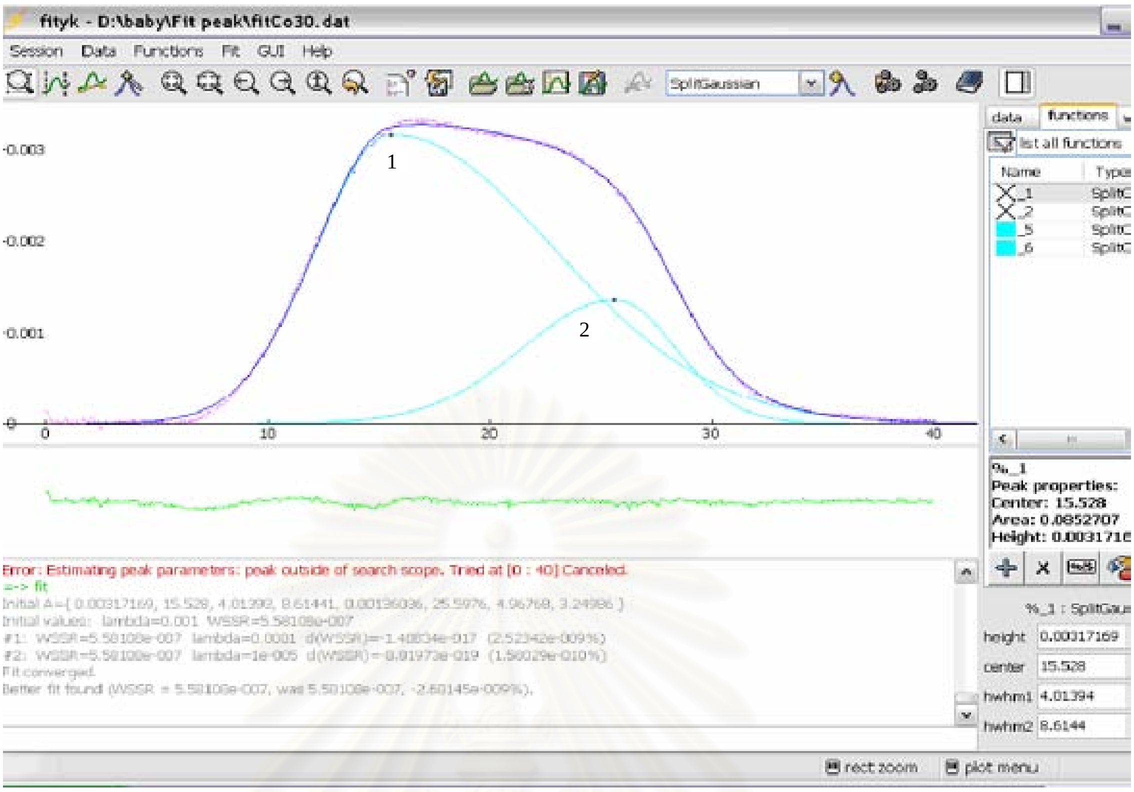
%_1 : SplitGaus

height 0.00296396
center 10.2473
hwhm1 3.90314
hwhm2 8.52169

Figure 4.11 Peak deconvolution of Co-TS-1 0.103 mol % of Co.

Data fit peak

Peak properties		**1**	**2**
Center	time (min)	16.9991	9.75641
	temp (°C)	149	228
Area		0.0784004	0.0105658
Height		0.00224097	0.00236636



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Error: Estimating peak parameters: peak outside of search scope. Tried at [0 : 40] Canceled.
=-> fit
Initial A={ 0.00317169, 15.528, 4.01392, 8.61441, 0.00136036, 25.5976, 4.96768, 3.24986 }
Initial values:  lambda=0.001  WSSR=5.58108e-007
#1:  WSSR=5.58108e-007  lambda=0.0001  d(WSSR)=-1.40834e-017  (2.52342e-009%)
#2:  WSSR=5.58108e-007  lambda=1e-005  d(WSSR)=-8.91973e-019  (1.60029e-010%)
Fit converged.
Better fit found (WSSR = 5.58108e-007, was 5.58108e-007, -2.60145e-009%).
```

```
%_1
Peak properties:
Center: 15.528
Area: 0.0852707
Height: 0.0031716
```

%_1 : SplitGau

height 0.00317169

center 15.528

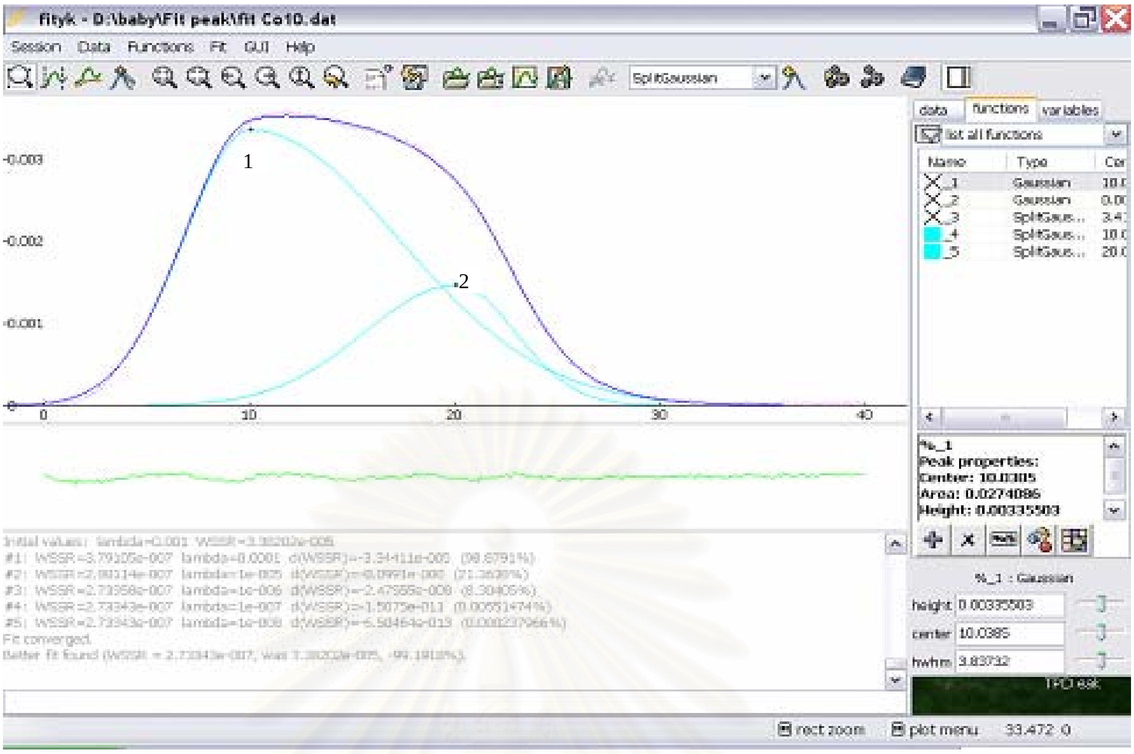
hwhm1 4.01394

hwhm2 8.6144

Figure 4.12 Peak deconvolution of Co-TS-1 0.217 mol% of Co.

Data fit peak

Peak properties		1	2
Center	time (min)	15.528	25.5976
	temp (°C)	141	236
Area		0.085277	0.0237989
Height		0.00317169	0.00136036



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Initial values:  lambda=0.001  WSSR=3.38202e-005
#1:  WSSR=3.79105e-007  lambda=0.0001  d(WSSR)=-3.34411e-005  (98.8791%)
#2:  WSSR=2.98114e-007  lambda=1e-005  d(WSSR)=-8.0991e-008  (21.3638%)
#3:  WSSR=2.73358e-007  lambda=1e-006  d(WSSR)=-2.47555e-008  (8.30405%)
#4:  WSSR=2.73343e-007  lambda=1e-007  d(WSSR)=-1.5075e-011  (0.00551474%)
#5:  WSSR=2.73343e-007  lambda=1e-008  d(WSSR)=-6.50464e-013  (0.000237966%)
Fit converged.
Better fit found (WSSR = 2.73343e-007, was 3.38202e-005, -99.1918%).
```

```
%_1
Peak properties:
Center: 10.0385
Area: 0.0274086
Height: 0.00335503
```

height 0.00335503
center 10.0385
hwhm 3.83732

Figure 4.13 Peak deconvolution of Co-TS-1 0.382 mol% of Co.

Data fit peak

Peak properties		**1**	**2**
Center	time (min)	10.0385	20.0429
	temp (°C)	145	240
Area		0.0878317	0.0271415
Height		0.00335503	0.00146456

4.2.2 2-Propanol oxidation

In this part, the oxidation properties of TS-1 and Co-TS-1 catalysts are studied by using the oxidation reaction of 5% 2-propanol in 8% O_2 system as the test reaction. The calculation (see Appendix C) shows that there is no effect of internal and external diffusion under the reaction condition used.

Figure 4.14 shows the catalytic activity of TS-1 catalyst for 2-propanol oxidation reaction. The conversion of 2-propanol increases from 2% to 85.69% at the temperature range 200-350 °C and rapidly increases to 90%. Above 350 °C, the conversion of 2-propanol approaches 100% at 500 °C. At the initial reaction temperature (200-350 °C) the main products are acetone, CO_2 and propylene. When the reaction temperature is further increased, the selectivity to acetone decreases to 54.88% while propylene selectivity gradually rises to a value around 11-12%. The selectivity of CO_2 gradually increases to 33.65% at 500 °C.

The effects of reaction temperature on the catalytic activity and product selectivities of 2-propanol over Co-TS-1 catalysts with Co 0.097 mol%, Co 0.107 mol%, Co 0.217mol%, Co 0.382 mol% of cobalt concentration in Co-TS-1, are shown in Figures 4.15-4.18 respectively. It is found that all the synthesized Co-TS-1 samples behave in a similar way. The difference between each catalyst is the amount of 2-propanol being converted to the products. In each experiment, the primary product is propylene with selectivity 23.25%, 23.18%, 30.17%, 26.46% at 100-350 °C for 0.097, 0.103, 0.217, 0.382 mol% Co, respectively. Carbon dioxide becomes another significant reaction product in the reaction temperature above 400 °C. The selectivities to carbon dioxide are around 30-40% in the reaction temperature range 400-500 °C. It should be noted here that in each experiment mentioned above, isopropyl ether (product of the dehydration between two 2-propanol molecules) was found in a very small amount. The formation of isopropyl ether, therefore, will not be considered in the further discussion.

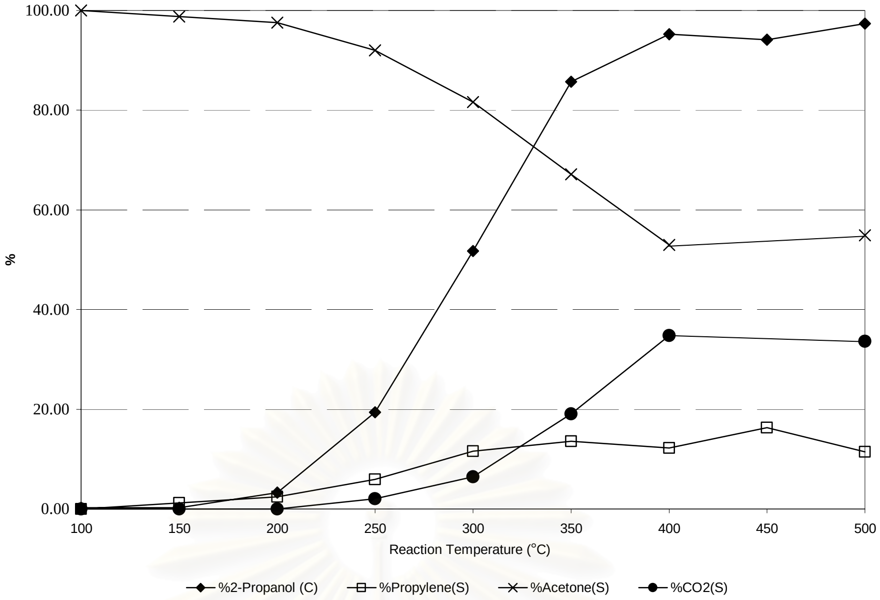


Figure 4.14 Product selectivities and conversion of 2-propanol over TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity).

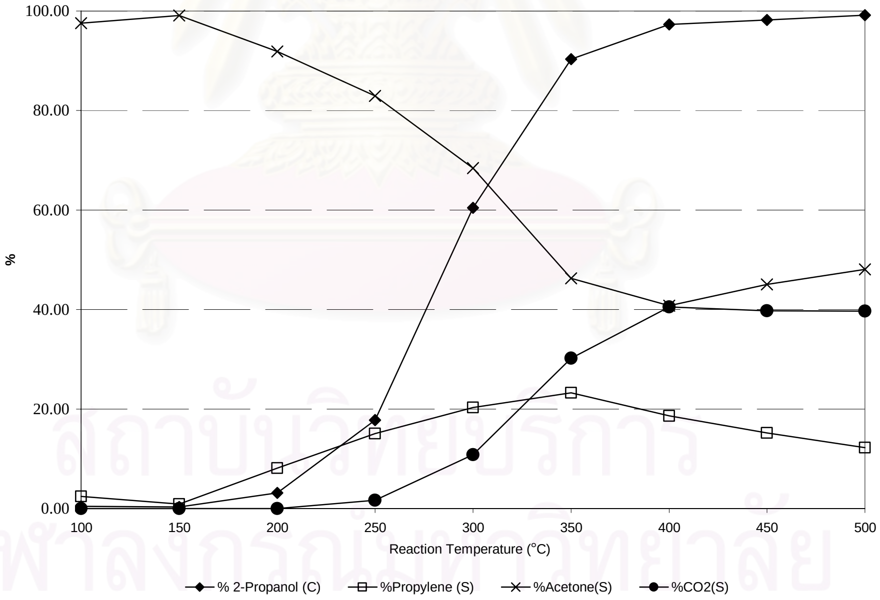


Figure 4.15 Product selectivities and conversion of 2-propanol over Co-TS-1 0.097 mol% for 8 vol% O_2 system (C-Conversion, S-Selectivity).

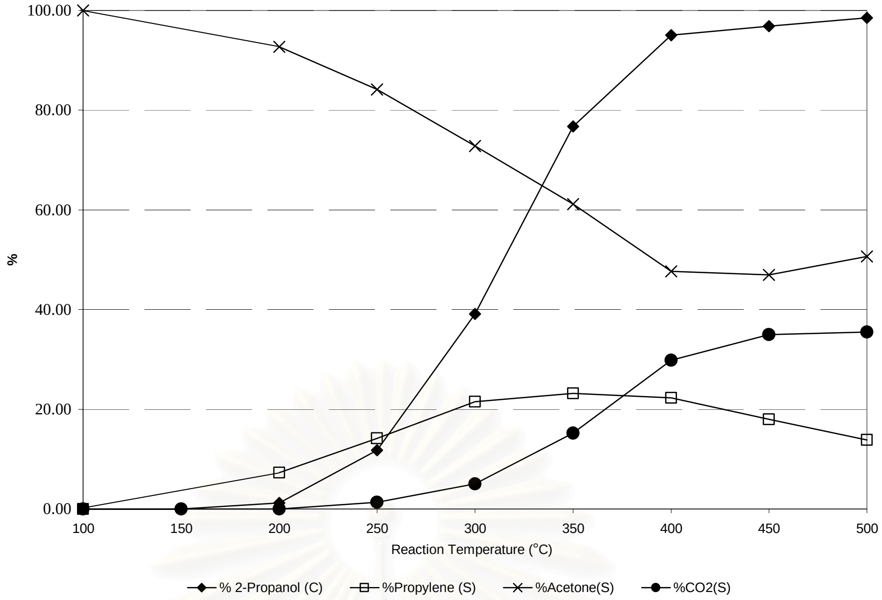


Figure 4.16 Product selectivities and conversion of 2-propanol over Co-TS-1 0.103 mol% for 8 vol% O_2 system (C-Conversion, S-Selectivity).

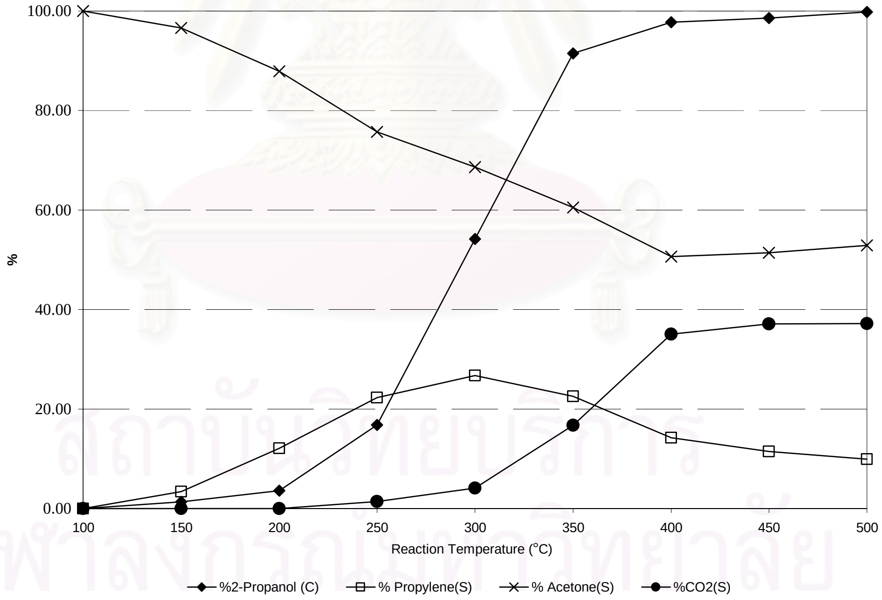


Figure 4.17 Product selectivities and conversion of 2-propanol over Co-TS-1 0.217 mol% for 8 vol% O_2 system (C-Conversion, S-Selectivity).

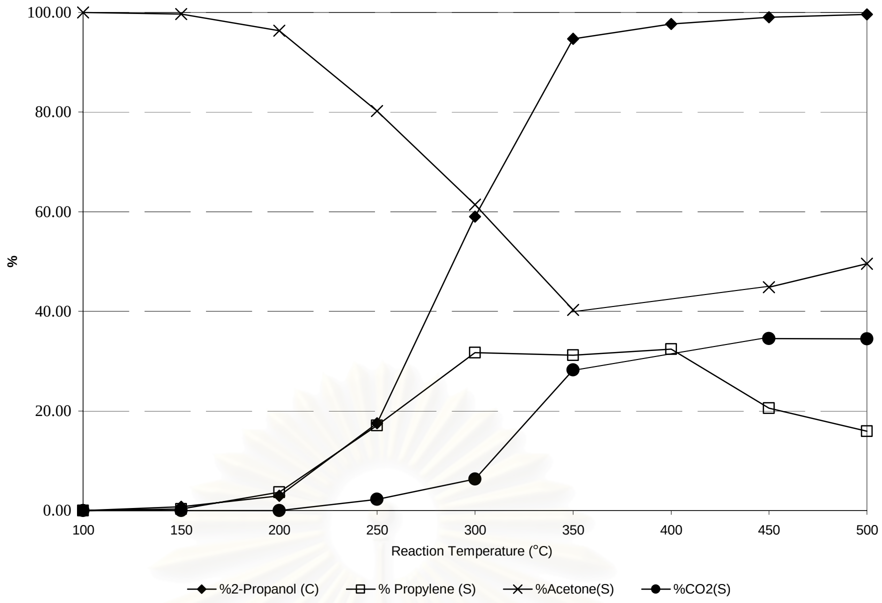


Figure 4.18 Product selectivities and conversion of 2-propanol over Co-TS-1 0.382 mol% for 8 vol% O_2 system (C-Conversion, S-Selectivity).

The reaction testing results described above indicate that the major role of cobalt on the oxidation of 2-propanol over modified TS-1 is the promotion of the dehydration of 2-propanol to propylene, as can be seen from the increase in propylene selectivity when the amount of cobalt increases. The added cobalt has no pronounce effect on the oxidation reaction since the selectivity to CO_2 is approximately the same for all the catalysts sample. In addition, since there is no small organic molecule (i.e. C1-C2 organic compounds) appears in the reaction product, it can be concluded that the added cobalt does not create a new reaction pathway nor inhibit the combustion pathway too. The changing in acetone selectivity can be the result of the further oxidation of acetone to CO_2 or the competitive reaction between the dehydration of 2-propanol to propylene and the oxidation of 2-propanol to acetone. Since the formation of CO_2 does not significantly change while the formation of propylene is significantly increased, the observed decrease of acetone selectivity is likely to be the result of loosing 2-propanol reactant to propylene rather than the loosing via the further oxidation of acetone to CO_2. This conclusion agrees with the finding reported in the NH_3-TPD section that the addition of cobalt significantly increases the amount of the weak acid site which is able to dehydrate but not able to oxidize 2-propanol.

From all of the above explained experimental results, the pathway of product formation in 2-propanol oxidation reaction over Co-TS-1 can be summarized in Figure 4.19 below. This model has been proposed before by Kedsuda (2004) using TS-1 as the oxidation catalyst. The present study finds that the pathway of 2-propanol oxidation over Co-TS-1 also follows this model too. The difference is the ratio the reactants proceed via each pathway.

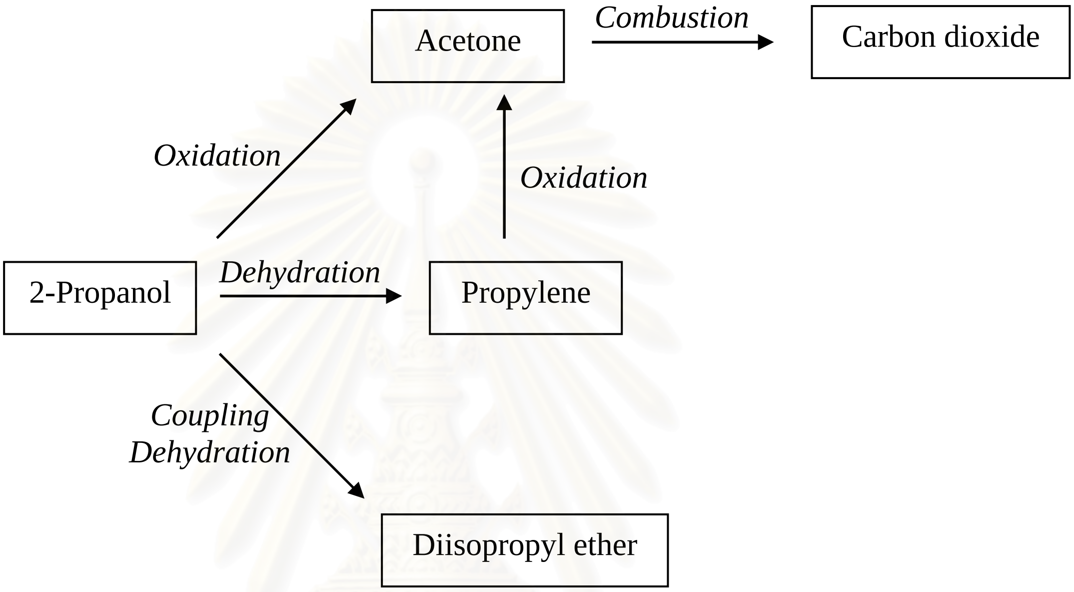


Figure 4.19 Schematic pathway of product formation in 2-propanol oxidation reaction.

CHAPTER V

CONCLUSION

5.1 Conclusions

The conclusions of the present research are the following:

1. The presence of $Co(NO_3)_2.6H_2O$ up to 0.382 mol% in the synthesis solution slightly affects the formation of TS-1 structure. The formed catalysts can still maintain the crystal structure as well as surface area and average pore size nearby TS-1.

2. The amount of $Co(NO_3)_2.6H_2O$ used in the preparation of the catalyst with the highest Co content (0.382 mol%) is about 15 times higher than the amount of $Co(NO_3)_2.6H_2O$ used in the synthesis of the catalyst with the lowest Co content (Co-TS-1 0.097 mol%), the amount of Co cation can be incorporated is only about 4 times different. The incorporation of Co in TS-1 framework does not linearly increase as the amount of $Co(NO_3)_2.6H_2O$ used during the synthesis is increase.

3. Co promotes the dehydration of 2-propanol to propylene rather than the oxidation of 2-propanol to acetone when compare with TS-1.

5.2 Recommendations for future studies

From the previous conclusions, the following recommendations for future studies can be proposed.

1. More characterization techniques such as X-ray absorption at fine structure (EXAFS) which can be used to investigate the environmental amorphous phase and small metal particle which are very difficult to study by other techniques and additional ESR study to confirm the oxidation state and cobalt within the MFI framework should be carried out.

2. The reaction study under commercial Fisher-Tropsch synthesis conditions using Co-TS-1 catalysts is also recommended.

3. It will be interesting to investigate the oxidation property of Co-TS-1 catalyst on other alcohol such as unsaturated alcohol or glycol.

REFFERENCE

Barakat, M.A., Hayes, G., and Shanh, S.I. "Effect of cobalt doping on the phase transformation of TiO_2 nano-particles". *J of nanoscience and Nanotechnology*. 2005, 1-7.

Boccuti, M.R., Rao, K.M., Zecchina, A., Leofanti, G., and Petrini, G., "Hydroxylation of Phenol over Ti-MCM-41 and TS-1", *Stud. Surf. Sci. Catal*., 1989, **48**, 133.

Ciaxia, Q., Akita, T., Okumura, M., and Haruta, M. "Epoxidation of propylene over gold catalysts supported on non porous silica" *Appl. Catal A:*. 2001, **218**, 81-89.

Duprey, E., Beaunier, P., Spring-Huet, M.A., Bozon-Verduraz, F., Fraissard, J., Mandi J. M., and Breault J. M. "Characterization of catalysts based on titanium silicalite, TS-1 by Physicochemical Techniques" *J. of catal.* 1997, **165**, 22-32.

Guo, X., Wang, R., Wang, X., Hao, J. "Effect of preparation method and precipitator on the propylene epoxidation over Ag/TS-1 in the gas phase" *Catal. Today*, 2004, 211-216.

Katsuda Chairat , "Oxidation reaction of alcohols over TS-1 catalyst", Master's thesis ,Department of Graduated school, Chulalongkorn University, 2004.

Karandikar, R.Dhanya, K.C., Deshande, Chandwadkar, A.J., Sivasanker, S., and Agashe, M. "Cu/Co-Salen immobilized MCM-41 characterization and catalytic reaction reaction". *Catal. Communications*. 2004**, 5**, 69-74.

Jentys, A., Pharn, N.H., Vinek, H.,Erglishch, M., and Lercher, J.A. "synthesis and characterization of mesopic materials containing highly dispersed cobalt". *Micro and Meso Master.* 1996, **6,** 13-17.

Jentys, A., Pharm, N.H., Vinek, H., Englisch, M., and Lercher, J.A. "structure of Co and Cu clusters in MCM-41". *Catal. Today* 1998**, 39**, 311-315.

Jenzer, G., Mallet, T., Maciejewski, M., Eigenmann, F., and Baiker, A. "Continuous epoxidation of propylene with oxygen and hydrogen on a Pd-Pt/TS-1 catalyst" *Appl. Catal. A:*. 2001, **208**, 125-133.

Hung, Liu, Guanxhang, Lu, and Hangjin, Hu. "Synthesis characterization and catalyticperformance of titanium silicalite-1 prepared in the presence of nonionic surfactants". *Mate Chem and Phys*. 2006.

Laufer, W., Meiers, R., and Holderich, W. “Propylene epoxidation with hydrogen peroxide over palladium containing titanium silicalite” *J.of Mole. Catal. A.*, 1999, 215-221.

Rafael, V. G., David, P. S., Juan, A. M., and Alicia, G. “ Effect of the solvent in the liquid phase rearrangement of 1,2-epoxyoctane over Al-MCM-41 and Al-TS-1 catalyst” *J. of Mole. Catal. A*:. 2004, **222**, 167-174.

Panpranot, J., Goodwin, J.G., Jr. and Sayari, A. “ Synthesis and characteristics of MCM-41 supported CoRu catalysts” *Catal Taday.* 2002, **77**, 269-284.

Panpranot, J., Goodwin, J.G., Jr. and Sayari, A. “Effect of the H2 partial pressure on surface reaction parameters during Co hydrogenatin on Ru-promoted silica-supported Co catalysts” *J. catal.* 2003, **213**, 78-85.

Pirutko, L.V., Uriarte, A.K., Chernyavsky, V.S., Kharitonov, A.S., and Panov, G.I. “Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by N_2O”, *Micr. and meso. Mater.*, 2001, **48**, 345-353.

Schieber, W., Vinek, H., and Jentys, A. “Catalytic reduction of NO_x over transition-metal-containing MCM-41”. *Catal. Lett.* 1998**, 56**, 189-194.

Song, C., and Reddy, K.M. “Mesoporous molecular sieve MCM-41 support Co-Mo catalyst for hydrosulfurization of dibenzothiophene in distillate fuels”. *Appl. Catal. A.* **176**, 1996, 1-10.

Suvanto, S., Hukkamaki, J., Pakkanen, T.T., and Pakkanen, T.A. “High-Cobalt – loaded MCM-41 via the Gas-phase Method Langmuir”, *Langmuir.* **16**, 2000, 4109-4115.

Suvanto, S., and Pakkanen, T.A. “Temperature programmed studied off Co on MCM-41 and SiO_2”. *J.Molecular Catal. A.* 2002**, 164,** 173-280.

Taramasso, M., Perego, G., and Notari, B. “Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides”, *United States Patent*, 1983, 4410501.

Teul, A. “Cryatllization of titanium silicalite-1(TS-1) from gels containing hexanediamine and tetrapropylammonium bromide” *Zeolites*, 1996, **16**,108-117.

Turaga, U.T., and Sang, C. “MCM-41-suupported Co-Mo catalysts for deep hydrodrfulfuriczation of light cycle oil”, *Catal. Today*.86 (2003)129-140.

Van der Pol, A.J.H.P. and Van Hooff, J.H.C. “Parameters affecting the synthesis of titanium silicalite-1”, *Appl. Catal. A*, 1992, **92**, 93-111.

Xinbin Ma, Jinlong Gong, Sheng Wang, Fei He, Hongli Guo, Xia Yong, and Genhui Xu. “Characterization and reactivity of stannum modified titanium silicalite TS-1 catalysts for transesterification of dimethyl oxalate with phenol”. *J. of Mole. Catal A: Chem*. 2005 ,**237**, 1-8.

Yin, D., Li, W., Yang, W. Xiang, H., Sun, Y. Zhang, B. ,and Reng, S. “Mesoporous HMS molecular sieve supported cobalt catalyst for Ficher-Tropsch synthesis”. *Micro. and Meso*. Mater, 2001**, 47**, 15-24.

APPENDICES

APPENDIX A

BASIC INFORMATION OF TS-1

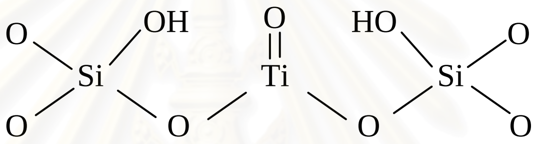
A1 Titanium Silicalite-1 [Notari (1989)]

Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been in several oxidation reactions with H_2O_2 as the oxidizing agent [Centi et al. (2001)].

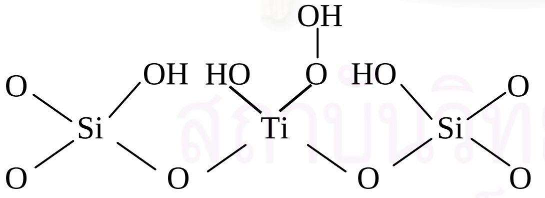
Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{IV} compounds immediately shows that Ti^{IV} has a strong tendency to assume a high coordination number : with oxygen, six groups in octahedral coordination form a stable and very frequently observed configuration, but to do this Ti^{IV} must have near neighbours capable of increasing their coordination number to satisfy at the same time titanium valency of four and coordination of six. When bulky groups are linked to Ti^{IV}, tetrahedral coordination is also observed. Coordination of seven in. a pentagonal pyramidal arrangement like in peroxo compounds and of eight like in $Ti(NO_3)_4$ are also observed.

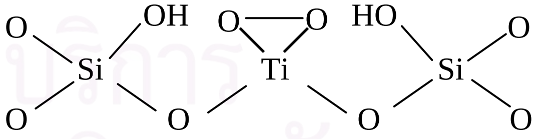
From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{IV} with Ti^{IV} it seems justified to represent TS-l as a silicalite in which few Ti^{IV} have taken the place of Si^{IV}. The interpretation of the catalytic activity of TS-l must take into consideration the role played by these few Ti^{IV}: in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-l crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{IV} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most Ti^{IV} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{IV} replaces a Si^{IV} it should be tetrahedrally coordinated by $O^{=}$: however, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the Ti = O group, whose streching frequency is 975 cm^{-1} with bond distances of 1.66 – 1.79 Å; furthermore, hydroxyl groups are present at the surface as shown by the increase in selectivity which is obtained upon silylation.

Finally, near neighbour positions of Ti^{IV} are occupied by Si^{IV} which in a field of $O^{=}$ is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be

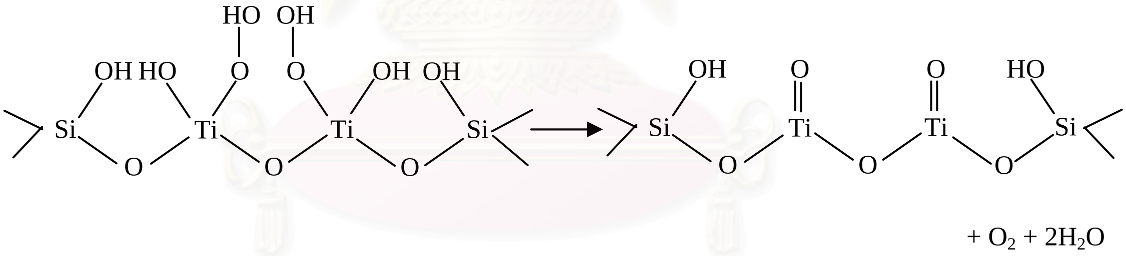


Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts. Ti^{IV} in TS-1 maintains the strong affinity of soluble Ti^{IV} salts for H_2O_2 and in fact the addition of H_2O_2 gives rise to a strong yellow colour which can be attributed to the formation of surface titanium peroxo compounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants.





Work carried out on Mo(VI) and W(VI) peroxo compounds [Amato et al. (1986)] has demonstrated that peroxo compounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess H_2O_2 the peroxo compound is regenerated and this accounts for the catalytic nature of the reaction. It seems reasonable to assume that a similar mechanism operates in the case of Ti(IV) peroxo compounds. The relevance of isolated Ti^{IV} and the connection with catalytic performances appears to hold also for the TiO_2/SiO_2 catalyst. In fact high epoxide selectivities are obtained when TiO_2 is distributed on high surface area SiO_2 and its concentration is limited to 2% [Sheldon, (1980)]. It is very likely that at this low concentration Ti^{IV} are isolated and surrounded by Si^{IV}. Furthermore, SiO_2 or TiO_2 alone, or physical mixtures of SiO_2 and TiO_2 or various metal titanates exhibit no significant activity. Similarly, supporting TiO_2 on carriers different from SiO_2 like Al_2O_3, MgO or ZrO_2 leads to catalysts whose activity is lower or nil. One piece of evidence seems very convincing: when the TiO_2 concentration on the catalyst is reduced from 4% to 0.4%, all other conditions being equal, an increase in epoxide selectivity is obtained. The only effect that a reduction in the concentration of TiO_2 can have is an increase in the degree of dispersion of each Ti^{IV}: chances for each Ti^{IV} of having Si^{IV} as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated Ti^{IV} and selectivity of the catalyst in epoxidation could be due to the fact that on Ti^{IV} having other Ti^{IV} as near neighbours, a mechanism proceeding through a bimolecular interaction of surface peroxo species could be operating which would give rise to a high decomposition rate of H_2O_2 or hydroperoxides to O_2. This mechanism could not operate on perfectly isolated Ti^{IV}.



Low decomposition of H_2O_2 (or hydroperoxides as well) means greater stability of titanium peroxo compound whose reduction can only be carried out by the organic substrate with increased yields of useful oxidized products. When the different results between TS-1 and TiO_2/SiO_2 in the hydroxylation of phenol are analyzed the existence of a “restricted transition state selectivity” must be assumed to explain the small amount of tars formed.

A2 Substitution of Si from Silica Lattice by Metals

In order for the isomorphic substitution of tetrahedrally coordinated Si^{4+} by other metals ions to take place, it is necessary for the metal ions to assume the same coordination as the ions being replaced. Based on the radius ratio rules, substitution of tetrahedrally coordinated Si^{4+} should be possible if the radius ratio of the cation and oxygen anion is between 0.225 and 0.414. Recent developments in this area show that framework substitution is also possible for larger metal cations, e.g. Mo, for which the radius ratio is slightly higher than 0.414. The first successful example was the isomorphic substitution of Si^{4+} with Ti^{4+} from a ZSM-5 silicalite framework, which was reported by Tiramisu et al. in 1983. As synthesized titanium incorporated ZSM-5 silicalite (TS-1) shows excellent catalytic properties in a number of catalytic oxidation reactions with aqueous hydrogen peroxide as the oxidant under mild conditions.

Based on the success of TS-1, other transition metals, such as, V, Fe , Mo, Zr, and Cr, have also been inserted into the silica lattice. .5 Ǻ Typical Catalytic Test Reaction: Phenol Hydroxylation two well known molecular sieves of MFI type are silicalite-1 and ZSM-5 Figure 1.1 shows a MFI –crystal with typical habit and the channel system and crystallographic axes the straight elliptical channels along the b-direction within the crystal have the dimention 5.6x5.3 Ǻ and the sinusoidial channels channel along the a-direction have the dimentions 5.5x5.1 Ǻ The difference between silicalite-1 and ZSM-5 ,is the aluminum content. The silicon/aluminum ratio for silicalite-1 is>200. The silicon/aluminum ratio within ZSM-5 is in the range of 10-200 Aluminum affects several properties of the zeolite, by adding charge to the framework. The charge framework renders the zeolite catalytically active, hydrophilic and an ionexchange.

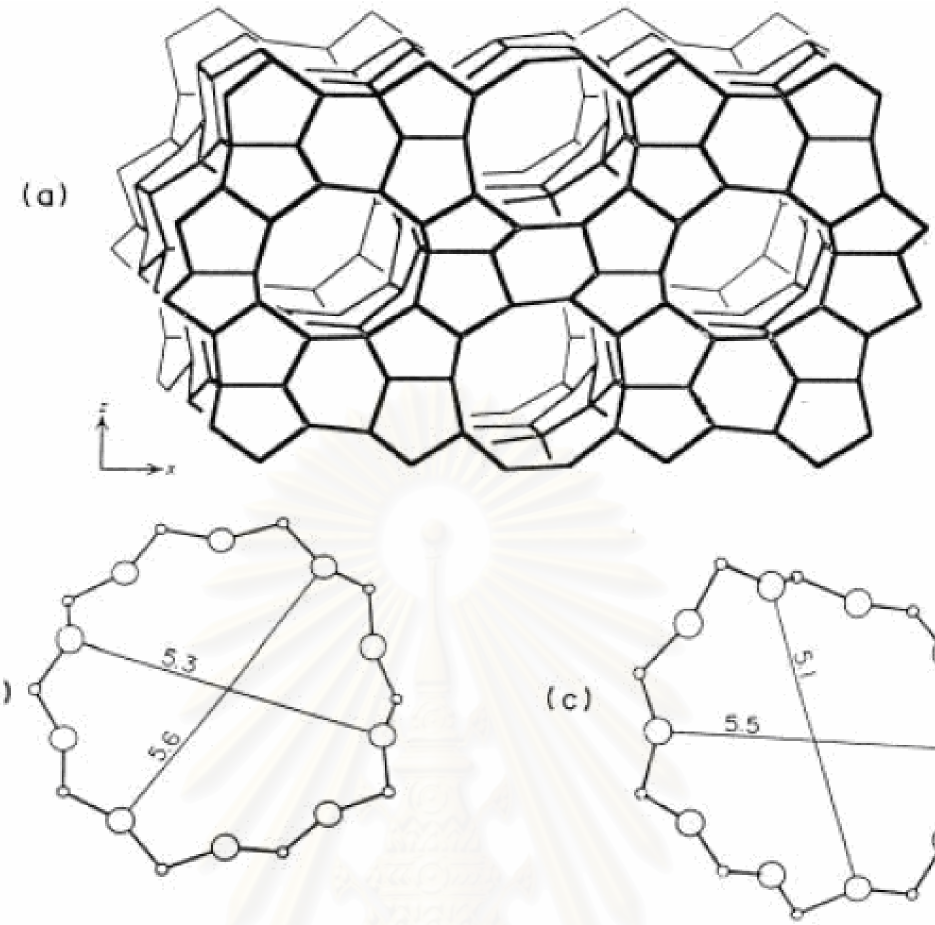


Figure A.1 Structure of MFI a) The MFI framework topology b) 10-ring viewed along [010] (straight channel) and c) 10-ring viewed along [100] sinusoidal channel

A3 Reaction of alcohols

Reaction of an alcohol can involve the breaking of either two bonds:the C-OH bond, with removal of the –OH group ; or the O-H bond, with removal of –H bond. Either kind of reaction can involve substitution, in which a group replace the –OH or –H, or elimination, in which a double bond is formed.

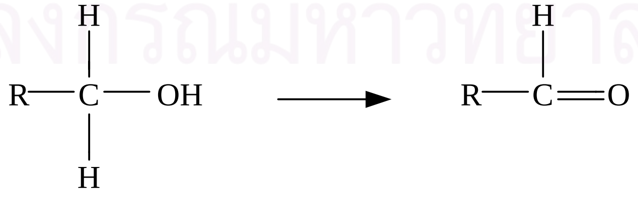
Reactions of alcohols

Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the -OH group ; or the O-H bond, with removal of -H bond. Either kind of reaction can involve substitution, in which a group replaces the -OH or -H, or elimination, in which a double bond is formed.

A3.1 Oxidation

The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

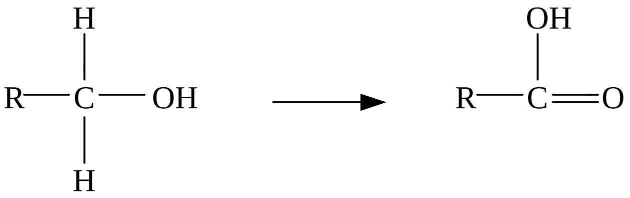
A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,



$$R-\overset{H}{\underset{H}{C}}-OH \longrightarrow R-\overset{H}{C}=O$$

A 1^{o}alcohol An aldehyde

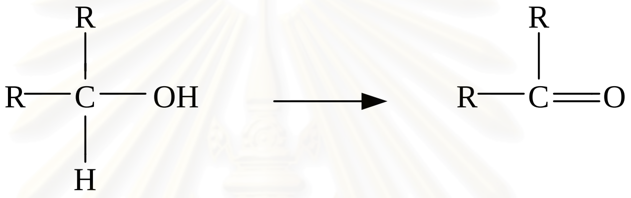
or both of them to form a carboxylic acid.



$$\mathrm{R{-}CH_2{-}OH} \longrightarrow \mathrm{R{-}C(OH){=}O}$$

A 1^{o} alcohol A carboxylic acid

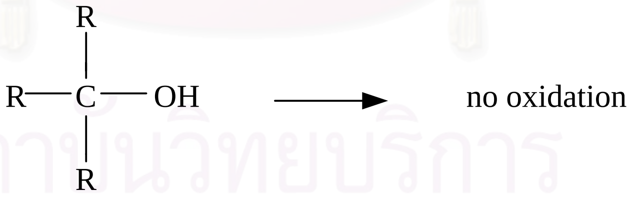
A secondary alcohol can lose its only α-hydrogen to form a ketone.



$$\mathrm{R_2CH{-}OH} \longrightarrow \mathrm{R_2C{=}O}$$

A 2^{o} alcohol A ketone

A tertiary alcohol contains no α-hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).

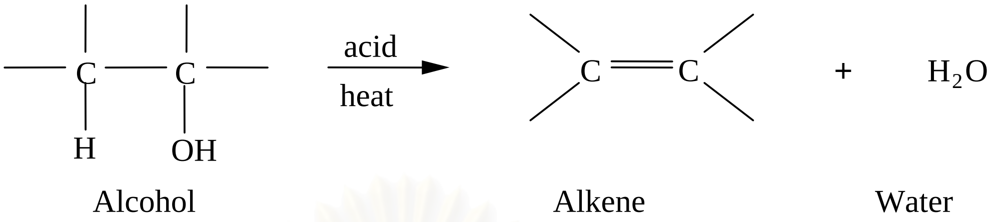


$$\mathrm{R_3C{-}OH} \longrightarrow \text{no oxidation}$$

A 3^{o} alcohol

A3.2 Dehydration

Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperature. An alcohol is converted into an alkene by dehydration (elimination of a molecule of water).



The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohol $3^o > 2^o > 1^o$

A4 Cobalt [Young (1960), Othmer (1991]

A4.1 General

Cobalt, a transition series metallic element having atomic number 27, is similar to silver in appearance.

Cobalt and cobalt compounds have expended from use colorants in glassed and ground coat frits for pottery to drying agent in paints and lacquers, animal and human nutrients, electroplating materials, high temperature alloys, hard facing alloys, high speed tools, magnetic alloys, alloys used for prosthetics, and used in radiology. Cobalt is also as a catalyst for hydrocarbon refining from crude oil for the synthesis of heating fuel.

A4.2 Physical Properties

The electronic structure of cobalt is [Ar]$3d^7 4s^2$. At room temperature the crystalline structure of the α (or ε) form, is close-packed hexagonal (cph) and lattice parameters are a = 0.2501 nm and c = 0.4066 nm. Above approximately 417 ºC, a face-cantered cubic (fcc) allotrope, the γ (or β) form, having alattice parameter a = 0.3544 nm, becomes the stable crystalline form. Physical properties of cobalt are listed in Table A.1.

The scale formed on unalloyed cobalt during exposure to air or oxygen at high temperature is double-layered. In the range of 300 to 900 ºC ,the scale consists of a thin layer of mixed cobalt oxide, Co_3O_4, on the outside and cobalt(II) oxide, CoO, layer next to metal. Cobalt (III) oxide, Co_2O_3 may be formed at temperature below 300 ºC. Above 900 ºC, Co_3O_4 decomposes and both layers, although of different appearance , are composed of CoO only. Scales formed below 600C and above 750 ºC appear to cracking on cooling, whereas those produced at 600-750 ºC crack and flank off the surface.

Cobalt forms numerous compounds and complexes of industrial importance. Cobalt, atomic weight 58.933, is one of the members of the first transition series of

Table A.1 Physical properties of the cobalt [Othmer (1991)]

Property	Value
Atomic number	27
Atomic weight	58.93
Transformation temperature, ºC	417
Heat of transformation, J/g^a	251
melting point, ºC	1493
latent heat of fusion, ΔH^{fus} J/g^a	395
boiling point, ºC	3100
latent heat of vaporization at bp, ΔH^{fus} J/g^a	6276
specific heat, J/(g^0 C)^a	
15-100 ºC	0.442
Molten metal	0.560
coefficient of the thermalexpansion, ºC^{-1}	
cph at room temperature	12.5
fcc at 417 ºC	14.2
thermal conductivity at 25 ^{o}C, W/(mK)	69.16
thermal neutrin absorption,Bohr atom	34.8
resistivity, at 20^0 C^b, 10^{-8} Ω.m	6.24
Curie temperature, ºC	1121
Saturation induction, 4¶I_s,T^c	1.870
Permeability, μ	
Initial	68
max	245
residual induction, T^c	0.490
coercive force, A/m	708
Young's modulus, Gpac	211
Poiison's ratio	0.32

Table A.1 Physical properties of cobalt (cont.)

Property		Value		
Hardnessf, diamond pyramid, of % Co		99.9	99.98e	
At 20 ºC		225	253	
At 300 ºC		141	145	
At 600 ºC		62	43	
At 900 ºC		22	17	
Strength of 99.99 % cobalt, Mpa[g]	as cast		annealed	sintered
Tensile	237		588	679
Tensile yield	138		193	302
Compressive	841		808	
Compressive yield	291		387	

[a] To convert J to cal, divided by 4.184.

[b] conductivity = 27.6 % of International Annealed Copper standard.

[c] To convert T to gauss, multiply by 10^4.

[d] To convert GPa to psi, multiply by 145,000.

[e] Zone refined.

[f] Vickers.

[g] To convert MPa to psi, multiply by 145.

Group9 (VIIIB). There are thirteen know isotopes, but only three are significant: ^{59}Co is the only stable and naturally occurring isotope; ^{60}Co has a half-life of 5.3 years and is a common source of γ-radioactivity; and ^{57}Co has a 270-d half-life and provides the source for MÖssbauer spectroscopy.

Cobalt exists in the +2 or +3 valance states for the major of its compounds and complexes. A multitude of complexes of the cobalt (III) ion exists, but few stable simple salt are known. Octahedral stereochemistries are the most common for cobalt (II) ion as well as for cobalt (III). Cobalt (II) forms numerous simple compounds and complexes, most of which are octahedral or tetrahedral in nature; cobalt (II) forms more tetrahedral complex than other transition-metal ions. Because of the small stability difference between octahedral and tetrahedral complexes of cobalt (II), both can be found equilibrium for a number of complexes. Typically, octahedral cobalt (II) salts and complexes are pink to brownish red; most of the tetrahedral Co(II) species are blue.

A4.4 Cobalt Oxides

Cobalt has three well-known oxides:

Cobalt (II) oxide, CoO, is olive green, cubic crystalline material. Cobalt (II) oxide is the final product formed when the carbonate or the other oxides are calcined to a sufficiently high temperature, preferably in a neutral or slightly reducing atmosphere. Pure cobalt (II) oxide is a difficult substance to prepare, since it readily takes up oxygen even at room temperature to re-form a higher oxide. Above about 850C, cobalt (II) oxide form is the stable oxide. The product of commerce is usually dark gray and contain 75-78 wt% cobalt. Cobalt (II) oxide is soluble in water ,ammonia solution, and organic solvents, but dissolves in strong mineral acids. It is used in glass decorating and coloring and is a precursor for the production of cobalt chemical.

Cobalt(III) oxide, Co_2O_3, is form when cobalt compounds are heated at a low temperature in the presence of an excess of air. Some authorities told that cobalt (III) oxide exists only in the hydrate form. The lower hydrate may be made as a black power by oxidizing neutral cobalt solutions with substance with substance like sodium hypochlorite. Co_2O_3 or $Co_2O_3.H_2O$ is completely converted to Co_2O_3 at temperature above 265 °C. Co_2O_3 will absorb oxygen in a sufficient quantity to correspond to the higher oxide Co_2O_3

Cobalt oxide, Co_2O_3, is form when cobalt compound, such as the carbonate or the hydrate sesquioxide, are air at temperature above approximately 265 °C and not exceedind 800 °C.

A4.5 Co-based Catalysts

Support cobalt (Co) catalysts are the preferred catalysts for the synthesis of hydrocarbons from natural gas based syngas (CO and H_2) because of the their high Ficher-Tropsh (FT) activity, high selectivity for linear hydrocarbons and low activity for the water-gas shift reaction. It is known that reduced cobalt metal, rather than its oxides or carbides, is the most active phase for CO hydrogenation in such catalysts. Investigations have been done to determine the nature of cobalt species on various supports such as alumina, silica, titania, magnesia, carbon, and zeolites. The influence various types of cobalt precursor used was also investigated. It was found that the used of organic precursors such as Co(III) acetate resulting in an increase of Co conversion compared to the that cobalt nitrate.

A4.6 Cobalt-Support Compound Formation (Co-SCF)

Compound formation between cobalt metal and the support can occur under pretreatment and/or reaction conditions, leading to catalyst deactivation. The compound formation of cobalt metal with support materials However, is difficult to predict because of the lack of sufficient thermodynamic data. Co-Support compound formation can be detected evidentially.

A4.7 Co-Aluminate Formation

Interaction of cobalt with its alumina support has been observed by many authors using various techniques including TPR, XRD, EXAFS, and XPS. The migration of cobalt ions into alumina lattice sites of octahedral or tetrahedral symmetry is limited to the first few layers of the support under normal calcinations conditions. The reaction of Co with γ-Al_2O_3 can form a surface spinel in Co/γ-Al_2O_3 catalysts. The surface spinel structure can not be observed by X-ray diffraction because it does not have long range, three dimensional order. It has been suggested that cobalt ions occupying surface octahedral site of γ-Al_2O_3 are reducible whole cobalt ions occupying tetrahedral sites are non-reducible, at least at temperature

≤900 °C. At lower calcinations temperatures, filling of the octahedral sites is more favorable. Filling of the tetrahedral site of γ- Al_2O_3 may be enhanced by an increase in calcinations temperature.

A4.8 Co-silicate Formation

The formation of cobalt silicates on Co/SiO_2 under hydrothermal conditions has been extensively studied by Kogelbauer et al. (1995). Hydrothermal treatment at 200 ºC led to a catalyst with lower reducibility due to the formation of both reducible and non-reducible (at-temperature ≤ 900 ºC) cobalt silicates. It was found that hydrothermal treatment of the reduced catalyst or hydrothermal treatment of the calcinations catalyst in the presence of hydrogen produces cobalt silicates, while hydrothermal treatment of the calcined catalyst in air does not result in their formation. Hydrothermal treatment of the calcined catalyst in inert gas also has little effect.

APPENDIX B

CALCULATION FOR CATALYST PREPARATION

The calculations is base on weight of Sodium Silicate ($Na_2O.SiO_2.H_2O$) in B1 and B2 solution.

Molecular weight of Si = 28.0855

Molecular weight of SiO_2 = 60.0843

Weight present of SiO_2 in Sodium Silicate = 28.5

Using Sodium Silicate 69g with 45 g of water as a B1 and B2 solution.

$$\text{Mole of Si used} = \text{wt. x } \frac{(\%)}{100} \text{ x } \frac{(\text{M.W. of Si})}{(\text{M.W. of } SiO_2)} \text{ x } \frac{(\text{1mole})}{(\text{M.W. of Si})}$$

$$= 69 \text{ x } (28.5/100) \text{ x } (1/60.0843)$$

$$= 0.3273 \text{ mole}$$

MFI catalyst

For example , to prepare Si/Ti atomic ratio of 50 by using $Ti[O(CH_2)_3CH_3]_4$ for titanium source.

Molecular weight of Ti = 47.88

Molecular weight of $Ti[O(CH_2)_3CH_3]_4$ = 340.36

Weight % purities of $Ti[O(CH_2)_3CH_3]_4$ = 97

Si/Ti atomic ratio = 50

Mole of $Ti[O(CH_2)_3CH_3]_4$ required = 0.3273/50

= 6.546×10^{-3} mole

amount of $Ti[O(CH_2)_3CH_3]_4$ = $(6.546 \times 10^{-3}) \times (340.36) \times (100/97)$

= 2.2970 g

For example, to prepare Si/Co atomic ratio of 30 by using $Co(NO_3)_2.6H_2O$ for cobalt source.

Molecular weight of Co = 58.93
Molecular weight of $Co(NO_3)_2.6H_2O$ = 291.03

Si/Ti atomic ratio = 30
Mole of $Co(NO_3)_2.6H_2O$ required =0.3273/30
= 1.091×10^{-2} mole
amount of $Co(NO_3)_2.6H_2O$ = $(1.091 \times 10^{-2}) \times (291.03)$
= 3.175 g

which used in A1 and A2 solutions.

APPENDIX C

DATA OF EXPERIMENTS

Table C1 Data of Figure [TS-1]

Reaction temperature (ºC)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.25	0.00	0.00	100.00	0.00
150	0.29	1.25	0.00	98.75	0.00
200	3.31	2.47	0.00	97.53	0.00
250	19.38	5.94	0.00	92.02	2.04
300	51.71	11.62	0.31	81.64	6.44
350	85.69	13.59	0.19	67.16	19.06
400	95.24	12.24	0.06	52.93	34.77
450	94.15	16.32	0.05	75.35	8.28
500	97.38	11.48	0.00	54.88	33.65

Table C2 Data of Figure [Co-TS-1(0.097 mol % of Co)]

Reaction temperature (ºC)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.45	2.47	0.00	97.53	0.00
150	0.31	0.91	0.00	99.09	0.00
200	3.14	8.12	0.00	91.88	0.00
250	17.81	15.08	0.33	82.91	1.68
300	60.43	20.27	0.47	68.42	10.84
350	90.34	23.25	0.27	46.25	30.23
400	97.28	18.62	0.06	40.82	40.50
450	98.20	15.21	0.03	45.01	39.75
500	99.13	12.23	0.00	48.09	39.67

Table C3 Data of Figure [Co-TS-1(0.103 mol % of Co)]

Reaction temperature (ºC)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	100.00	0.00
150	0.03	14.19	0.00	85.81	0.00
200	1.21	7.30	0.00	92.70	0.00
250	11.81	14.19	0.35	84.13	1.33
300	39.13	21.53	0.60	72.82	5.05
350	76.77	23.18	0.43	61.17	15.23
400	95.06	22.32	0.14	47.70	29.84
450	96.86	17.98	0.05	46.98	34.99
500	98.52	13.84	0.02	50.64	35.50

Table C4 Data of Figure [Co-TS-1(0.214 mol% of Co)]

Reaction temperature (ºC)	Component				
	% 2-propanol C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.07	0.00	0.00	100.00	0.00
150	0.10	0.00	0.00	100.00	0.00
200	2.49	2.17	0.00	91.23	6.60
250	14.40	13.74	0.00	85.65	0.61
300	24.30	23.23	0.31	72.63	3.82
350	60.92	30.17	0.29	60.76	8.78
400	90.86	27.29	0.24	51.18	21.30
450	97.37	18.87	0.12	46.40	34.61
500	99.17	15.67	0.03	48.20	36.10

Table C5 Data of Figure [Co-TS-1(0.382 mol% of Co)]

Reaction temperature (ºC)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	100.00	0.00
150	0.00	0.00	0.00	100.00	0.00
200	3.59	2.49	0.00	97.51	0.00
250	7.27	20.11	0.00	77.60	2.30
300	33.93	18.33	0.19	69.03	12.45
350	71.04	26.46	0.13	64.81	8.60
400	95.28	20.29	0.05	50.38	29.27
450	98.37	15.71	0.03	53.02	31.24
500	98.74	15.92	0.03	51.52	32.54

APPENDIX D

CALIBRATION CURVE

Flame ionization detector gas chromatograph, model 8A, was used to analyze the concentrations of oxygenated compounds. 2-propanol, acetone, propylene, and isopropyl ether were analyzed by GC model 8A with using 15% Carbowax 1000.

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO, CO_2 by using Molecular Sieve 5A and Porapak-Q columns respectively.

The calibration curves 2-propanol, acetone, propylene, isopropyl ether, and CO_2 are illustrated in the following figures.

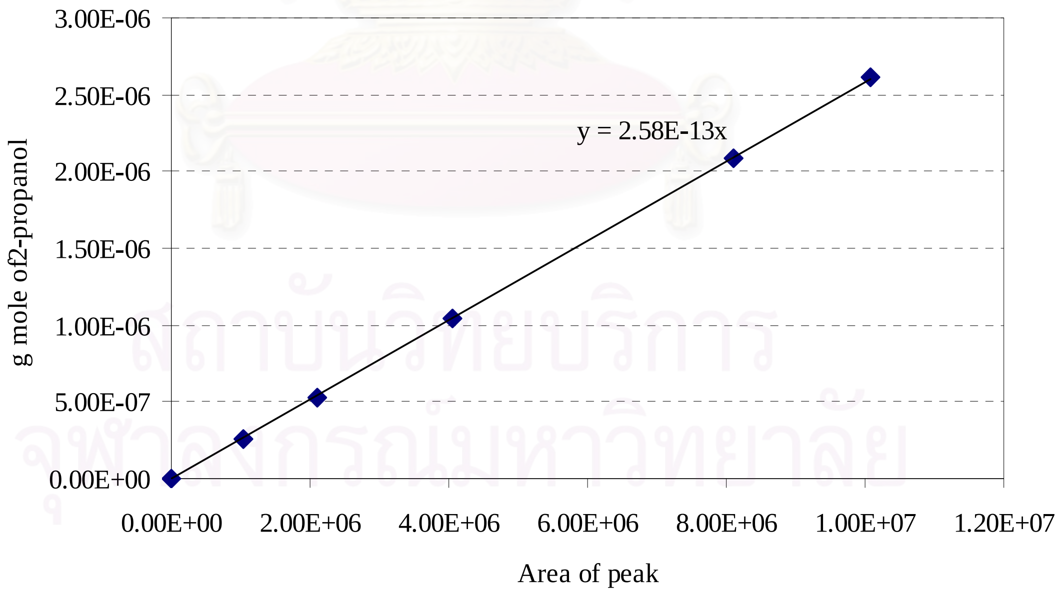


Figure D1 The calibration curve of 2-propanol.

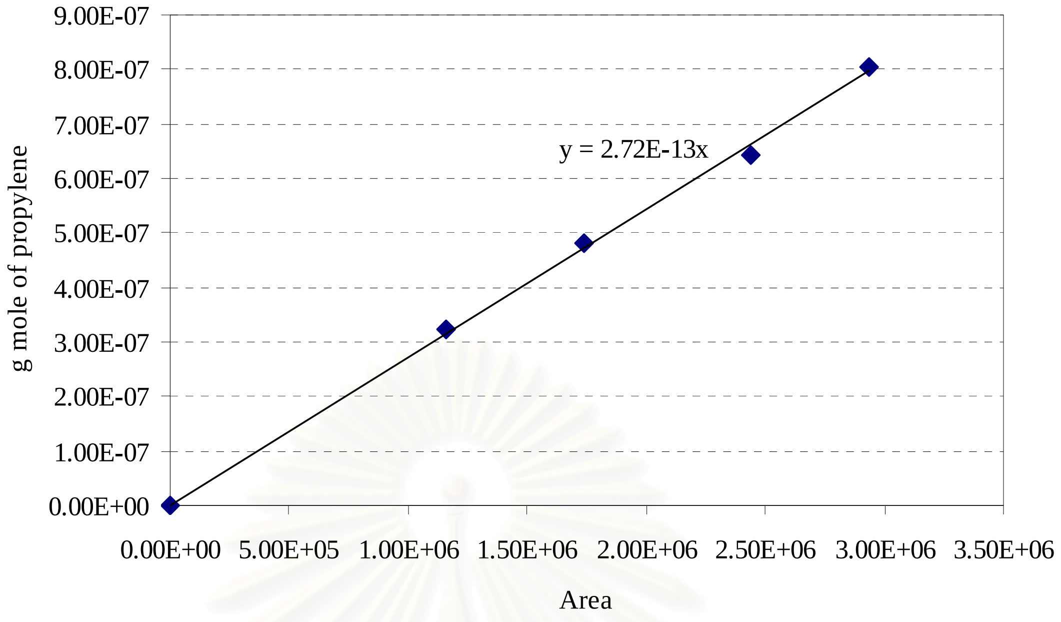


Figure D2 The calibration curve of propylene.

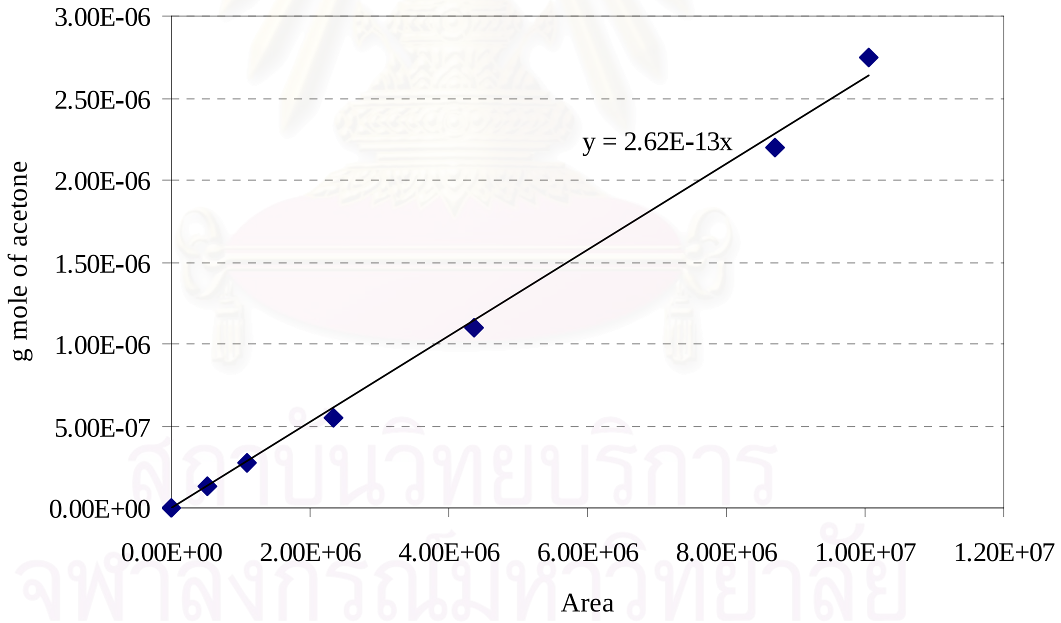


Figure D3 The calibration curve of acetone.

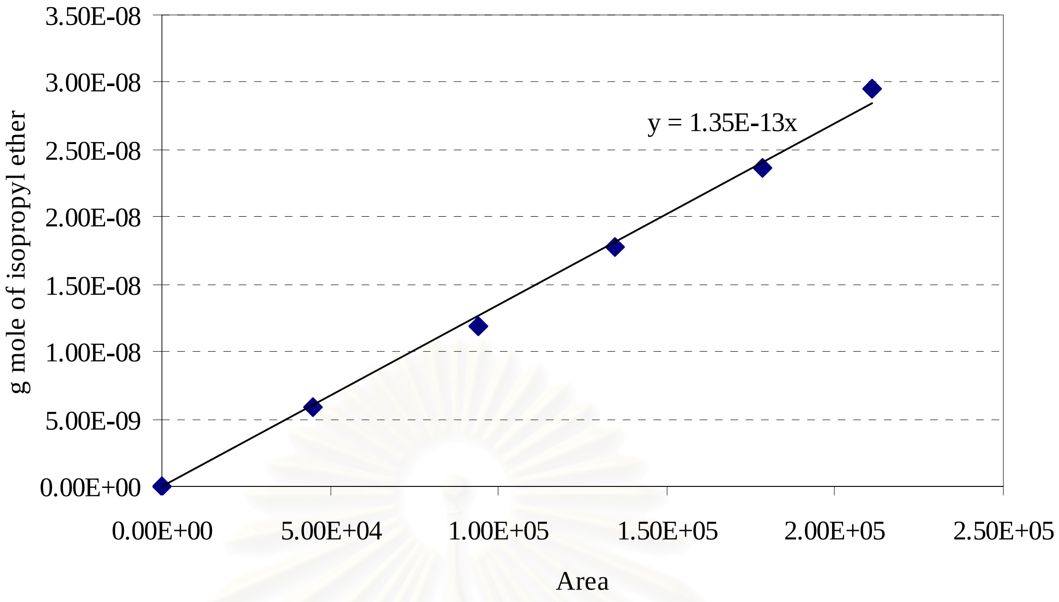


Figure D4 The calibration curve of isopropyl ether.

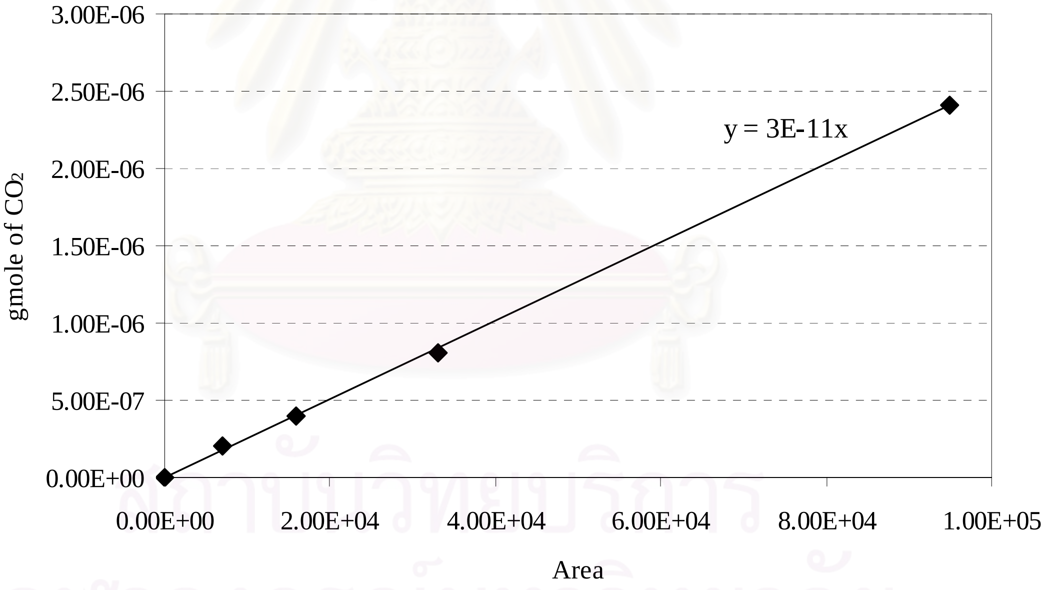


Figure D5 The calibration curve of CO_2.

APPENDIX E

MATERIAL SAFETY DATA SHEET

Titanium (IV) n-butoxide

Safety data for titanium (IV) n-butoxide

General

Synonyms: Tetra-n-butyl titanate; TNBT; Titanium(IV) n-butoxide (TYZOR TNBT); Tetra-n-butyl orthotitanate for synthesis; titanium tetrabutanolate; Titanium(IV)n-butoxide (TYZOR TBT); Butyl Titanate; Titaniumbutoxidecolorlessliq; Titanium n-butoxide; Titanium (IV) n-butoxide, 99+%; Tetra-n-butoxytitanium(IV)~Tetra-n-butyl orthotitanate; Titanium tetrabutoxide; Triethoxy Methane; Titanium tetrabutylate; Orthotitanic acid tetrabutyl ester

Molecular formula: $C_{16}H_{36}O_4Ti$

Chemical formula: $Ti[O(CH_2)_3CH_3]_4$

Physical data

Boiling point	:	310-314 °C
Flash point	:	78 °C
Density	:	1.486 g/cm^3

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

Tetrapropylammonium bromide

Safety data for tetrapropylammonium bromide

General

Synonyms: 1-Propanaminium, N, N, N-tripropyl, bromide or Tetra-n-propylammonium bromide or TPBr or TPABr

Molecular formula: $C_{12}H_{28}N.Br$

Chemical formula: $(C_3H_7)_4NBr$

Physical data

Solubility in Water	:	60% (20 °C)
pH	:	5 - 10 for solution
Melting Point	:	275-278 ºC (decomposes)

Stability and reactivity

Stable at ambient temperatures. Do not expose to high temperatures. Oxidizers should be tested for compatibility before use.

Hazardous decomposition

In fire conditions: Carbon monoxide, Hydrobromic acid and Nitrogen oxides. If heated to decomposition, tripropylamine may be released.

Potential health effect

Inhalation : May cause irritation.

Eye Contact : May cause irritation.

Skin Contact : May cause irritation.

Ingestion : No toxicity or other health effects information available.

Chronic : May cause irritation. No additional information available.

First aid measure

Inhalation: Remove to fresh air. If breathing has stopped, give artificial respiration. Consult a physician.

Eye Contact: Immediately flush with water until no evidence of chemical remains (at least 15-20 minutes) and consult a physician.

Skin Contact: Immediately flush with water with sufficient volume until there is no evidence of the chemical on the affected area.

Ingestion: If person is conscious and able to swallow, have them drink a large volume of water and milk and induce vomiting. Contact a physician.

Fire fighting measures

Wear S.C.B.A. May use water spray, carbon dioxide, dry chemical or chemical foam to fight fire.

Hazardous product combustion

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

Sodium chloride

Safety data for Sodium chloride

General

Synonyms: extra fine 200 salt, extra fine 325 salt, H.G. blending, salt, sea salt, table salt, common salt, dendritis, rock salt, top flake, white crystal, saline, halite, purex, USP sodium chloride

Molecular formula: NaCl

Physical data

Appearance : colourless crystals or white powder
Melting point : 804 ºC
Boiling point : 1413 ºC
Vapour pressure : 1 mm Hg at 865 ºC
Specific gravity : 2.16 g cm^{-3}
Solubility in water : 35.7 g/100g at ºC

Stability

Stable. Incompatible with strong oxidizing agents.

Toxicology

May cause skin, eye or respiratory irritation.

Personal protection

Not believed to present a significant hazard to health.

Sodium hydroxide

Safety data for Sodium hydroxide

General

Synonyms: caustic soda, soda lye, lye, white caustic, aetznatron, ascarite, Collo-Grillrein, Collo-Tapetta, sodium hydrate, fotofoil etchant, NAOH, STCC 4935235, sodium hydroxide pellets, Lewis red devil lye

Molecular formula: NaOH

Physical data

Appearance : odourless white solid (often sold as pellets)
Melting point : 318 ºC
Boiling point : 1390 ºC
Vapour pressure : 1 mm Hg at 739 ºC
Specific gravity : 2.12
Water solubility : High (Note: dissolution in water is highly exothermic)

Stability

Stable. Incompatible with a wide variety of materials including many metals, ammonium compounds, cyanides, acids, nitro compounds, phenols, combustible organics. Hygroscopic. Heat of solution is very high and may lead to a dangerously hot solution if small amounts of water are used. Absorbs carbon dioxide from the air.

Toxicology

Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or by inhalation of dust. Typical TLV 2 mg m^{-1}.

Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

Sodium silicate

Safety data for Sodium silicate

General

Synonyms: silicic acid sodium salt, water glass, sodium water glass, soluble glass, silicate of soda, silicon sodium oxide, sodium orthosilicate, sodium sesquisilicate, sodium silicate glass, agrosil S, barasil S, britesil, carsil 2000, chemfin 60, chemsilicate, crystal 79, crystal 96, ineos 140, inosil Na 4237, portil A, pyramid 8, vitrosol N40, ZhS 3, very large number of further trade names

Molecular formula: Na_4O_4Si

Physical data

Appearance : colourless liquid as usually supplied (solution)
Boiling point : ca. 102 °C for a 40% aqueous solution
Specific gravity : approximately 1.3 for a ca. 40% solution

Stability

Stable. Incompatible with acids, most metals, many organic materials.

Toxicology

Harmful by ingestion. Corrosive - may cause burns through skin or eye contact. Very destructive of mucous membranes.

Personal protection

Safety glasses, gloves.

Sulfuric acid

Safety data for Sulfuric acid

General

Synonyms: oil of vitriol, mattling acid, vitriol, battery acid, dipping acid, electrolyte acid, vitriol brown oil, sulphuric acid

Molecular formula: H_2SO_4

Physical data

Appearance : Colourless oily liquid
Melting point : -2 °C
Boiling point : 327 °C
Specific gravity : 1.84
Vapour pressure : <0.3 mm Hg at 20 °C (vapour density 3.4)
Water solubility : miscible in all proportions

Stability

Stable, but reacts with moisture very exothermically, which may enhance its ability to act as an oxidizing agent. Substances to be avoided include water, most common metals, organic materials, strong reducing agents, combustible materials, bases, oxidising agents. Reacts violently with water - when diluting concentrated acid, carefully and slowly add acid to water, not the reverse. Reaction with many metals is rapid or violent, and generates hydrogen (flammable, explosion hazard).

Toxicology

Extremely corrosive, causes serious burns. Highly toxic. Harmful by inhalation, ingestion and through skin contact. Ingestion may be fatal. Skin contact can lead to extensive and severe burns. Chronic exposure may result in lung damage and possibly cancer.

Personal protection

Safety glasses or face mask; acid-resistant gloves. Suitable ventilation. In the UK use of this material must be assessed under the COSHH regulations.

cobalt (II) nitrate hexahydrate

safety for cobalt nitrate hexahydrate

General

Synonyms: cobalt dinitrate hexahydrate, cobalt nitrate hexahydrate, nitric acid cobalt (+2) salt, cobaltous nitrate hexahydrate

Molecular formula: $Co(NO_3)_2\ 6H_2O$

Physical data

Physical State	: Solid
Appearance	: red
Odor	: odorless
pH	: Not available.
Vapor Pressure	: Negligible.
Vapor Density	: Not available.
Evaporation Rate	: Negligible.
Viscosity	: Not applicable.
Boiling Point	: Not available.
Freezing/Melting Point	: 55-56 ºC
Autoignition Temperature	: Not applicable.
Flash Point	: Noncombustible.
Decomposition Temperature	: 74 deg C
NFPA Rating	: (estimated) Health: 2; Flammability: 0; Reactivity: 1
Explosion Limits, Lower	: Not available.
Upper	: Not available.
Solubility	: Soluble.
Specific Gravity/Density	: 2.49
Molecular Formula	: $Co(NO_3)_2.6H_2O$
Molecular Weight	: 291.0234 Physical data

Stability

Chemical Stability: Stable. However, may decompose if heated.

Conditions to Avoid: Incompatible materials, excess heat, combustible materials, reducing agents, temperatures above 100°C.

Incompatibilities with Other Materials: Reacts violently if mixed with reducing agents, organic matter, and other flammable and combustible materials including wood, paper, sulfur, aluminum, phosphorus, hydroxylamine, phosphinates, alky esters, ammounium hexacyanoferrate (4-), carbon, tin (II) chloride, and flammable liquids.

Hazardous Decomposition Products: Nitrogen oxides, irritating and toxic fumes and gases.

Hazardous Polymerization: Has not been reported. Stable. Strong oxidizer - incompatible with reducing agents.

Toxicology

Harmful if swallowed or inhaled.

Eye: Causes eye irritation.

Skin: Prolonged and/or repeated contact may cause irritation and/or dermatitis. May cause skin sensitization, an allergic reaction, which becomes evident upon re-exposure to this material.

Ingestion: Causes gastrointestinal irritation with nausea, vomiting and diarrhea. May be harmful if swallowed. Excessive ingestion may increase red blood cells and decrease blood pressure. May cause sensation of heat and enlargement of the thyroid.

Inhalation: Dust is irritating to the respiratory tract. May cause methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea (labored breathing), and death. May cause asthmatic attacks due to allergic sensitization of the respiratory tract.

Chronic: Repeated exposure may cause allergic respiratory reaction (asthma).

Personal protection

Eyes : Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations

Skin : Wear appropriate gloves to prevent skin exposure.

Clothing : Wear appropriate protective clothing to prevent skin exposure

2-Propanol

Safety data for 2-Propanol

General

Synonyms : Isopropanol, Isopropyl alcohol
Molecular formula : C_3H_8O
Chemical formula : $CH_3CH(OH)CH_3$

Physical data

Melting point : -89.5 °C
Boiling point : 82.4 °C
Ignition temperature : 425°C
Flash point : 12°C
Explosion limits : 2 % - 12.7 %
Vapor pressure : 31.68 mm (14.7 °C)
Relative vapor density: 2.07
Density : 0.786 g/cm^3 (20 °C)
Solubility in water : soluble (20 °C)

Stability

Conditions to be avoided: Strong heating.

Substances to be avoided: alkali metals, alkaline earth metals, aluminium in powder form, oxidizing agent, organic nitro compounds, aldehydes, amines, fuming sulfuric acid, phosgene.

Hazardous decomposition products: no information available.

Further information: highly inflammable; hygroscopic, explosive with air in a vapor/gas state.

Toxicology

Further toxicological information

After inhalation: Irritation symptoms in the respiratory tract Drowsiness

After skin contact: degreasing effect on the skin possibly followed by secondary inflammation.

After eye contact: Irritations.

After swallowing: after accidental swallowing the substance may pose a risk of aspiration. Passage into the lung can result in a condition resembling pneumonia

After absorption: headache, dizziness, inebriation

After uptake of large quantities: respiratory paralysis, coma.

Personal protection

Personal protective equipment: Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Industrial hygiene: Change contaminated clothing. Application of Skin-protective barrier cream recommended. Should be wash hands after working with substance.

APPENDIX F

LIST OF PUBLICATION

Eakawut Poompichate, Darunee Sookhom, Rattanawalee Sunphloi, Nitiporn Sangngaen, and Tharathorn Mongkhonsi$^+$, “Synthesis and Characterisation of Metal Modified TS-1”, Proceedings of the Thai Institute of Chemical Engineering and Applied Chemical Conference 15th, Chonburi, Thailand, Oct., 27-28, 2005, Ref. No CA-09

Synthesis and Characterisation of Metal Modified TS-1

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ABSTRACT

Titaniumsilicalite-1 synthesized by a hydrothermal method was modified by adding Cu, Co, Cr, or V during the synthesis step. The synthesized catalysts was characterized using XRF, XRD, XPS, FT-IR, BET, and SEM. The results indicate that the second metal ions and titanium ion can simultaneously and homogeneously incorporated into the framework of TS-1.

Keywords: Metal modified TS-1, TS-1

1. INTRODUCTION

Nowadays, a popular structure of industrial catalysts is the MFI structure. The pore structure of a MFI type catalyst leads to various types of shape selectivity, *e.g.* reactant shape selectivity, product shape selectivity and transition state shape selectivity. The three dimensional pore structure of the MFI type catalyst is considered to be responsible for its long catalyst life. A catalyst having the MFI structure is titaniumsilicalite-1 or TS-1.

In general, the MFI type catalyst is usually loaded with another metal, especially transition metals, to modify some properties of the synthesized catalyst. Several methods for loading another metal onto a catalyst exist, and incorporation method is one of them. It is known that the second cation can partially replace the parent cation of the MFI structure without destroying the original structure. Important things have to be considered are the amount of the second cation to be loaded and loading procedure.

In a published research, an attempt has been done to loaded some transition metals to TS-1 [1] to modify properties of TS-1. It has been reported that loading transition metals to TS-1 still maintained the MFI structure. However, the state of transition metals in TS-1 catalyst and the effect of the amount of transition metals containing in TS-1 catalyst have never been studied before. Therefore, the aim of this research is to investigate the effect of the amount of transition metals loaded by incorporation method on MFI structure, surface area, oxidation state of transition metal, and morphology.

2. EXPERIMENTAL

2.1 Preparation of catalysts

The unmodified TS-1 catalyst was prepared using a hydrothermal technique. Sodium silicate solution and titanium (IV) butoxide 97% were used as silicon and titanium sources, respective. Diluting water and an organic template were carefully mixed, and NaOH was used to adjust the pH of the mixture to be between 9-11. The solution obtained contained solution of silicon and titanium alkoxides with molar ratio of Si/Ti equals to 50. The mixture was then transferred to a autoclave and heated up to 483 K for crystallization. Once the crystallization was completed, the autoclave was cooled, the sediment was filtered and dried in air at 393 K. After drying, the dried sediment was calcined by heating in air for 7 h at 823 K to remove the remaining organic materials.

A similar method was used to prepare TS-1 modified by the second cation. In this study, Co, Cu, Cr and V were used as the second cation. The incorporation of the second cation was performed by adding the desired amount of the appropriate metal salts ($(CoNO_3)_2.6H_2O$, $Cu(NO_3)_2$, VCl_3, or $Cr(NO_3).9H_2O$) while mixing the solution of sodium silicate and titanium alkoxide with NaOH. The following nomenclature is used for samples designation: M/TS-1(x), where M is the modifying metal, and (x) is its content in wt%

2.2. Characterization methods

The crystallinity of the standard and modified TS-1 was checked by powder x-ray diffraction technique. The analysis was performed using an x-ray diffractometer, SIEMENS D5000 using Cu Kα radiation with Ni filter. The chemical composition of the catalysts was determined by x-ray fluorescence spectroscopy, Bruker SRS 3400. Scanning electron microscopy, JEOL JSM-35CF, was used to determine the catalyst granule morphology.

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100. The surface area (A_{BET}) and micropore volume (V_μ) of the samples were calculated using BET technique, Micromeritics ASAP 2020.

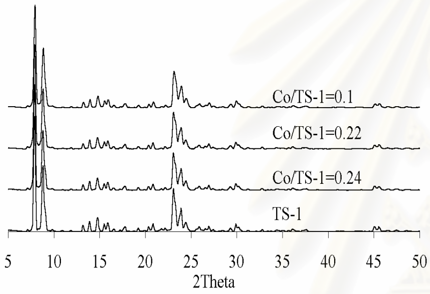
Chemical valence states of metals in the catalysts were measured by XPS technique using an AMICUS instrument with Mg Kα radiation as excitation source. The binding energy shift was calculated using the C 1s peak at 286.7 eV as reference.

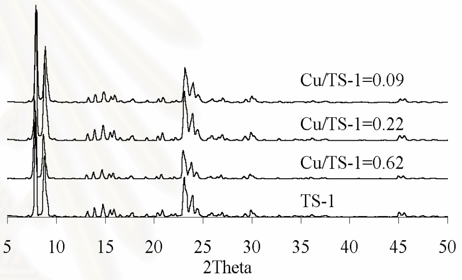
3. RESULTS AND DISCUSSION

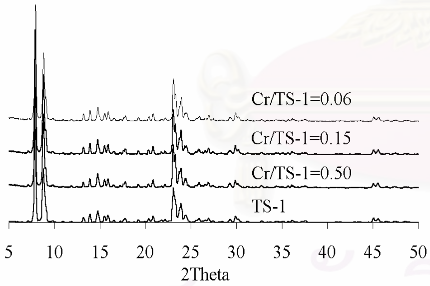
The compositions of the catalysts as well as surface areas and pore volumes are listed in table 1. The structures of the catalysts determined by XRD are shown in figure 1. The six main characteristic peaks at 2θ 8, 8.8, 14.8, 23.1, 24 and 29.5 indicate the MFI structure [2]. All catalysts which have the same structure as TS-1 posses surface area around 300 m^2/g and micropore volume around 0.2 ml/g, except V/TS-1(0.70) which does not have the MFI structure has much lower surface area and micropore volume. It should be noted here that when the Si/Ti mole ratios of the catalysts incorporated with Cr are rather high *i.e.* less Ti in the MFI structure.

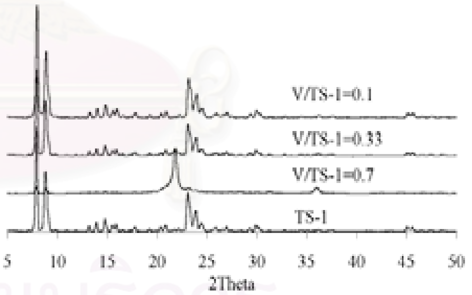
Table 1 Physico-chemical characteristics of modified TS-1 samples

Sample	Si/Ti	A_{BET} (m^2/g)	V_μ (ml/g)
TS-1	72.8	323	0.195
Co/TS-1(0.24)	62.30	336	0.261
Co/TS-1(0.22)	89.96	336	0.222
Co/TS-1(0.10)	61.50	322	0.238
Cu/TS-1(0.62)	93.49	302	0.177
Cu/TS-1(0.22)	66.78	310	0.217
Cu/TS-1(0.09)	50.10	334	0.195
Cr/TS-1(0.50)	204.52	332	0.180
Cr/TS-1(0.15)	145.68	340	0.187
Cr/TS-1(0.06)	123.53	324	0.195
V/TS-1(0.70)	91.60	27	0.019
V/TS-1(0.33)	53.03	246	0.162
V/TS-1(0.10)	71.77	324	0.195









SEM photographs of some prepared catalyst are illustrated in figure 2. It was observed that all the prepared samples have a rather uniform orthorhombic crystallite shape with sizes in the range 1-7 μm.

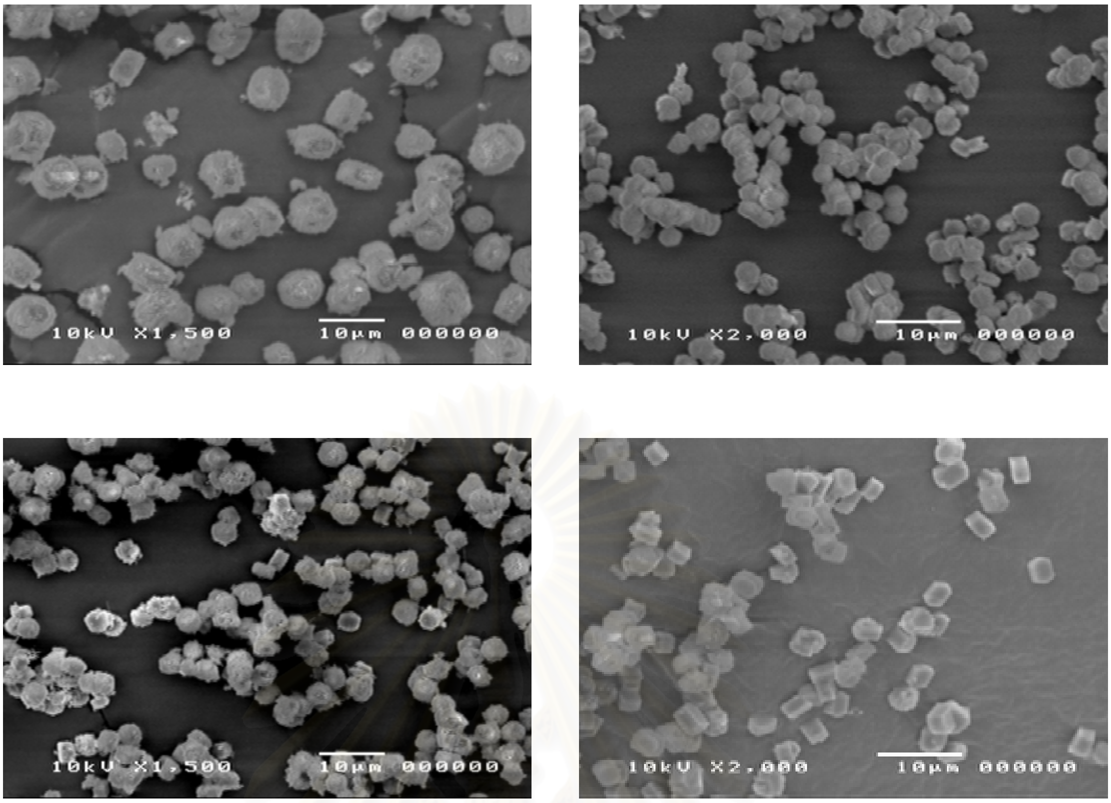


Figure 2 SEM photo of Top left : Co/TS-1, Top right : Cu/TS-1, Bottom left : Cr/TS-1 and Bottom right : V/TS-1

IR spectroscopy (figure 3) of the unmodified TS-1 shows a shoulder around 960-975 cm^{-1}, characteristic of Ti^{4+} in silicalite lattice [2]. This absorption band less appears for the modified TS-1 samples. For some reactions, it has been suggested that presence of 960-975 cm^{-1} band is a necessary, but not a sufficient, condition for catalytic activity of TS-1 [3].

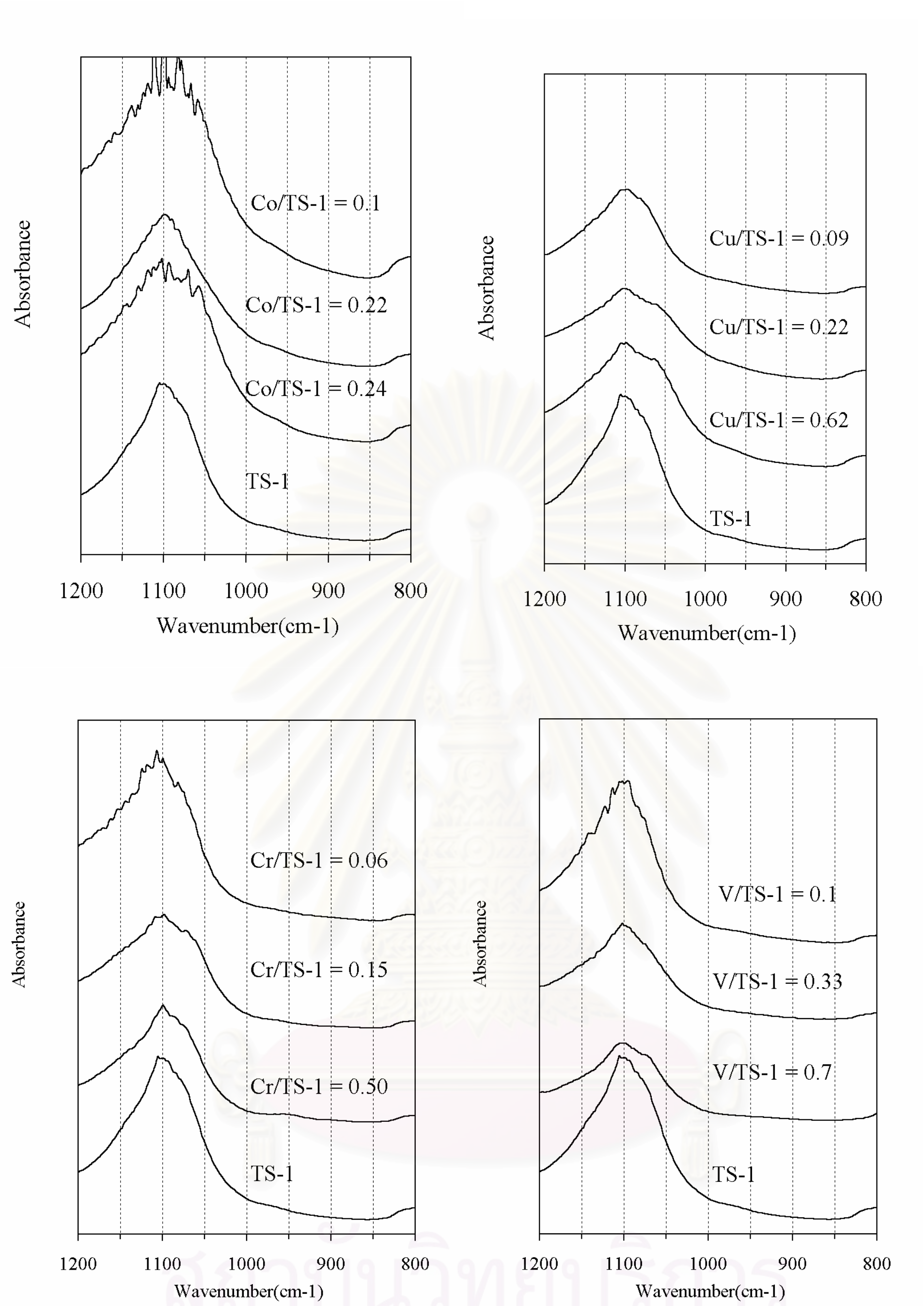


Figure 3 IR absorption spectra of modified and unmodified TS-1 samples.

Chemical states of various elements on the surface were analyzed by the XPS technique. The preliminary results are shown in table 2. The binding energy shift of each element is calculated using C 1s peak at 286.7 eV as reference. The binding energy of Co, Cu, Cr and V in metal form (M^0) is also shown in the table for comparison (ref). It is found that in all samples the second metals exist as cation. The exception is Cu/TS-1(0.09) in which the binding energy shift of Cu is about zero. This indicates that Cu in Cu/TS-1(0.09) may exists as Cu^0 while Cu in Cu/TS-1(0.22) and Cu/TS-1(0.62) is likely to exist in the form Cu^{2+}. The state of Co cation in Co/TS-1(0.1) and Co/TS-1(0.22) is likely to be Co^{3+} while both Co^{2+} and Co^{3+}. may exists in Co/TS-1(0.24). The oxidation state of vanadium in V/TS-1 may vary V^{5+} in

V/TS-1(0.7) down to V^{3+} in V/TS-1(0.1). The largest binding energy shift of Cr/TS-1(0.5) possibly dues to Cr^{6+} while the lower binding shifts of Cr/TS-1(0.15) and Cr/TS-1(0.06) suggest the present of both Cr^{3+} and Cr^{6+} or only Cr^{3+}. The exact oxidation state of each element in each sample, however, has yet to be confirmed.

Table 2 Binding energy (B.E.) of Co, Cu, Cr and V in the modified TS-1 samples. C 1s peak at 286.7 eV is used as reference for binding energy shift.

Sample	B.E (eV)	Shift (eV)	Sample	B.E. (eV)	Shift (eV)
Co $2p_{3/2}$ (ref)	**779.5**		Cu $2p_{3/2}$ (ref)	934.4	
Co/TS-1(0.24)	784.04	4.54	Cu/TS-1(0.62)	935.15	0.75
Co/TS-1(0.22)	784.8	5.3	Cu/TS-1(0.22)	935.35	0.95
Co/TS-1(0.1)	785.4	5.9	Cu/TS-1(0.09)	934.25	-0.15
Cr $2p_{3/2}$ (ref)	575.7		V $2p_{3/2}$ (ref)	513.55	
Cr/TS-1(0.5)	579.8	4.1	V/TS-1(0.7)	518.8	5.25
Cr/TS-1(0.15)	578.6	2.9	V/TS-1(0.33)	518.3	4.75
Cr/TS-1(0.06)	577	1.3	V/TS-1(0.1)	517.4	3.85

Conclusion

Co, Cu, Cr and V can be incorporated into TS-1 framework by adding the appropriate metal salt into the solution before crystallization by hydrothermal technique. It is observed that the oxidation state of the second transition metals vary with the amount of the second transition metal loaded. For vanadium modified TS-1, adding vanadium to 0.7 wt% leads to the formation of new structure rather than the MFI structure.

Acknowledgements

The funding of this research was obtained from the Graduated School, Chulalongkorn University and The Thailand Research Fund (TRF).

References

[1] Pirutko, L.V., Uriarte, A.K., Chernyavsky, V.S., Kharitonov, A.S., and Panov, G.I.,
, *Microporous and mesoporous materials* 2001, **48**, 345-353.

[2] Taramasso, M., Perego, G., and Notari, B., *United States Patent*, 1983, **4410501**.

[3] Huybrechts, D.R.C., Vaesen, I., Li, H.X. and Jacobs, P.A., *Catal.Lett.*, 1991, **8**, 237-244.

VITA

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