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PREPARATION OF CHROMIUM-TITANIUM SILICALITE-1

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เอกวุฒิ ภูมิพิเชฐ : การเตรียมตัวเร่งปฏิกิริยาโครเมียม-ไทเทเนียมซิลิกาไลต์-1
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งานวิจัยฉบับนี้ได้ทำการสังเคราะห์และตรวจสอบคุณสมบัติของตัวเร่งปฏิกิริยาโครเมียม-ไทเทเนียม ซิลิกาไลต์-1 ที่มีไทเทเนียมประมาณ 2.22 % โมล และโครเมียมไม่เกิน 0.5 % โมล โดยตัวเร่งปฏิกิริยาทั้งหมดได้สังเคราะห์ขึ้นด้วยวิธีอินคอร์เปอร์เรชัน จากการตรวจสอบด้วยเทคนิควิเคราะห์พบว่า ตัวเร่งปฏิกิริยาที่สังเคราะห์ขึ้นนั้นมีโครงร่างผลึกในรูปแบบของเอ็มเอฟไอ และมีสัณฐานเป็นออร์โทรอมบิค โครเมียมและไทเทเนียมที่อยู่ในโครงร่างผลึกของตัวเร่งปฏิกิริยาจะสร้างพันธะกับอะตอมของออกซิเจนด้วยรูปแบบของเตตระฮีดรัล โดยเลขโคออร์ดิเนชันของไทเทเนียมและโครเมียมในโครงร่างผลึกมีค่าเป็น +4 และ +5 ตามลำดับ ในขณะที่ไทเทเนียมและโครเมียมบางส่วนจะอยู่ในรูปของออกไซด์บนพื้นผิวของตัวเร่งปฏิกิริยา ปริมาณโครเมียมที่มากขึ้นจะส่งผลให้โครเมียมเข้าไปอยู่ในโครงร่างผลึกได้มากขึ้น สัดส่วนพื้นที่สำหรับการเกิดปฏิกิริยาซึ่งมีสภาพเป็นกรดอ่อนบนพื้นผิวของตัวเร่งปฏิกิริยาเพิ่มมากขึ้น และทำให้ปริมาณของโครเมียมที่มีสถานะออกซิเดชันสูงบนพื้นผิวของตัวเร่งปฏิกิริยาเพิ่มขึ้น จากคุณสมบัติดังกล่าวทำให้เมื่อใช้ปฏิกิริยาออกซิเดชันของ 2-โพรพานอลเป็นปฏิกิริยาทดสอบตัวเร่งปฏิกิริยาที่สังเคราะห์ขึ้นพบว่าปริมาณโครเมียมที่มากขึ้นทำให้ค่าการเลือกเกิดของโพรพิลีนมีแนวโน้มสูงขึ้น ยกเว้นตัวเร่งปฏิกิริยาที่มีโครเมียม 0.15 % โมล ซึ่งเป็นปริมาณที่อยู่ในช่วงกลางระหว่างปริมาณโครเมียมที่น้อยที่สุดและมากที่สุดสำหรับงานวิจัยนี้ จะให้ค่าการเลือกเกิดของอะซิโตนที่สูง ซึ่งจากการตรวจสอบพื้นผิวของตัวเร่งปฏิกิริยาดังกล่าวพบว่าตัวเร่งปฏิกิริยานั้นน่าจะมีการกระจายของไทเทเนียม (4+) ในโครงร่างผลึกที่ดีกว่าตัวเร่งปฏิกิริยาอื่นๆในการทดลอง ส่งผลให้ค่าการเลือกเกิดของอะซิโตนจากปฏิกิริยาทดสอบดังกล่าวมีค่าสูง

ภาควิชา..............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต..
สาขาวิชา............วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา..........................
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EAKAWUT POOMPICHATE: PREPARATION OF CHROMIUM-TITANIUM SILICALITE-1 CATALYST. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D. 84 pp. ISBN: 974-17-5878-2

This research has studied preparation and characterization of chromium-titanium silicalite-1 catalysts. In our study, every catalyst prepared by incorporation method composed of titanium about 2.22 %mol and chromium not over 0.5 %mol. From characterization, all synthesized samples have MFI structure and orthorhombic crystalline shape. Titanium and chromium atoms in the catalyst framework exist in form of tetrahedral, coordination number of both atoms are 4+ and 5+ respectively. Unlikely, some parts of chromium and titanium atoms are mantled in oxide form on the synthesized catalyst surface. Higher amount of loaded chromium increased the amount of Cr^{5+} in the catalyst framework; in addition, weak acid site ratio and high oxidation state of chromium on the catalyst surface are also increased. Because of those properties, when the catalyst sample with higher loaded chromium is tested by 2-propanol oxidation, high selectivity of propylene is achieved. Only the sample with 0.15 % Cr yields high selectivity to acetone. To investigate on this sample, the surface analysis results suggest that the satisfied dispersion of Ti^{4+} in the catalyst framework should be the reason for its unusual behavior.

Department……Chemical Engineering… Student's signature…Eakawut Poompichate…
Field of study….Chemical Engineering… Advisor's signature…………………...
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Finally, he would like to dedicate the achievement of this work to his parents, who have always been the source of his support and encouragement.

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CHAPTER I

INTRODUCTION

Titanium silicate (TS-1) is a zeolite catalyst with MFI structure obtained by isomorphic substitution of titanium atoms in the framework of crystalline silicates (SiO_2). TS-1 was firstly developed by Taramasso and co-workers in 1983. In the present, TS-1 plays a role as a catalyst in chemical industries especially oxidation reaction process because of its satisfied activity on oxidation reaction produced by Ti^{4+} in TS-1. TS-1 can make many oxidation reactions occur at low temperature and pressure. Moreover, good thermal stability and non-corrosive nature which are properties of MFI structure also make TS-1 favor in chemical industries, i.e. selective oxidation of alkenes to epoxides, α-olefins via epoxidation to 1,2-diols, styrene oxide to phenylaldehyde and manufacture of epichlorohydrin.

From many benefits of TS-1 that are stated above, they indicated that loading metal into catalyst framework can change catalyst properties to proper for some reactions. In case of TS-1, titanium atoms loaded into SiO_2 framework changed that one to active for oxidation reaction. Unfortunately, to meet designed product selectivity from oxidation reaction does not only depend on oxidation ability of catalyst, but also depend on other properties such as acidity, surface area and pore volume of catalyst. Therefore, second metal was introduced to TS-1 framework to improve TS-1 properties as we see in former researches. (see Table 1.1)

In this study, metal modified TS-1 is synthesized by incorporation method, both of titanium atoms and second metals are loaded directly into the framework simultaneously with SiO_2 framework forming. Then, properties of synthesized catalyst will be investigated. Since titanium atom can be loaded into TS-1 framework, therefore, principal of second metal selection for this study is that the second metal should have atomic and ionic radius nearly to that of titanium. In addition, the second metal should be non-corrosive nature. As a result, chromium atom is chosen as second metal for this study because of its properties corresponding with our principal. From the former studies, chromium was used to load into many supports which have their structure like ZSM-5 including MFI. (see Table 1.2) Moreover, some evidences had already appeared to confirm that chromium atom could be loaded into TS-1 framework as we see in Table 1.2. Cr-TS-1 was successfully synthesized by incorporation method; however, the effect of amount of chromium on Cr-TS-1 properties has yet to be explored. Therefore, the main objective of this research is to investigate the changing of Cr-TS-1 properties which are affected from the various amount of chromium loaded into TS-1 by incorporation method. Surface area, pore volume, morphology structure, oxidative active site, oxidation state of chromium and acidity of Cr-TS-1 are the catalyst properties in our investigations. Consequently, both of different characterization techniques and some reaction tests are used to investigate Cr-TS-1 properties.

In the recent years, most of reaction tests used to explore TS-1 properties were usually in liquid phase as we see in Table 1.3. Hydrogenperoxide (H_2O_2) was used as oxidant. However, several problems such as other phase existence from mixing between two or more reactants and separation of catalyst can occur in liquid phase operation. To avoid these problems, oxidation in gas phase is therefore selected to be the test reaction used to explored Cr-TS-1 properties in our study. This research has been scoped as follows:

1) Preparation of Cr-TS-1 catalysts at various of Si/Cr by using the incorporation method.

2) Catalytic reactions in gas phase oxidation of 2-propanol at 100 - 500°C and atmospheric pressure to determine catalytic activity.

3) Characterization of Cr-TS-1 catalysts by using the various techniques.

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

Author (year)	2nd metal	Synthesized method	Effect of 2nd metal	Advantage
Pirutko *et al.* (2001)	Fe	Incorporation	Form α-site in high concentration.	Catalyze the oxidation of benzene to phenol with high activity and selectivity.
Taylor *et al.* (2005)	Au	deposition-precipitation	Contribute to formation of H_2O_2.	Improve the epoxidation of propylene.
Xinbin *et al.* (2005)	Sn	Impregnation	Increase weak acid site of catalyst.	Increase selectivity of diphynyl- oxalate from transesterification of dimethyloxalate with phenol.
Prasetyoko *et al.* (2005)	Nb	Impregnation	Increase Bronstated acid site.	Increase selectivity of 1,2-octanediol from 1-octene oxidation.

Table 1.2 Former researches of ZSM-5 catalyst containing Cr in framework

Author (year)	Catalyst framework	Structure	Synthesized method
Kucherov *et al.* (1995)	Cr-SiO_2	ZSM-5	incorporation
Giannetto *et al.* (1997)	Cr-Al-SiO_2	ZSM-5 (MFI)	impregnation
Pirutko *et al.* (2001)	Cr-TS-1	ZSM-5 (MFI)	incorporation
Araujo *et al.* (2002)	Pt-Cr-SiO_2	ZSM-5	ion-exchange
Gaspar *et al.* (2005)	Cr-SiO_2	ZSM-5	impregnation

Table 1.3 Phase of oxidation reaction used for testing TS-1 including modified TS-1 in former researches

Author (year)	Reaction phase	Reactant / oxidant
van der Pol *et al.* (1993)	liquid	linear alcohol / H_2O_2
Joseph *et al.* (1994)	liquid	oximes / H_2O_2
Gontier and Tuel (1994)	liquid	aniline / H_2O_2
Reddy and Sayari (1995)	liquid	propylamine / H_2O_2
Hulea *et al.* (1998)	liquid	cyclopentene / H_2O_2
Atoguchi and Yao (2001)	liquid	phenol / H_2O_2
Jenzer *et al.* (2001)	gas	propylene / O_2
Schuster *et al.* (2001)	gas	propane / O_2
Sooknoi and Limtrakul (2002)	liquid	cyclohexane / H_2O_2
Wang *et al.* (2004)	gas	propylene / O_2
Zhuang *et al.* (2004)	liquid	styrene / H_2O_2
Wan *et al.* (2005)	liquid	aniline / H_2O_2
Wróblewska *et al.* (2005)	liquid	methyl alcohol / H_2O_2

This present work is organized as follows:

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

Chapter II presents some methods for catalyst evaluation.

Procedures of catalyst preparation, catalyst characterization and catalytic reaction in gas phase oxidation are presented in chapter III.

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

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

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

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 methods

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

Characterization method	Measured properties
X-ray fluorescence spectroscopy (XRF)	Chemical compositions
Scanning electron microscopy (SEM)	Morphology
X-ray diffraction technique (XRD)	Phase structure
Multipoint BET techniques (BET)	Surface area and pore volume
Infrared spectroscopy (IR)	Orthorhombic silicalite defection
Electron spin resonance (ESR)	Transition metal state in catalyst framework
Temperature program desorption (TPD)	Acid site and acid strength
X-ray photoelectron spectroscopy (XPS)	Oxidation state on catalyst surface

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 homogenous reactions of the reactants should be kept as minimum as possible in order to prevent the interference of the undesired reaction on result interpretation.

2. The reactant should not too inert to cause the tested catalysts behave like an inactive catalyst.

3. The reactant should not extremely reactive in order that the results of performance comparison between different catalysts will be clear.

4. To help in tracing the reaction pathway, the reactant should have only one active functional group and selected reaction should not produce many intermediate agents in the system.

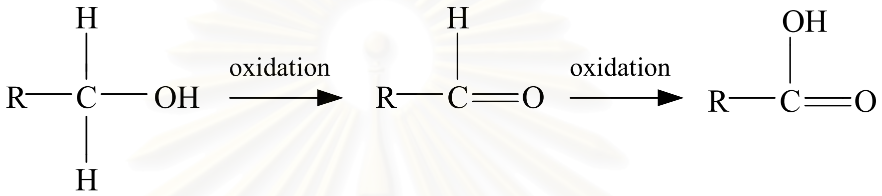
5. The reactant should not cause catalyst deactivation such as poising and coking.

In practice, the reaction corresponding to all the listed criteria above may not available.

For criteria about functional group and reactivity, alcohol is therefore one of the best choice to use as reactant in our study. Alcohol is an organic chemical containing –OH group as its functional group. In addition, alcohol is also reactive for gas phase oxidation which is used as test reaction in this study as we described in previous chapter.

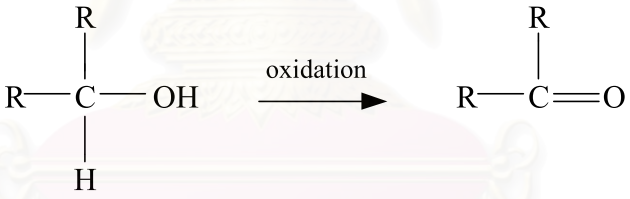
The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde. Consequently, an formed aldehyde can be oxidized to a carboxylic acid.



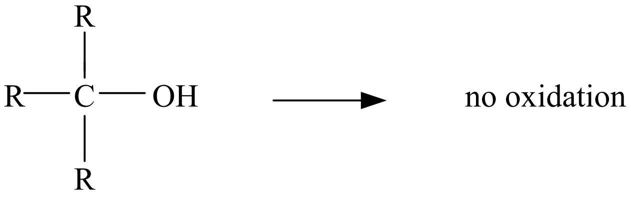
1°alcohol aldehyde carboxylic acid

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



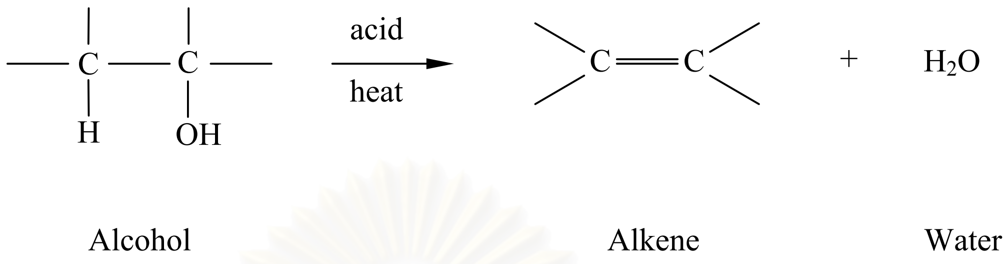
2° alcohol ketone

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).



3° alcohol

Furthermore, Dehydration can occur in the system involving the presence of an acid and the application of heat. An alkene is produced from elimination of a molecule of water in an alcohol.



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

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

As stated above, we found that oxidation of secondary alcohol does not produce intermediate agent unlike oxidation of primary alcohol. Therefore, it is advantage to evaluate tested catalysts with oxidation of secondary alcohol. In addition, because of any convenience and safety to prepare reactant in gas phase, 2-propanol is therefore selected to use as reactant in our test reaction.

CHAPTER III

EXPERIMENTS

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into three sections, i.e., catalyst preparation, catalyst characterization and catalytic reaction. The chemicals, apparatus and procedures for catalyst preparation are explained in section 3.1. The composition, structure and surface properties of the catalyst characterized by various techniques are discussed in section 3.2. Finally, the details of the catalytic reaction are illustrated in section 3.3.

3.1 Catalyst preparation

3.1.1 Chemicals

The details of chemicals used in the preparation procedure of titanium silicalite-1 (TS-1) and chromium-titanium silicate-1 (Cr-TS-1) are shown in Table 3.1.

Table 3.1 The chemicals used in the catalyst preparation

Chemical	Grade	Supplier
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
Chromium nitrate nanohydrate	-	Aldrich

3.1.2 Preparation Procedures

Titanium silicalite-1 (TS-1) and various samples of chromium-titanium silicate-1 (Cr-TS-1) ascribed as Cr-TS-1 no.1 - no.5 were prepared according to the incorporation method discussed in details below.

3.1.2.1 Preparation of Solution

Solution for crystallization was prepared by mixing of prepared gel and decant solution. Various solutions which were involved with preparation of gel and decant solution were listed in Table 3.2. Also, The amount of chromium nitrate nanohydrate contained in solution A1 and A2, including the desired ratio of Si/Ti and Si/Cr for synthesizing our desired catalysts were showed in Table 3.3.

- *Gel preparation*

Gel was prepared by dropping solution A1 coupling with solution B1 into solution C1, meanwhile pH value of mixed solution were controlled in range of 9-11 during this step. Mixed solution were further stirred for 2 hours and then be centrifuged to derive gel.

- *Decant solution preparation*

Decant solution was prepared by dropping solution A2 coupling with solution B2 into solution C2, meanwhile pH value of mixed solution were also controlled in range of 9-11 during this step. Mixed solution were further stirred for 2 hours and then be centrifuged to derive gel.

Mixing of prepared gel and decant solution leads to derive solution for crystallization in the next step.

Table 3.2 The compositions of each solution for preparation of gel and decant solution

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g	$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g
TPABr	5.72	g	TPABr	7.53	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	$Cr(NO_3)_3{\cdot}9H_2O$	x	g
$Cr(NO_3)_3{\cdot}9H_2O$	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	ml			
H_2SO_4 (conc.)	1.55	ml			

Table 3.3 The amount of $Cr(NO_3)_3{\cdot}9H_2O$ indicated as ‘x’ ,and the desired ratio of Si/Ti and Si/Cr for synthesizing various catalyst samples

Sample	X (g)	Si/Ti	Si/Cr
TS-1	0	50	α
Cr-TS-1 no.1	0.873	50	150
Cr-TS-1 no.2	1.31	50	100
Cr-TS-1 no.3	2.62	50	50
Cr-TS-1 no.4	6.55	50	20
Cr-TS-1 no.5	13.10	50	10

3.1.2.2 Crystallization

The mixture of solution from the previous step was filled in a 250 ml Pyrex glass. The glass container was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm^2 gauge. The mixture was heated from room temperature to 160 ^oC with a heating rate of 2 $^oC/min$ and was further heated from 160 ^oC to 210 ^oC with a heating rate of 2 $^oC/10$ min, followed by cooling the mixture to room temperature in the autoclave. The product crystals were washed with de-ionized water until the pH of the washing water decreased from about 10 to 7. Then the crystals were dried in an oven at 110 ^oC for 24 h.

3.1.2.3 Calcination

The dry crystals were calcined in an air stream at 550 ^oC and held at that temperature for 6 h, by heating them from room temperature to 550 ^oC with heating rate 8.6 $^oC/min$. The organic templates were burned off leaving cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature and stored in a dessicator for later use.

3.2 Catalyst characterization

3.2.1 Determination of composition content of catalysts

0.5 gram of the catalyst sample was examined by x-ray fluorescence spectroscopy (XRF) using Bruker SRS 3400 at the Department of Science Service Ministry of Science Technology and Environment.

3.2.2 Scanning electron microscopy (SEM)

A few amount of the catalyst sample which is coated with gold was examined using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 10 kV.

3.2.3 X-ray diffraction (XRD)

The holder filled with the catalyst sample was placed into X-ray diffractometer, SIEMENS D5000, using Cu Kα radiation with Ni filter, and the signal during analyzing was reported on a microcomputer. The operating conditions of measurement are shown below :

2θ range of detection :	$6\text{-}40^{o}$
Resolution :	0.02^{o}
Number of scan :	10

3.2.4 BET surface area and pore volume measurement

The sample cell which contained 0.3 gram of sample was placed into degas port of BET Micromeritrics ASAP 2020. After completion of degas step, the degased cell was transfered to the analytical port of that one for processing the analyzing step.

3.2.5 Fourier transform infrared (FT-IR)

The holder filled with the catalyst sample was placed into FT-IR spectroscopy using Nicolet model Impact 6700. Infrared spectra were recorded between 400 and 1200 cm^{-1} on a microcomputer. The samples were characterized in a diffuse reflectance mode.

3.2.6 Electron spin resonance (ESR)

A tube containing 0.8 gram of the catalyst sample was placed into ESR spectrometer using JEOSL, model JES – RE2X. X band with 8.8-9.6 GHz were used as microwave unit, and spectra were recorded between 300 and 350 mT on a microcomputer at Science and Technological Research Equipment Centre, Chulalongkorn university.

3.2.7 Temperature programmed desorption (TPD)

Sample cell which contained 0.1 gram of sample was placed to Micromeritrics Chemisorb 2750. Helium gas with flow rate at 15 ml/min was released to flow through our sample. The sample was heated from room temperature to 550 ^{o}C with a heating rate of 10 ^{o}C/min and hold for 1 hour. Then, the sample was cooled down to 80 ^{o}C and also hold for another hour. In the next step, 15 vol% ammonium gas with flow rate at 15 ml/min flowed through sample instead of helium, and hold for 15 minutes. Adsorption of 15 vol% ammonium on the catalyst surface occured in this step. Consequently, helium gas at the same flow rate flowed through our sample instead of ammonium and also hold for another hour. In the final step which was the desorption step, our sample was heated from 80 ^{o}C to 550 ^{o}C with a heating rate of 10 ^{o}C/min. The signal from this step was recorded every 0.1 seconds and reported on a microcomputer.

3.2.8 X-ray photoelectron spectroscopy (XPS)

A few amount of the catalyst sample was examined using XPS AMICUS. The binding energy was calculated using the C 1s peak at 284.6 eV as reference.

3.3 The catalytic activity measurements

3.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 3.1. 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. Argon 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 4.4.

Table 3.4 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 °C	70 °C
- Final	100 °C	120 °C
Heating rate	-	4 °C/min
Detector temperature	130 °C	120 °C
Injector temperature	130 °C	120 °C
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, 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 argon.

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, 2-propanol, isopropyl ether, acetone and CO_2 by calibration curves in Appendix D.

4. The result of catalytic test was calculated in the term of

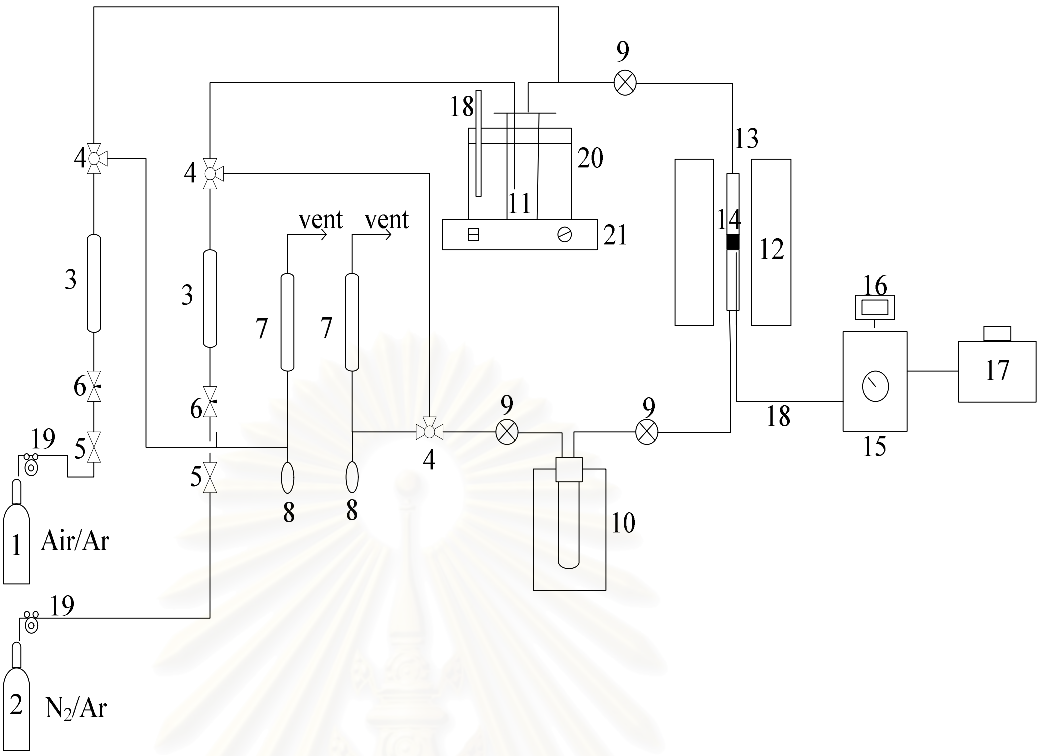
$$\%\ \text{A conversion (C)} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

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

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

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 3.1 Flow diagram of the oxidation reaction system.

CHAPTER IV

RESULTS AND DISCUSSION

Results from investigation of the synthesized catalyst properties will be interpreted in this chapter. Some physical and chemical properties of synthesized Cr-TS-1 catalysts, including effects of the amount of chromium in the samples are revealed by the characterization methods and the reaction test.

For convenience of discussion in this chapter, Cr-TS-1 no.1 - no.5 stated in Chapter III are renamed as Cr(0.06 %)-TS-1, Cr(0.08 %)-TS-1, Cr(0.15 %)-TS-1, Cr(0.40 %)-TS-1 and Cr(0.50 %)-TS-1, respectively. The ratio numbers in the brackets indicate the various ratios by mole of chromium contained in Cr-TS-1 samples which are detailed in the first section of this chapter. Then, other properties of the synthesized catalysts are discussed in sections 4.2 - 4.9.

4.1 Determination of chemical compositions of the synthesized TS-1 and Cr-TS-1 samples

Chemical compositions of synthesized catalysts were analyzed by x-ray fluorescence spectroscopy. Those results are presented in Table 4.1.

From Table 4.1, we can see that the ratios of Si/Ti and Si/Cr of various Cr-TS-1 samples are different from the desired ratio values showed in Table 3.3. The amount of titanium and chromium in the synthesized catalyst samples are less than the amounts loaded during synthesizing. One of the reason causing that problem may be the reaction time in the autoclave during synthesizing. The reaction time used in our experiment may not long enough for titanium and chromium forming into framework in a large amount. Consequently, some retained transition metals were eliminated during washing step; transition metals contained in synthesized samples are therefore less than the desired values. However, trend of chromium contained in the synthesized samples is correspond to the mixing step in our experiment, more chromium loaded in the mixing step, more chromium contained in the synthesized Cr-TS-1 samples.

Table 4.1 Chemical composition ratios by mole of the synthesized TS-1 and Cr-TS-1 samples

Sample	Chemical composition ratios by mole				
	Si (%)	Ti (%)	Cr (%)	Si/Ti	Si/Cr
TS-1	32.152	0.442	0	73	α
Cr(0.06 %)-TS-1	32.327	0.262	0.057	124	563
Cr(0.08 %)-TS-1	32.360	0.232	0.083	139	389
Cr(0.15 %)-TS-1	32.348	0.222	0.151	146	215
Cr(0.40 %)-TS-1	32.036	0.206	0.396	156	81
Cr(0.50 %)-TS-1	32.188	0.157	0.495	205	65

Another point from this section, a large amount of chromium loaded during the mixing step cause titanium contained in our samples slightly decreases. High concentration of chromium in the mixture during the mixing step may increase the interaction between chromium and SiO_2; as a result, decreases the interaction between titanium and SiO_2. Hence, titanium contained in our sample is slightly decreased.

From consideration of every synthesized Cr-TS-1 samples in Table 4.1, we will see that the decreasing of the amount of titanium from Cr(0.06%)-TS-1 to Cr(0.50%)-TS-1 is so small when we compare with the increasing of the amount of chromium. In other words, only one half fold of titanium are reduced from Cr(0.06%)-TS-1 to Cr(0.50%)-TS-1, meanwhile eight fold of chromium are increased. Therefore, it is reasonable to state that the amount of titanium in every Cr-TS-1 samples is rather constant.

Unfortunately, the existence of chromium and titanium in the catalyst framework can not be determined by this technique, because the reported values are also include the amount of transition metals in oxide form occurred by calcination step. Hence, other techniques are necessary for our study.

4.2 Morphology

Morphology of synthesized catalysts were analyzed by Scanning Electron Microscopy, SEM. Those results are represented in figure 4.1a – 4.1f.

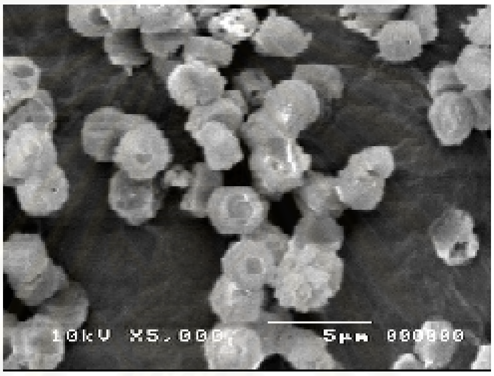


Figure 4.1a SEM photo of TS-1

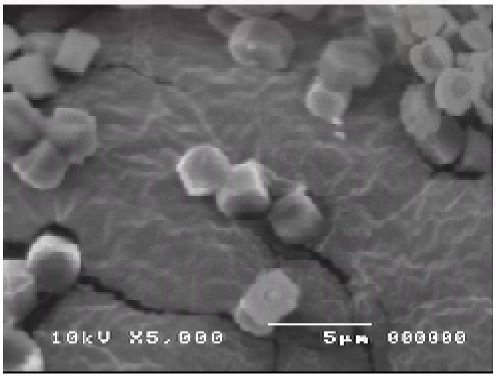


Figure 4.1b SEM photo of Cr(0.06 %)-TS-1

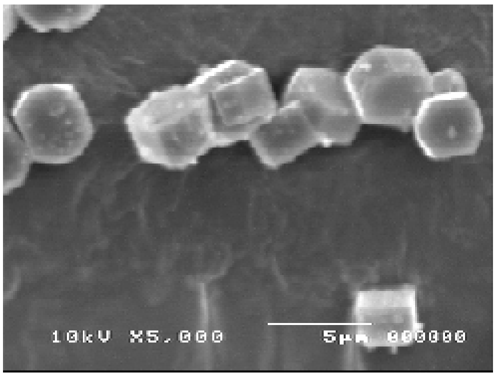


Figure 4.1c SEM photo of Cr(0.08 %)-TS-1

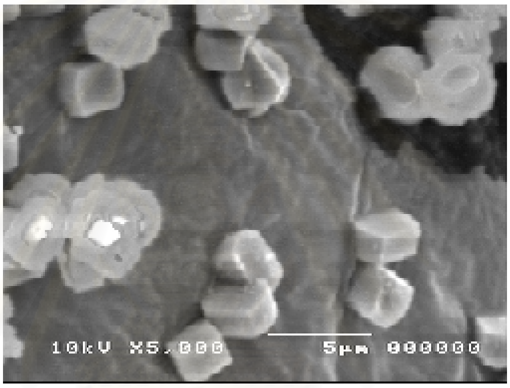


Figure 4.1d SEM photo of Cr(0.15 %)-TS-1

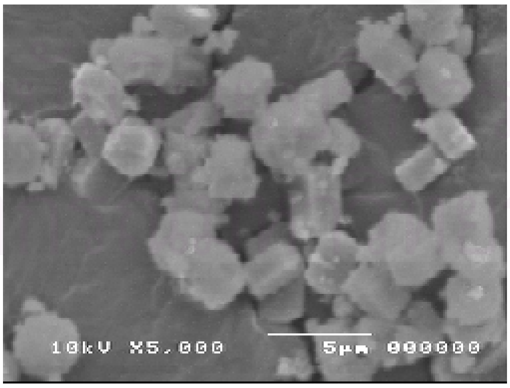


Figure 4.1e SEM photo of Cr(0.40 %)-TS-1

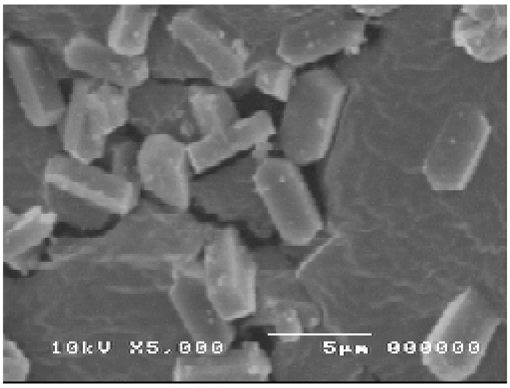


Figure 4.1f SEM photo of Cr(0.50 %)-TS-1

From all of SEM photos above, they are observed that all of the synthesized samples have a rather uniform orthorhombic crystalline shape with sizes in range 1-7 μm. Since, the amount of loaded metals, titanium and chromium, are so small, SiO_2 which is major part of Cr-TS-1 and TS-1 clearly demonstrates its morphology. As a result, we see orthorhombic crystalline shape in all synthesized samples.

4.3 Crystalline structure

Crystalline structures of all samples were investigated by powder x-ray diffraction technique, XRD. XRD patterns of the synthesized TS-1 and Cr-TS-1 samples are illustrated in figure 4.2. These 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.

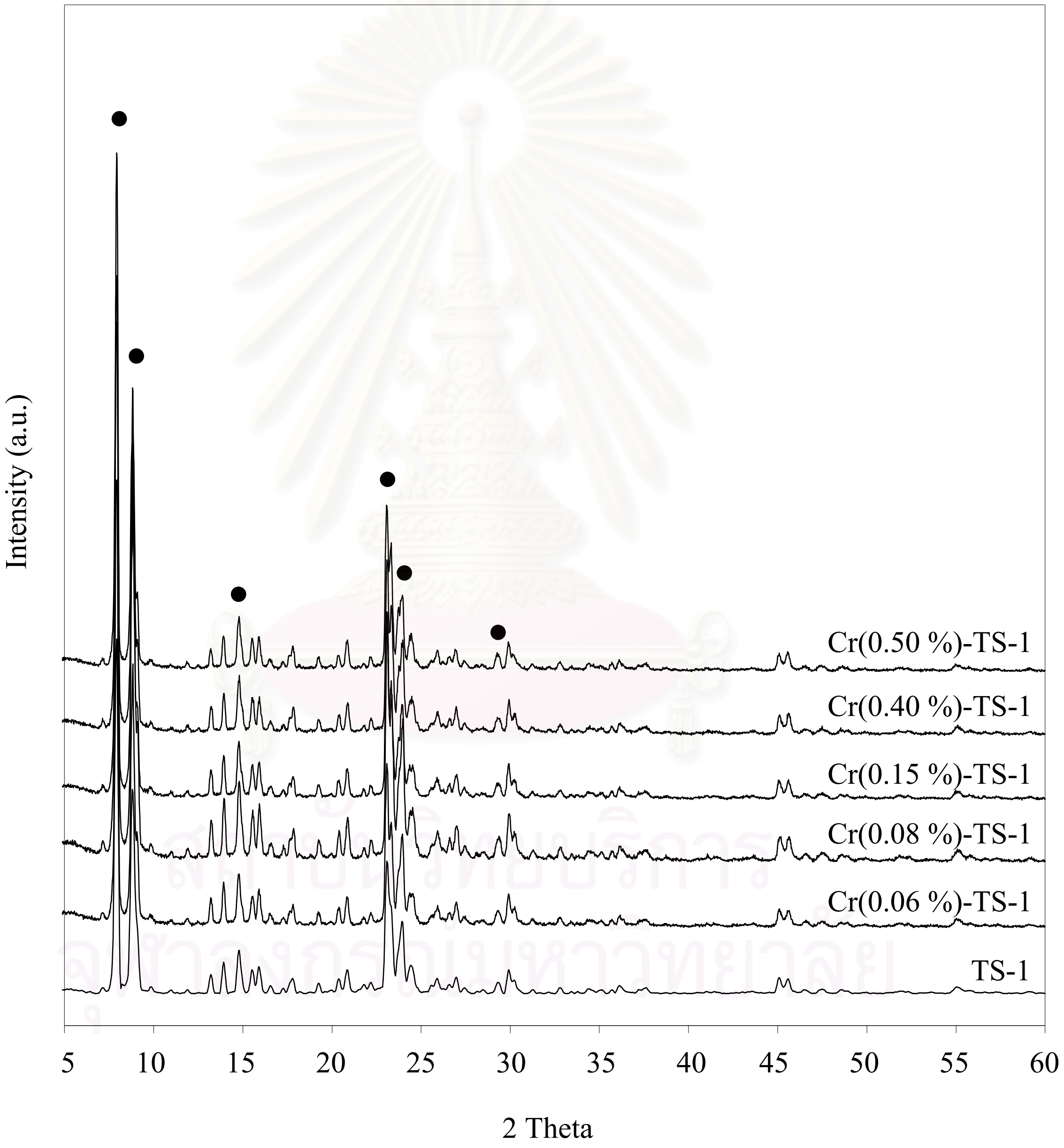


Figure. 4.2 X-ray diffraction patterns of the synthesized TS-1 and Cr-TS-1 samples

From reported XRD pattern, peak at 2θ as 8, 8.8, 14.8, 23.1, 24 and 29.5 degree which indicate the MFI structure appear in all of the synthesized samples. Hence, our synthesized samples have the MFI structure.

4.4 BET surface area and pore volume of the synthesized TS-1 and Cr-TS-1 samples

BET surface area and pore volume of each sample was measured by BET technique. The measured values of all samples are reported in Table 4.2.

Table 4.2 BET surface area and pore volume of the synthesized TS-1 and Cr-TS-1 samples

Sample	BET surface area (m^2/g)	Pore volume (ml/g)
TS-1	323	0.195
Cr(0.06 %)-TS-1	324	0.195
Cr(0.08 %)-TS-1	323	0.187
Cr(0.15 %)-TS-1	340	0.187
Cr(0.40 %)-TS-1	327	0.215
Cr(0.50 %)-TS-1	332	0.180

From Table 4.2, surface area and pore volume of the synthesized Cr-TS-1 samples are similar to those of TS-1 sample.

From previous results, morphology, crystalline structure, surface area and pore volume of Cr-TS-1 samples are not different from those of TS-1. Because of low amount of loaded transition metals in Cr-TS-1 and TS-1 samples, we therefore see the physical characteristics of SiO_2 in mainly, not see many differences in each sample.

4.5 Silicate framework defection

To investigate SiO_2 framework, Fourier Transform Infrared Spectroscopy, FT-IR, was used in our study. Defection of SiO_2 framework can be revealed at 900-1000 cm^{-1} region. Smooth spectrum, no peak appear, at that region indicate that our catalyst framework is composed of SiO_2 only, if not, some defections occur in our framework. [Perego et al. (1986)]

In our experiment, the spectra of all samples were measured around 400-1200 cm^{-1} by FT-IR. Those results are represented by figure 4.3.

From figure 4.3, it is clearly seen that some peaks appear around 960-980 cm^{-1}. From previous study [Huybrechts et al. (1991)], peak around 960-975 cm^{-1} indicates that Ti^{4+} exists in silicate framework. Unlikely, peak shape of Cr-TS-1 occuring around 960-980 cm^{-1} are wider when compared with that of TS-1 sample. This difference implies that not only Ti^{4+} exists in silicate framework but also other ions can be there. Some transition states of chromium may exist in silicate framework. However, existence of Ti^{4+} and chromium ion in silicate framework needs other techniques to confirm.

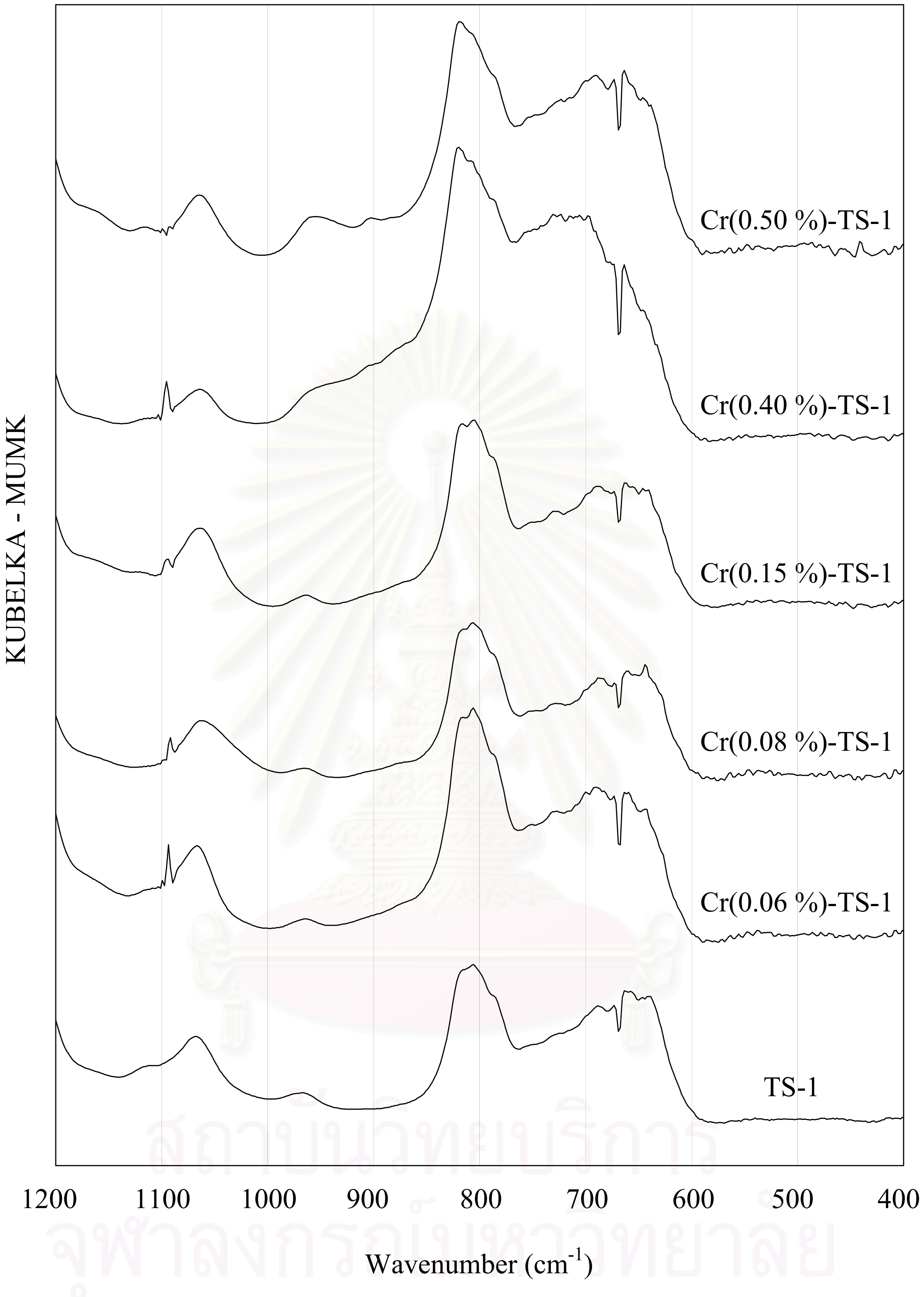


Figure 4.3 IR spectra of the synthesized TS-1 and Cr-TS-1 samples

4.6 Chromium status in Cr-TS-1 framework

This part demonstrates some evidences which indicative of chromium existence in Cr-TS-1 framework. Chromium status in Cr-TS-1 framework was investigated by electron spin resonance, ESR. Their results are presented in figure 4.4.

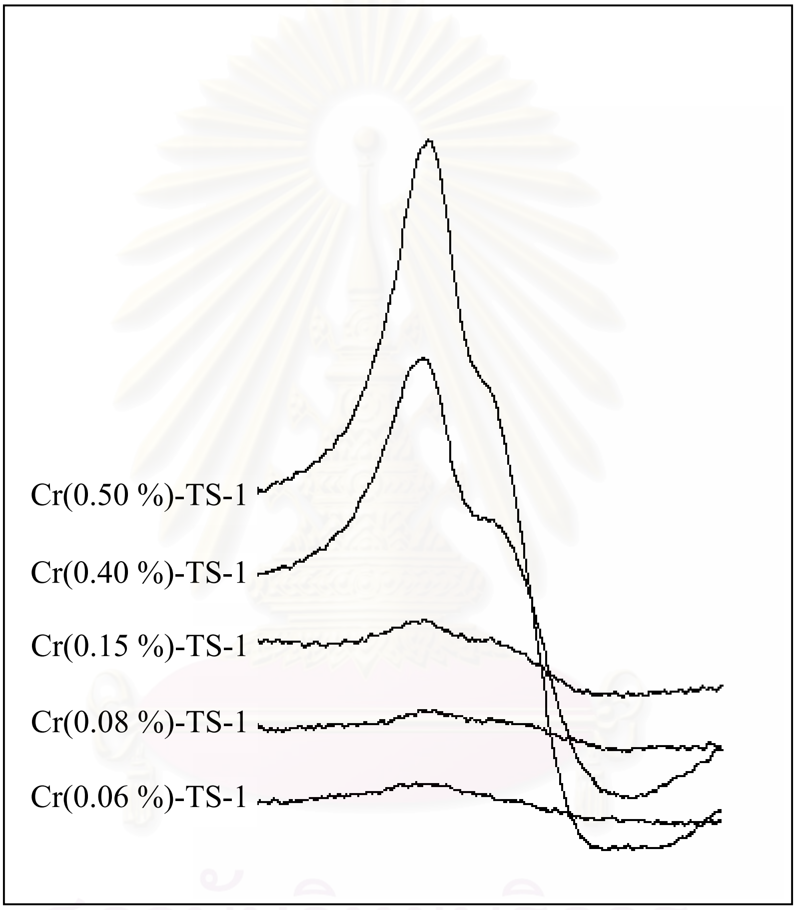


Figure 4.4 ESR spectra of the synthesized Cr-TS-1 samples

As we see in figure 4.4, the spectra from all samples compose of one peak with shoulder. Each magnetic field at the appearances of the peak and shoulder will be converted to g value, g_1 and g_2 respectively, as showed in Table 4.3.

Table 4.3 g value of the synthesized Cr-TS-1 samples

Sample	g_1	g_2
Cr(0.06 %)-TS-1	1.986	-
Cr(0.08 %)-TS-1	1.987	-
Cr(0.15 %)-TS-1	1.987	1.978
Cr(0.40 %)-TS-1	1.986	1.977
Cr(0.50 %)-TS-1	1.986	1.979

To label the species of chromium ion in SiO_2 framework, the obtained g values are compared to the values reported by Giannetto et al. (1997). This group has studied ESR of chromosilicate sample and reported the g value at 1.987 and 1.977. From their study, g value at 1.987 was ascribed to tetrahedral coordinated Cr^{5+} substituting Si atoms in the framework, meanwhile g value at 1.977 was ascribed to octahedral coordinated Cr^{5+} acting as a compensation ion outside the framework structure.

In our study, it is clearly seen that g values of all samples are around 1.987 and some of them are also around 1.977 which correspond to the values reported by Giannetto et al. (1997). These results confirm that loading chromium ion to the synthesized Cr-TS-1 with incorporation method successfully leads chromium ion into catalyst framework, especially being as tetrahedral coordinated Cr^{5+} in the framework. Nevertheless, in this part, we have also known that the increasing of the amount of loaded chromium raise the number of tetrahedral coordinated Cr^{5+} in the framework as we see the increased spectrum intensity in figure 4.4. This observation also supports IR spectra of Cr(0.50 %)-TS-1, highest loaded chromium, which illustrates the highest peak around 960-980 cm^{-1}.

4.7 Catalytic properties

To test the synthesized catalysts with 2-propanol oxidation reaction which composes of 2-propanol and oxygen in our system at 100-500 °C and 1 atm, will encounter three reactions. Selective oxidation, dehydration and combustion reactions will be involved to our system. In the experiment, the selective oxidation ability of the synthesized catalysts was evaluated by the selectivity of acetone. In addition, dehydration ability and combustion ability were evaluated by the selectivities of propylene and carbondioxide, respectively.

In our experiment, we collected sample to analyze with gas chromatography, GC, technique described in chapter III. Consequently, raw data from GC results were converted to conversion and selectivity values as showed in Appendix C. Those values from our reaction tests with synthesized Cr-TS-1 and TS-1 samples are showed in figures 4.5a - 4.5f.

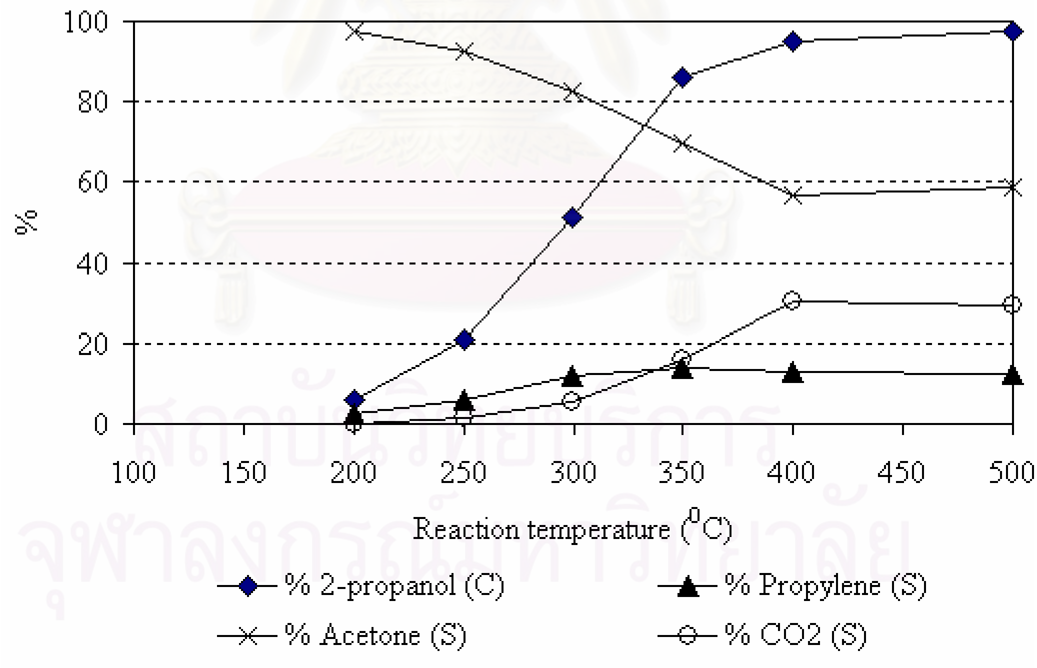


Figure 4.5a Product selectivities of 2-propanol oxidation over TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

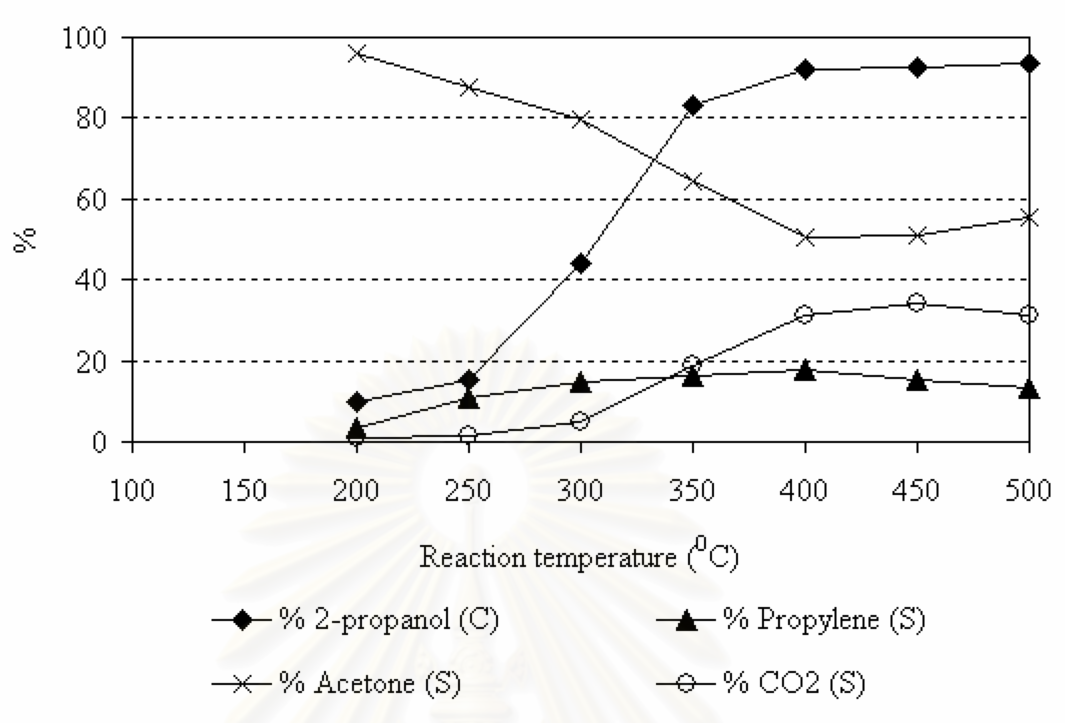


Figure 4.5b Product selectivities of 2-propanol oxidation over Cr(0.06 %)-TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

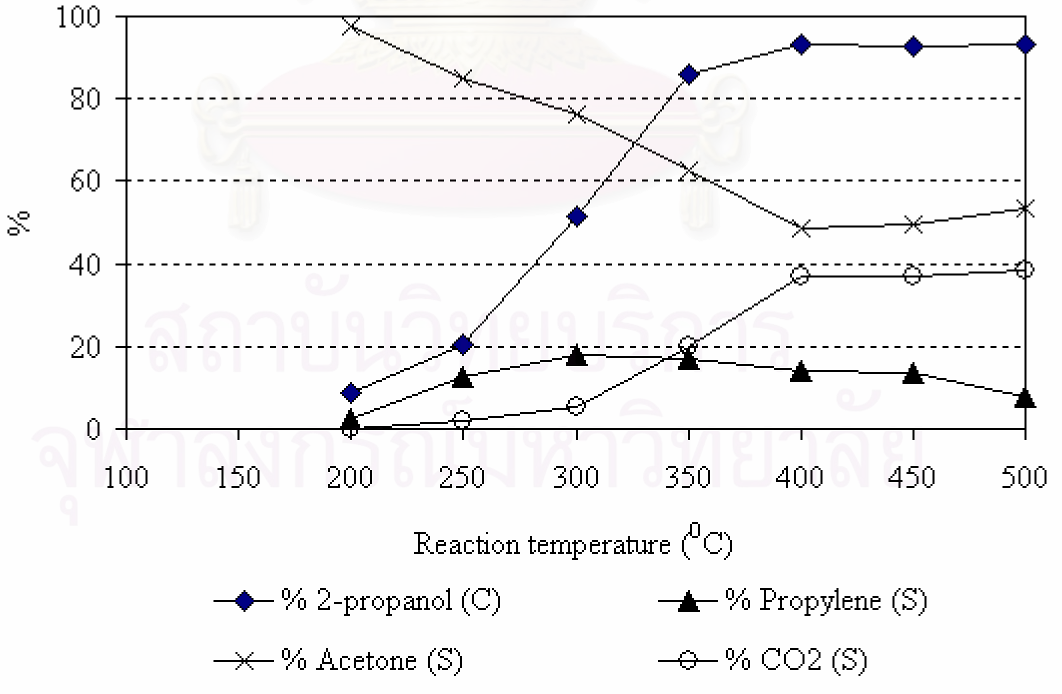


Figure 4.5c Product selectivities of 2-propanol oxidation over Cr(0.08 %)-TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

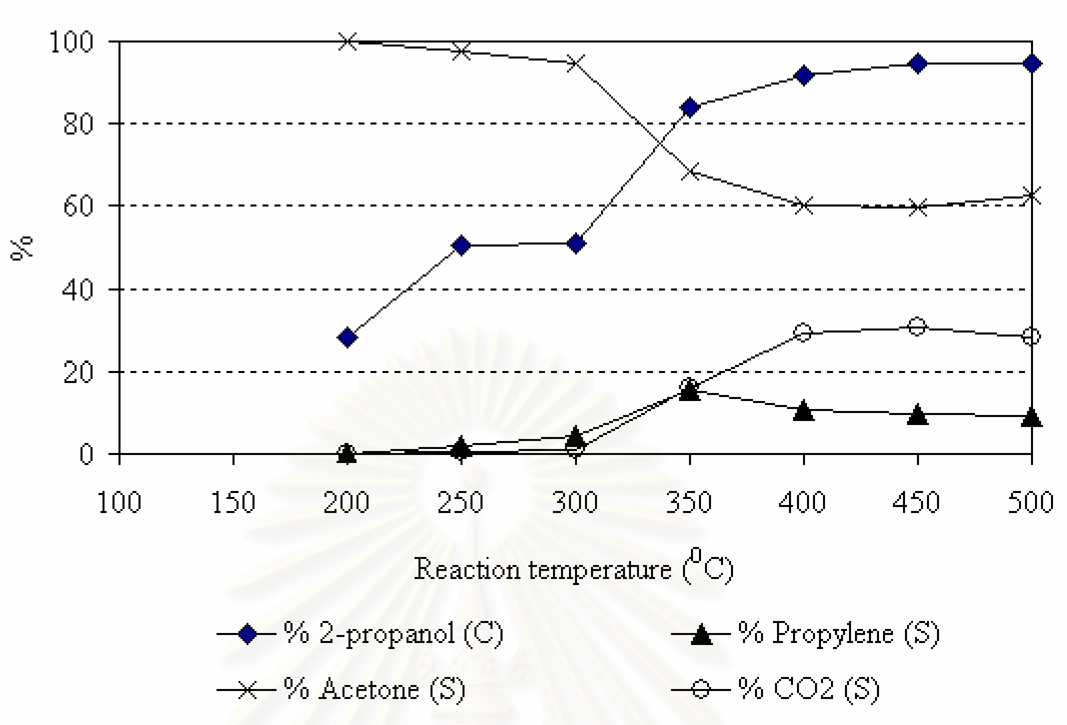


Figure 4.5d Product selectivities of 2-propanol oxidation over Cr(0.15 %)-TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

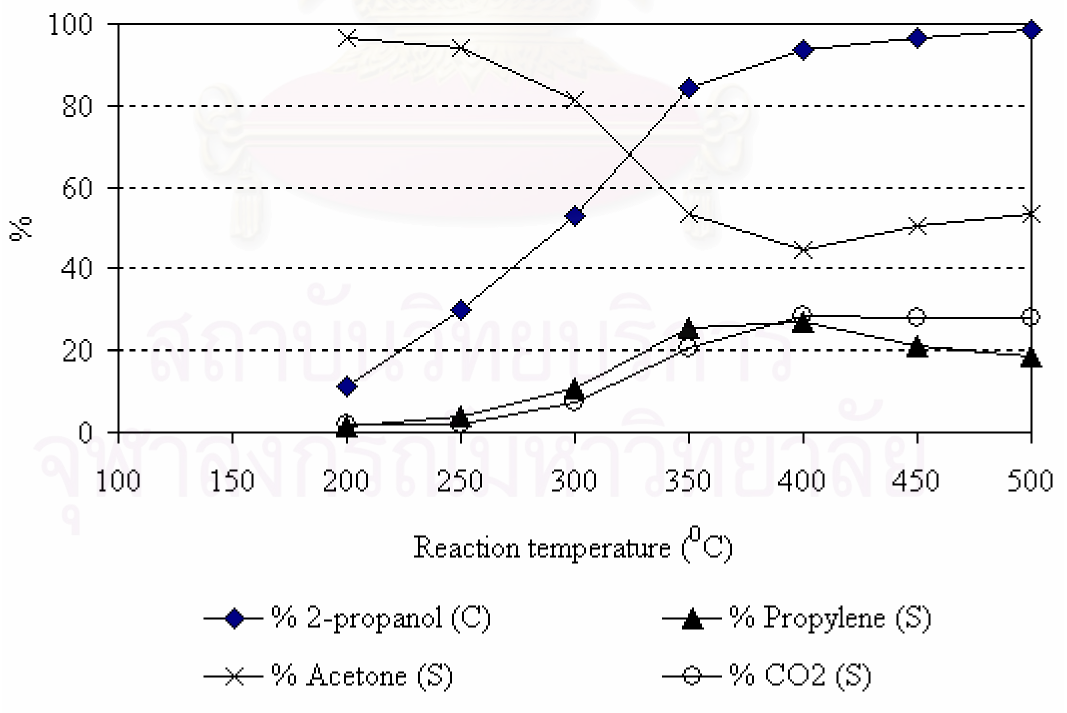


Figure 4.5e Product selectivities of 2-propanol oxidation over Cr(0.40 %)-TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

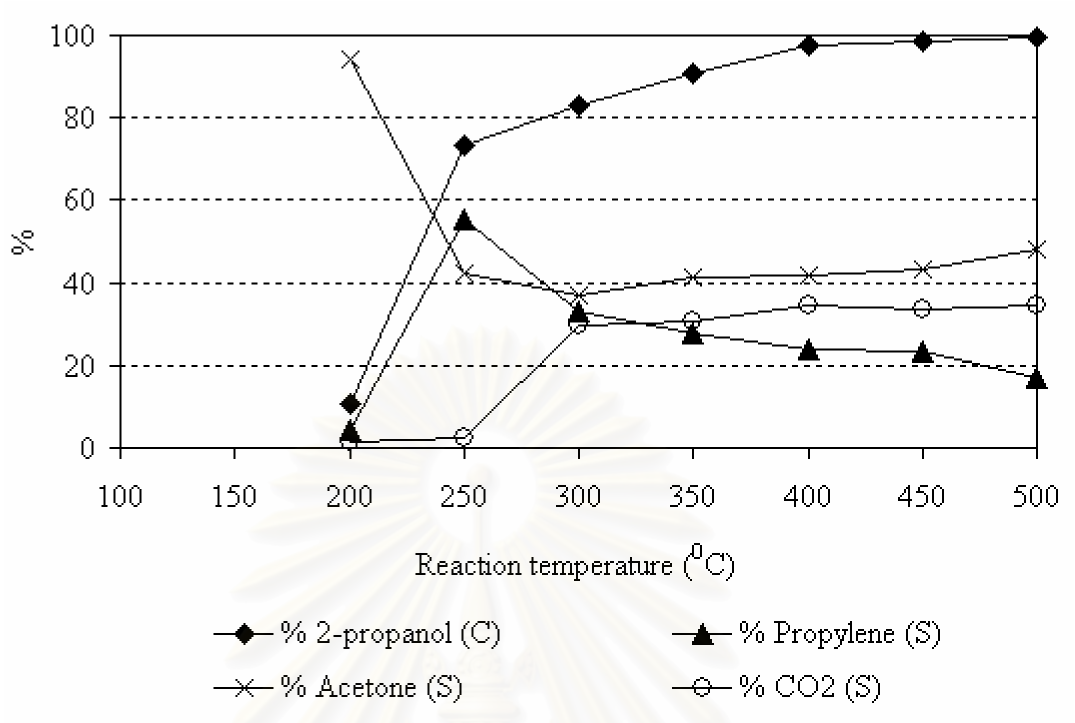


Figure 4.5f Product selectivities of 2-propanol oxidation over Cr(0.50 %)-TS-1 for 8 vol% O_2 system (C-Conversion, S-Selectivity)

To evaluate the performance of the synthesized catalysts, interpretation is divided to three following sections, dehydration ability, selectivity oxidation and combustion ability.

4.7.1 Dehydration ability

Dehydration is a reaction which can progress without oxygen, but need suitable acidity. More quantities of acid sites, more dehydration can occur. OH^- group and H atom attached to carbon atom linked with OH^- group will be eliminated to get molecule of alkenes and water as described in chapter II. In case of dehydration of 2-propanol, propylene and water become our products. From our reaction test with Cr-TS-1 samples which have nearly amount of titanium, we found that propylene selectivity is rather higher with increased amount of chromium in Cr-TS-1 samples, except Cr(0.15 %)-TS-1. These results imply that increased amount of Cr-TS-1 may increase acid sites which satisfy for dehydration reaction.

4.7.2 Selective oxidation ability

Selective oxidation is a reaction which depends on oxygen. In case of TS-1, Ti^{4+} in silicate framework is the location for selective oxidation. Comparison between synthesized TS-1 and Cr-TS-1 with lowest amount of chromium, Cr(0.06 %)-TS-1, we found that the trend of selectivities of both samples are almost the same. Acetone selectivity of Cr(0.06 %)-TS-1 is lower when we compare with that of TS-1 sample because of the lower amount of titanium for Cr(0.06 %)-TS-1. This comparison also confirms that Ti^{4+} exists in Cr-TS-1 framework from the appearance of acetone.

From the results showed in figures 4.5a - 4.5f, we see that acetone selectivity will drop with increasing of chromium in the synthesized Cr-TS-1 samples except Cr(0.15 %)-TS-1. The reason may be the reducing of active site for selective oxidation on the catalyst surface. Surface area of the synthesized catalysts may be shared by active site which is formed by loaded chromium; as a result, active site for the selective oxidation formed by Ti^{4+} in the silicate framework is decreased.

In case of Cr(0.15 %)-TS-1, acetone selectivity is the highest compared with other Cr-TS-1 samples as we see in figure 4.5d. Ti^{4+} in silicate framework of this sample may well disperse that causes surface area rich by active site for selective oxidation. Another reason for good selectivity of acetone may involve with CrO_3 on the catalyst surface. Cr^{6+} in CrO_3 is a strong oxidizer which may involve oxidation of 2-propanol without oxygen from gas feed. However, two assumptions for unusual selectivities of this sample have to be further explored.

4.7.3 Combustion ability

Combustion is a complete oxidation reaction which also needs oxygen. From each figure in this part, we will see that CO_2 selectivity is increased simultaneous with decreasing of acetone and propylene selectivities. It can be interpreted that some parts of acetone and propylene are burned with oxygen. In addition, CO_2 selectivity will be limited at 40% because of the limited amount of oxygen in our system.

The combustion of propylene well occur in reaction test with Cr(0.50 %)-TS-1, the highest loaded chromium, as we see in figure 4.5f. Oxygen burns propylene which is produced in high amount; consequently we see the raising of CO_2 selectivity coupling with high conversion at 300 °C as shown in figure 4.5f.

From our experiment until now, we have known that all of the synthesized Cr-TS-1 samples have Ti^{4+} and Cr^{5+} in the silicate framework. In addition, we have also known that loading chromium may increase acid sites for dehydration. However, some compound or transition state of chromium on catalyst surface which may effect on acid site and any reasons for unusual behavior of Cr(0.15 %)-TS-1 have to be further investigated.

4.8 Acid quantities and acid strength

Most of reactions occur at catalyst surface; therefore, investigation of active site on catalyst surface is useful for interpretation of reaction pathway. In our study, two main reactions, selective oxidation and dehydration need active sites being acid. Hence, we investigated the active site of our synthesized catalysts by explore acid site on the catalyst surface.

To find quantities of acid sites and acid strength on the catalyst surface, ammonium temperature program desorption, NH_3-TPD, was selected to our best method. The results which are calculated from raw data of NH_3-TPD with some helps of peak fitting program as showed in Appendix E are presented in Table 4.4.

Table 4.4 Desorption temperature and acid site quantities of the synthesized TS-1 and Cr-TS-1 samples

Sample	% Mole of Ti	Desorption temperature (°C)		Acid site quantities		
		Weak acid	Strong acid	Total (μmol H^+ / g catalyst)	Weak acid (%)	Strong acid (%)
TS-1	0.442	134	226	235	57.41	42.59
Cr(0.06 %)-TS-1	0.262	138	235	243	80.25	19.75
Cr(0.08 %)-TS-1	0.232	140	235	248	83.43	16.57
Cr(0.15 %)-TS-1	0.222	138	222	191	57.89	42.11
Cr(0.40 %)-TS-1	0.206	142	238	242	85.57	14.43
Cr(0.50 %)-TS-1	0.157	141	237	371	93.11	6.89

From Table 4.4, we will see that the ratio of strong acid site on the catalyst surface is decreased with more loaded chromium in Cr-TS-1 samples except Cr(0.15 %)-TS-1. Comparison between TS-1 and Cr(0.06 %)-TS-1, it should be noted that the amount of Ti^{4+} in the silicate framework of Cr(0.06 %)-TS-1 are less than that of TS-1, confirmed by acetone selectivity of both sample as described in section 4.7.2. It is clearly seen that the number of Ti^{4+} in the silicate framework relates to the number of strong acids in the same direction, in other words, Ti^{4+} in the silicate framework causes the strong acid site on the catalyst surface. Furthermore, we also know that high ratio of strong acid site leads to increase selective oxidation ability from interpretation of section 4.7.2 and Table 4.4

Another relation between type of acid site and type of reaction are disclosed. From Table 4.4, we found that the increased weak acid sites correspond to increasing of dehydration ability. As a result, we will get the highest selectivity of propylene from reaction test with Cr(0.50 %)-TS-1, highest loaded chromium and highest ratio of weak acid sites.

For Cr(0.15 %)-TS-1, we found that the ratio of strong acid on the catalyst surface is as high as that of TS-1, corresponding to high ability of selective oxidation described in section 4.7.2. Cr^{6+} and satisfied dispersion of Ti^{4+} in the silicate framework are still our assumptions for this unusual behavior. One of them will be eliminated in the next part.

4.9 Oxidation state of chromium on the synthesized Cr-TS-1 surface

In this part, the oxidation states of chromium ion on the catalyst surface and reasons for unusual behavior of Cr(0.15 %)-TS-1 will be revealed. The oxidation states of chromium ion on Cr-TS-1 surface were detected by x-ray photoelectron spectroscopy, XPS. C 1s peak at 284.6 eV is used as reference for binding energy shift. These results are presented in Table 4.5.

Table 4.5 Binding energy of chromium in the synthesized Cr-TS-1 samples

Sample	Binding energy (eV)	FWHM (eV)
Cr(0.06 %)-TS-1	576.000	8.664
Cr(0.08 %)-TS-1	576.192	6.475
Cr(0.15 %)-TS-1	576.431	5.650
Cr(0.40 %)-TS-1	576.862	6.093
Cr(0.50 %)-TS-1	577.620	4.724

Table 4.5 reveals that the binding energy of chromium in Cr-TS-1 samples are around 576 - 578 eV. A previous study by Gaspar et al. (2005) ascribed binding energy of Cr^{3+} and Cr^{6+} as 576.3 and 579.3 eV, respectively. Therefore, this information can predict our oxidation state on our catalyst surfaces that Cr^{3+} and Cr^{6+} are possible to exist. Cr^{3+} and Cr^{6+} on the catalyst surface are in the form of Cr_2O_3 and CrO_3, respectively. Especially for Cr-TS-1 samples with high loaded chromium, more Cr^{6+} will be detected as we see higher binding energy from aboved table.

For Cr(0.15 %)-TS-1, its binding energy of chromium is closed to that of Cr^{3+}, 576.3 eV; therefore Cr^{3+} should be the main oxidation state of chromium on its surface. Consequently, the assumption stated that Cr^{6+} cause the high ratio of strong acid site will be discarded. Alternatively, the satisfied dispersion of Ti^{4+} in silicate framework should be the best reason for its unusual behavior.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions of the present research are the following:

1. Preparation of Cr-TS-1 catalyst by incorporation method has been successful, Chromium and titanium can be exist in the catalyst framework and also maintain MFI structure and octahedral crystal shape.

2. Cr^{5+} and Ti^{4+} are the status of chromium and titanium, respectively, in tetrahedral framework of Cr-TS-1 catalyst.

3. Higher amount of chromium used for synthesizing will increase the amount of Cr^{5+} in the catalyst framework, including weak acid site ratio and CrO_3 on Cr-TS-1 catalyst surface.

5.2 Recommendations for future studies

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

1. Reaction time during crystallization should be varied to investigate composition ratio of chromium and titanium in the synthesized catalyst.

2. The properties of Cr-TS-1, with varying of the amount of chromium, prepared by incorporation method should be compared with the properties of that one prepare by ion-exchange and impregnation methods.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of Si/Ti and Si/Cr Atomic Ration for TS-1 and Cr-TS-1 samples

The calculation is based on weight of sodium silicate for Si source.

Molecular Weight of Si = 28.0855

Molecular Weight of silicon oxide = 60.0843

Concentration of SiO_2 in sodium silicate = 28.5 %

Using sodium silicate 69 g

$$\text{mole of Si used} = \frac{28.5}{100} \times \frac{69}{60.0843}$$

$$= 0.3272 \text{ mole}$$

For example, to prepare TS-1 at Si/Ti atomic ratio of 50 by using titanium butoxide 97 %, $Ti[O(CH_2)_3CH_3]_4$, for Ti source.

Molecular Weight of Ti = 47.88

Molecular Weight of titanium butoxide = 340.26

Si/Ti atomic ratio = 50

$$\text{mole of titanium required} = 0.3272/50$$

$$= 6.546 \times 10^{-3} \text{ mole}$$

$$\text{amount of titanium butoxide 97\% required} = 6.546 \times 10^{-3} \times 340.26 \times \frac{100}{97}$$

$$= 2.2962 \text{ g}$$

which is used in Topic 3.1.2.1.

For example, to prepare Cr-TS-1 at Si/Cr atomic ratio of 50 by using chromium nitrate nanohydrate , $CrNO_3{\cdot}9H_2O$, for Cr source.

Molecular Weight of Cr = 51.99

Molecular Weight of $CrNO_3{\cdot}9H_2O$ = 400.15

Si/Cr atomic ratio = 50

mole of chromium required = 0.3272/50

= 6.546×10^{-3} mole

amount of $CrNO_3 \cdot 9H_2O$ required = $6.546 \times 10^{-3} \times 400.15$

= 2.62 g

which is also used in Topic 3.1.2.1.

APPENDIX B

CALCULATION OF G VALUE

G value is the best index for determination of transition metal state in the catalyst framework and derived from the following equation.

$$g = 71.448\left(\frac{\text{mT}}{\text{MHz}}\right)\times\frac{\text{frequency (MHz)}}{\text{magnetic field (mT)}}$$

For example, Cr(0.06 %)-TS-1, peak of spectra by ESR appears at magnetic field of 339.62 mT with 9.44 MHz. Consequently, g_1 value for Cr(0.06 %)-TS-1 can be calculated from

$$g_1 = 71.448\left(\frac{\text{mT}}{\text{MHz}}\right)\times\frac{9.44\text{ (MHz)}}{339.62\text{ (mT)}}$$

$$g_1 = 1.986$$

APPENDIX C

DATA OF CATALYTIC EXPERIMENTS

Table C1 Data of Figure 4.5a

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	1.50	0.00	0.00	100.00	0.00
150	0.99	1.25	0.00	98.75	0.00
200	6.21	2.47	0.00	97.53	0.00
250	20.94	5.96	0.00	92.37	1.67
300	51.33	11.75	0.31	82.61	5.33
350	85.82	14.08	0.20	69.58	16.15
400	95.09	13.07	0.06	56.51	30.35
500	97.29	12.23	0.00	58.46	29.31

Table C2 Data of Figure 4.5b

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	3.13	1.76	0.00	98.24	0.00
150	2.43	0.90	0.00	99.10	0.00
200	9.67	3.29	0.00	95.85	0.86
250	15.49	10.75	0.00	87.65	1.60
300	44.21	15.06	0.24	79.68	5.03
350	82.99	16.47	0.29	64.46	18.78
400	92.10	17.90	0.16	50.57	31.36
450	92.60	15.23	0.08	50.77	33.92
500	93.33	13.32	0.03	55.53	31.12

Table C3 Data of Figure 4.5c

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	1.37	0.00	0.00	100.00	0.00
150	4.60	1.25	0.00	98.75	0.00
200	8.73	2.54	0.00	97.46	0.00
250	20.58	12.54	0.38	85.16	1.92
300	51.34	17.86	0.46	76.34	5.34
350	85.89	17.21	0.30	62.74	19.75
400	93.19	14.18	0.13	48.57	37.12
450	92.51	13.63	0.08	49.42	36.87
500	92.98	7.81	0.04	53.61	38.55

Table C4 Data of Figure 4.5d

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	4.94	1.33	0.00	98.67	0.00
150	19.48	0.05	0.00	99.95	0.00
200	28.34	0.22	0.00	99.78	0.00
250	50.36	2.00	0.05	97.40	0.55
300	51.16	4.14	0.13	94.85	0.88
350	84.22	15.58	0.11	68.41	15.90
400	91.77	10.66	0.05	60.14	29.15
450	94.57	9.69	0.00	59.64	30.67
500	94.79	9.37	0.00	62.52	28.10

Table C5 Data of Figure 4.5e

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	1.74	2.00	0.00	98.00	0.00
150	3.99	0.68	0.00	99.32	0.00
200	11.29	1.56	0.00	96.40	2.04
250	30.12	4.08	0.00	93.90	2.01
300	53.05	10.94	0.16	81.45	7.45
350	84.42	25.68	0.22	53.64	20.46
400	93.79	26.90	0.22	44.49	28.39
450	96.51	21.31	0.12	50.61	27.96
500	98.54	18.69	0.05	53.31	27.95

Table C6 Data of Figure 4.5f

Reaction temperature (^{0}C)	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO_2 (S)
100	0.30	0.00	0.00	100.00	0.00
150	1.93	0.31	0.00	99.69	0.00
200	10.90	4.48	0.00	94.26	1.26
250	73.10	55.47	0.08	42.06	2.39
300	83.09	32.96	0.29	37.10	29.65
350	90.68	27.66	0.38	41.24	30.73
400	97.50	23.96	0.10	41.63	34.31
450	98.77	23.33	0.04	43.18	33.45
500	99.56	17.00	0.03	48.29	34.69

APPENDIX D

CALIBRATION CURVE

Flame ionization detector gas chromatograph, model 8A, was used to analyze the concentrations of oxygenated compounds. 2-propanol, propylene, isopropyl ether and acetone were analyzed by GC model 8A with using Carbopack B/3% SP-1500.

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO_2 by using molecular sieve 5A and porapak-Q columns respectively.

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

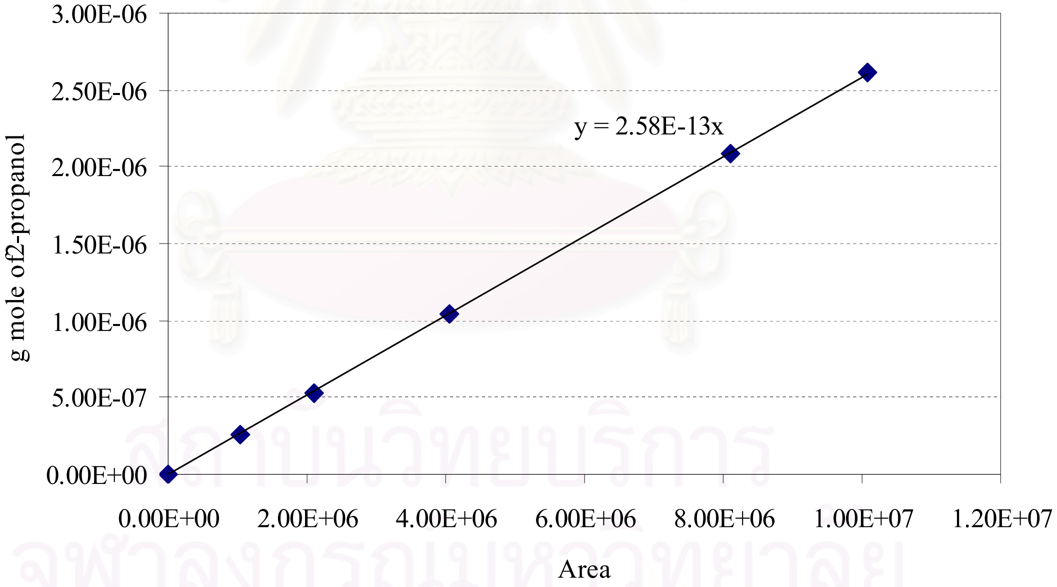


Figure D1 The calibration curve of 2-propanol

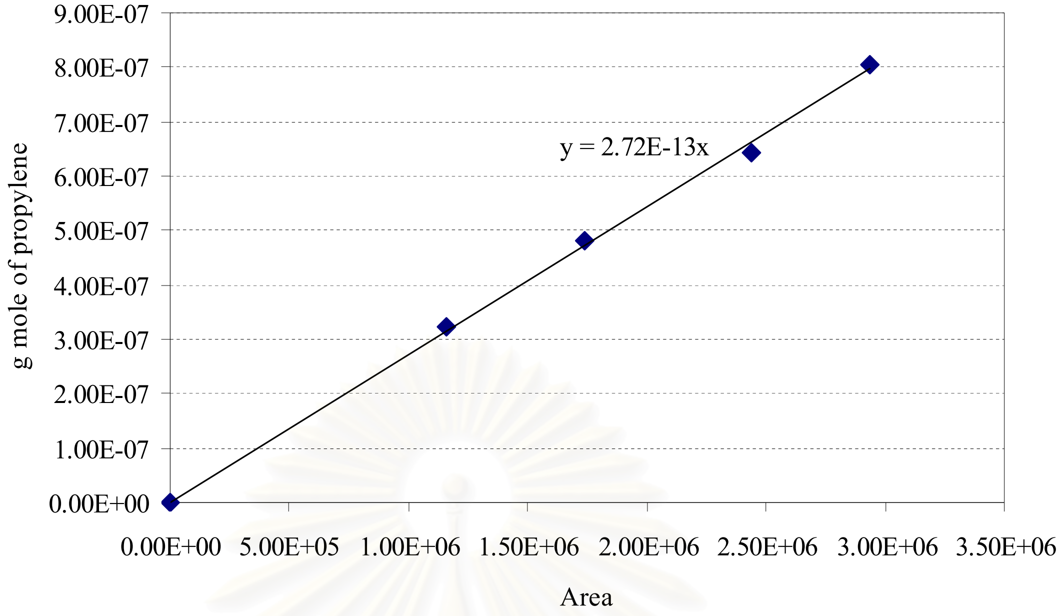


Figure D2 The calibration curve of propylene

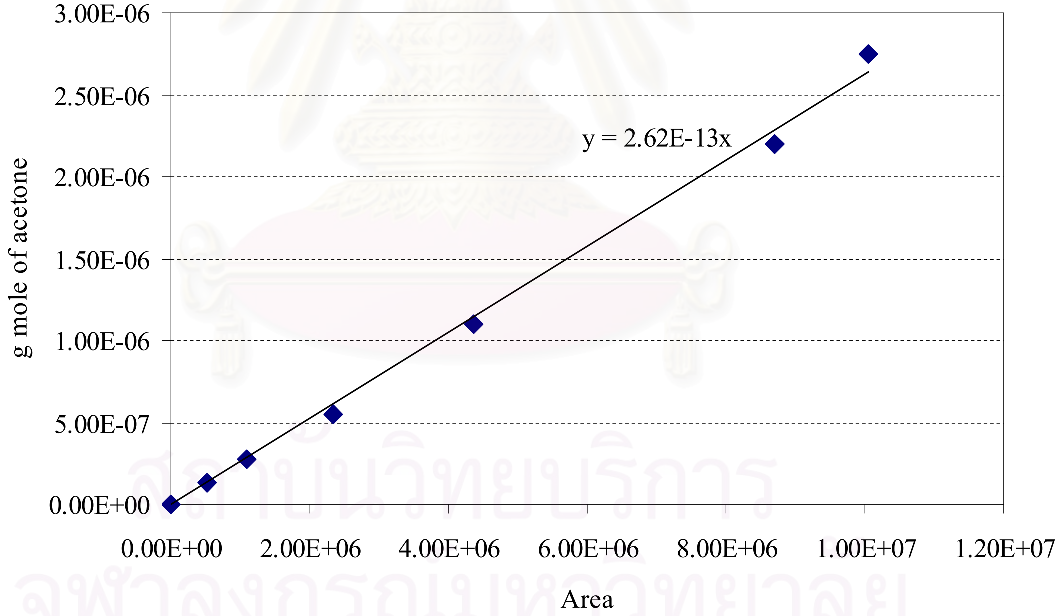


Figure D3 The calibration curve of acetone

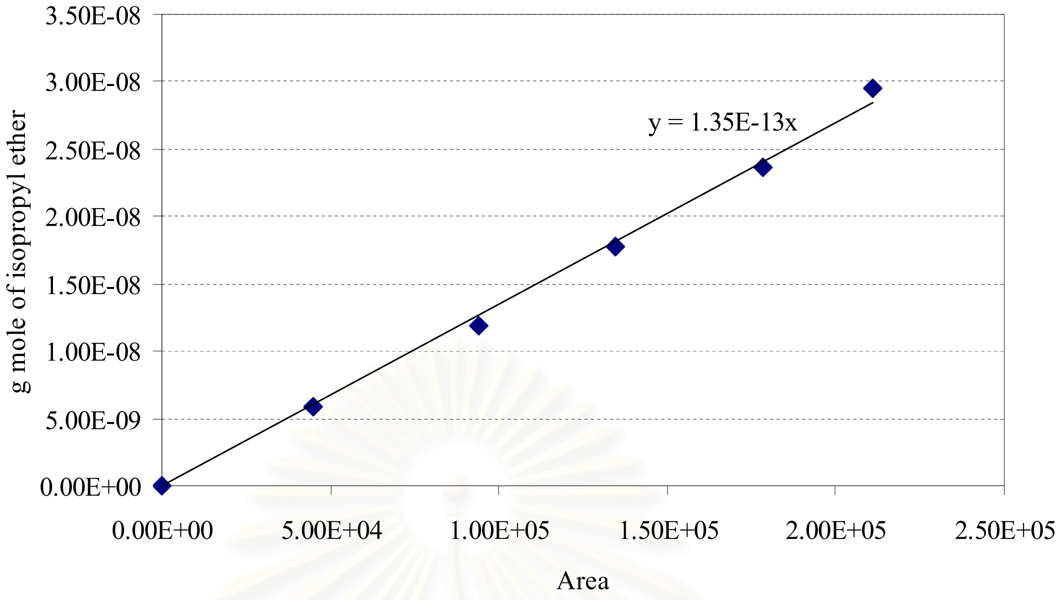


Figure D4 The calibration curve of isopropyl ether

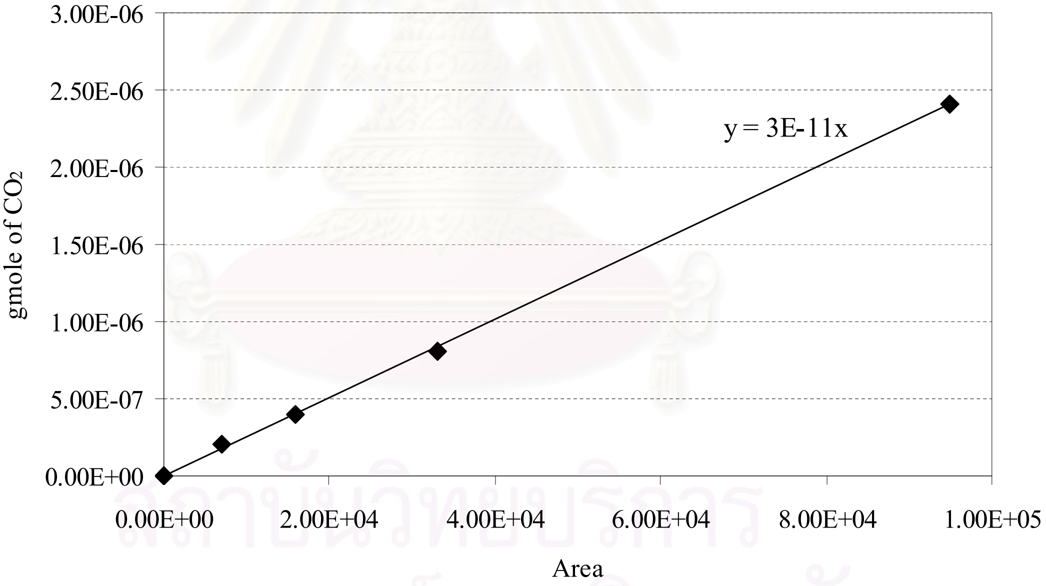


Figure D5 The calibration curve of CO_2

APPENDIX E

DATA AND CALCULATION OF ACID SITE

Table E1 Reported total peak area from Micromeritrics Chemisorb 2750

Sample	Reported total peak area
TS-1	0.0496108
Cr(0.06 %)-TS-1	0.051177
Cr(0.08 %)-TS-1	0.0528528
Cr(0.15 %)-TS-1	0.0412312
Cr(0.40 %)-TS-1	0.0518725
Cr(0.50 %)-TS-1	0.0783981

Calulation of total acid sites

For example, TS-1, total acid site is calculated from the following step.

1. Conversion of total peak area to peak volume

Conversion factor from Micromeritrics Chemisorb 2750 is equal to 77.57016 ml/area unit. Therefore, total peak volume is derived from

$$\begin{aligned} \text{Total peak volume} &= 77.57016 \times \text{total peak area} \\ &= 77.57016 \times 0.0496108 \\ &= 3.84832 \text{ ml} \end{aligned}$$

2. Calculation for adsorbed volume of 15% NH_3

$$\text{adsorbed volume of 15\% } NH_3 = 0.15 \times \text{total peak volume}$$

$$= 0.15 \times 3.84832 \text{ ml}$$

$$= 0.57725 \text{ ml}$$

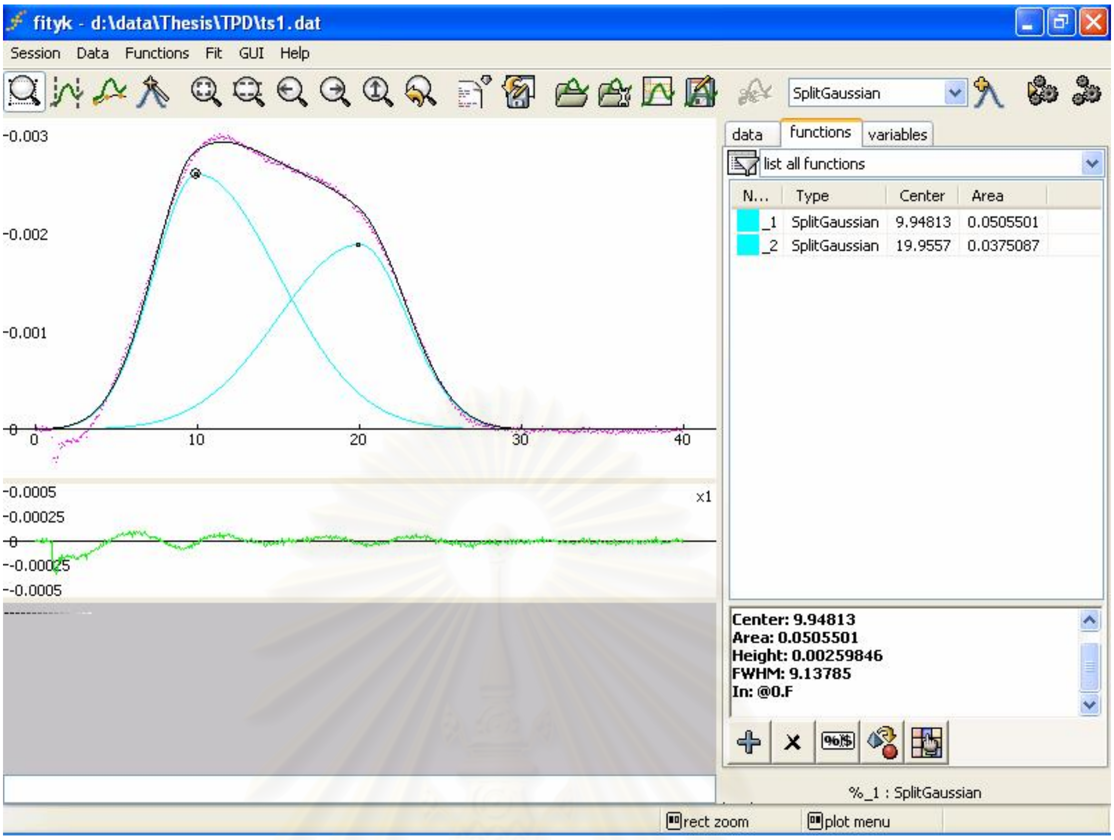
3. Total acid sties are calculated from the following equation

$$\text{Total acid sites} = \frac{(\text{Adsorbed volume, ml}) \times 101.325\ \text{Pa}}{\left(8.314 \times 10^{-3}\ \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298\ \text{K} \times (\text{weight of catalyst, g})}$$

For TS-1 sample, 0.1006 g of this one was measured, therefore

$$\text{Total acid sites} = \frac{0.57725\ \text{ml} \times 101.325\ \text{Pa}}{\left(8.314 \times 10^{-3}\ \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298\ \text{K} \times (0.1006\ \text{g})}$$

$$= 235\ \mu\text{mol H}^{+}/\text{g}$$

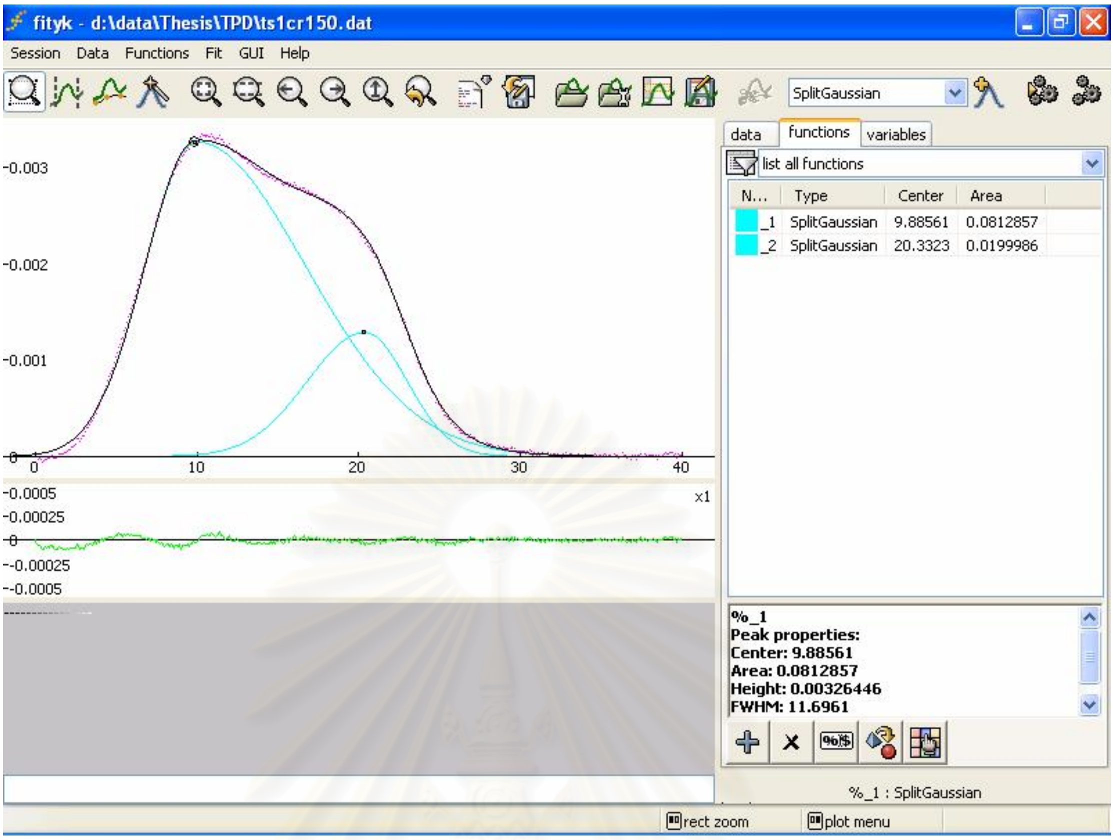


N...	Type	Center	Area
_1	SplitGaussian	9.94813	0.0505501
_2	SplitGaussian	19.9557	0.0375087

Center: 9.94813
Area: 0.0505501
Height: 0.00259846
FWHM: 9.13785
In: @0.F

%_1 : SplitGaussian

Figure E1. Data for calculating of acid site ratio of TS-1 from peak fitting program

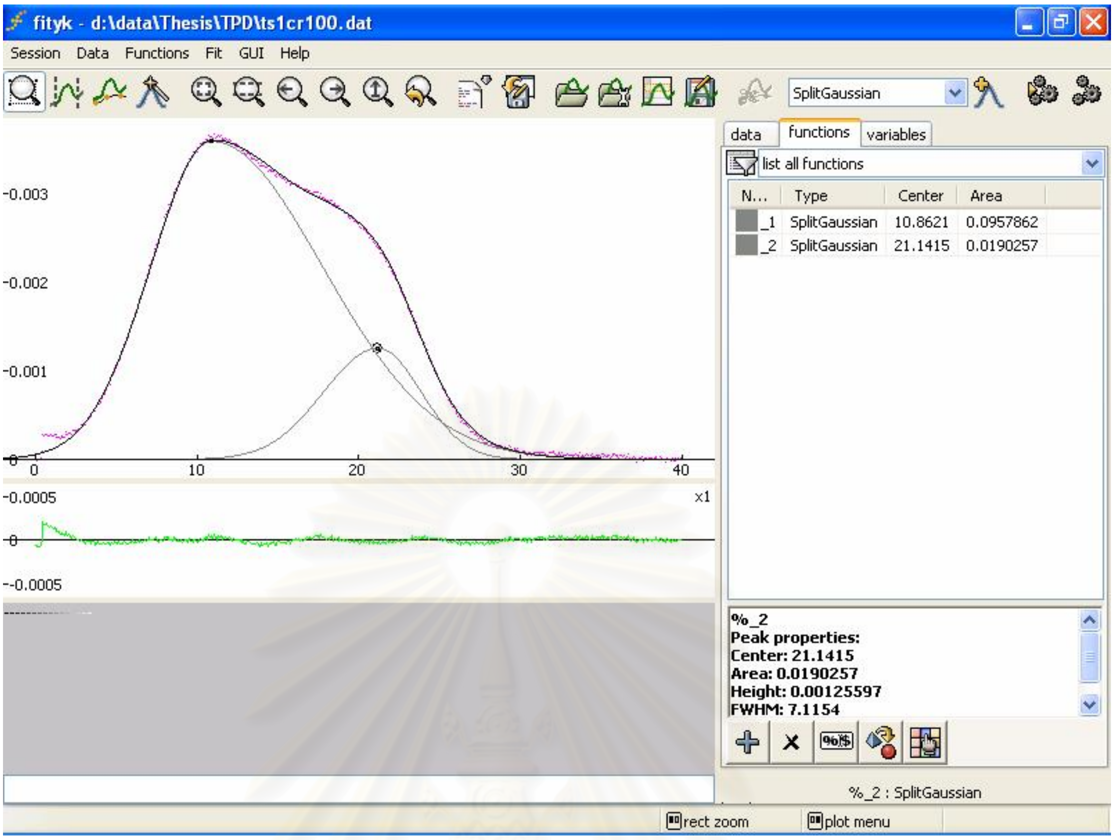


N...	Type	Center	Area
_1	SplitGaussian	9.88561	0.0812857
_2	SplitGaussian	20.3323	0.0199986

%_1
Peak properties:
Center: 9.88561
Area: 0.0812857
Height: 0.00326446
FWHM: 11.6961

%_1 : SplitGaussian

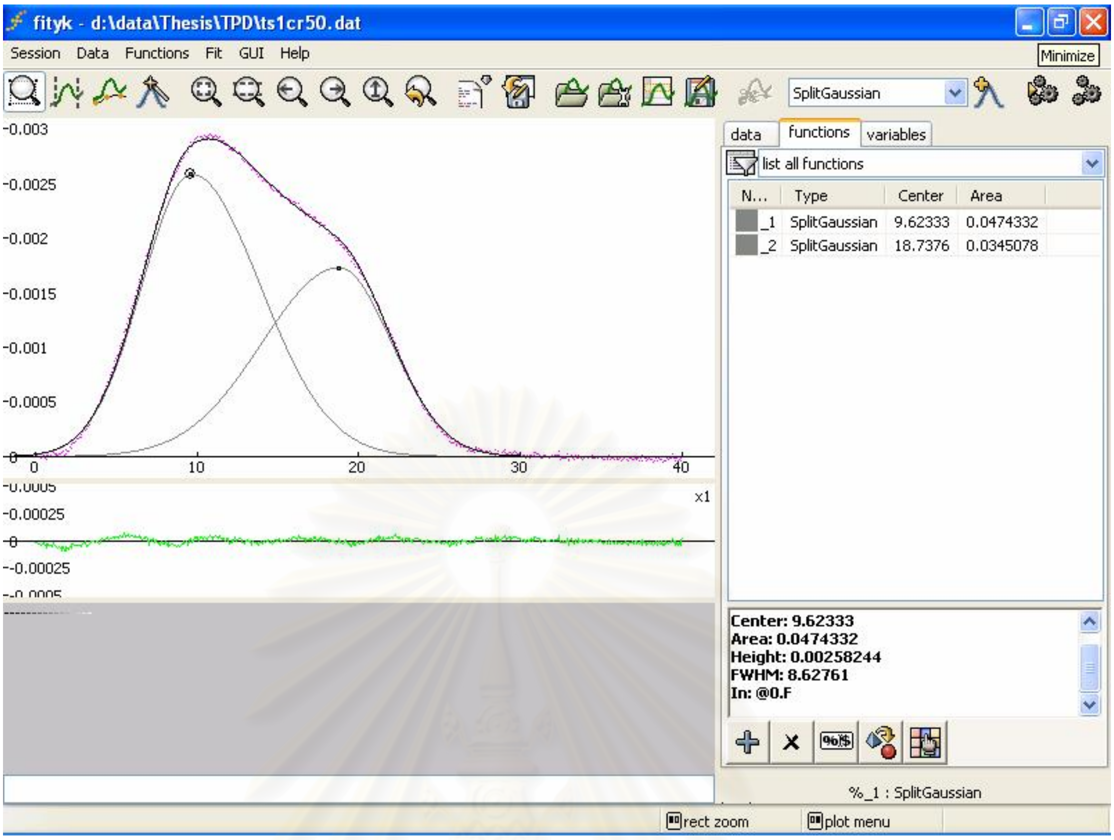
Figure E2. Data for calculating of acid site ratio of Cr(0.06 %)-TS-1 from peak fitting program



N...	Type	Center	Area
_1	SplitGaussian	10.8621	0.0957862
_2	SplitGaussian	21.1415	0.0190257

%_2
Peak properties:
Center: 21.1415
Area: 0.0190257
Height: 0.00125597
FWHM: 7.1154

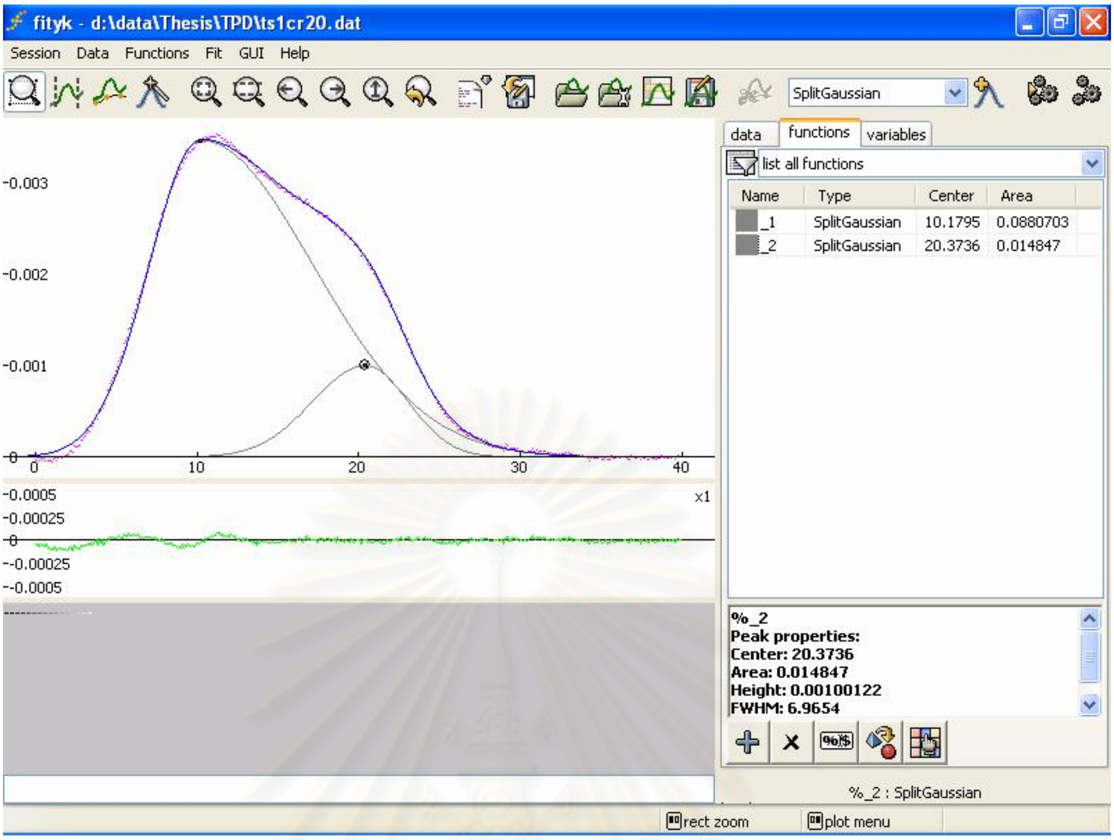
Figure E3. Data for calculating of acid site ratio of Cr(0.08 %)-TS-1 from peak fitting program



N...	Type	Center	Area
_1	SplitGaussian	9.62333	0.0474332
_2	SplitGaussian	18.7376	0.0345078

Center: 9.62333
Area: 0.0474332
Height: 0.00258244
FWHM: 8.62761
In: @0.F

Figure E4. Data for calculating of acid site ratio of Cr(0.15 %)-TS-1 from peak fitting program

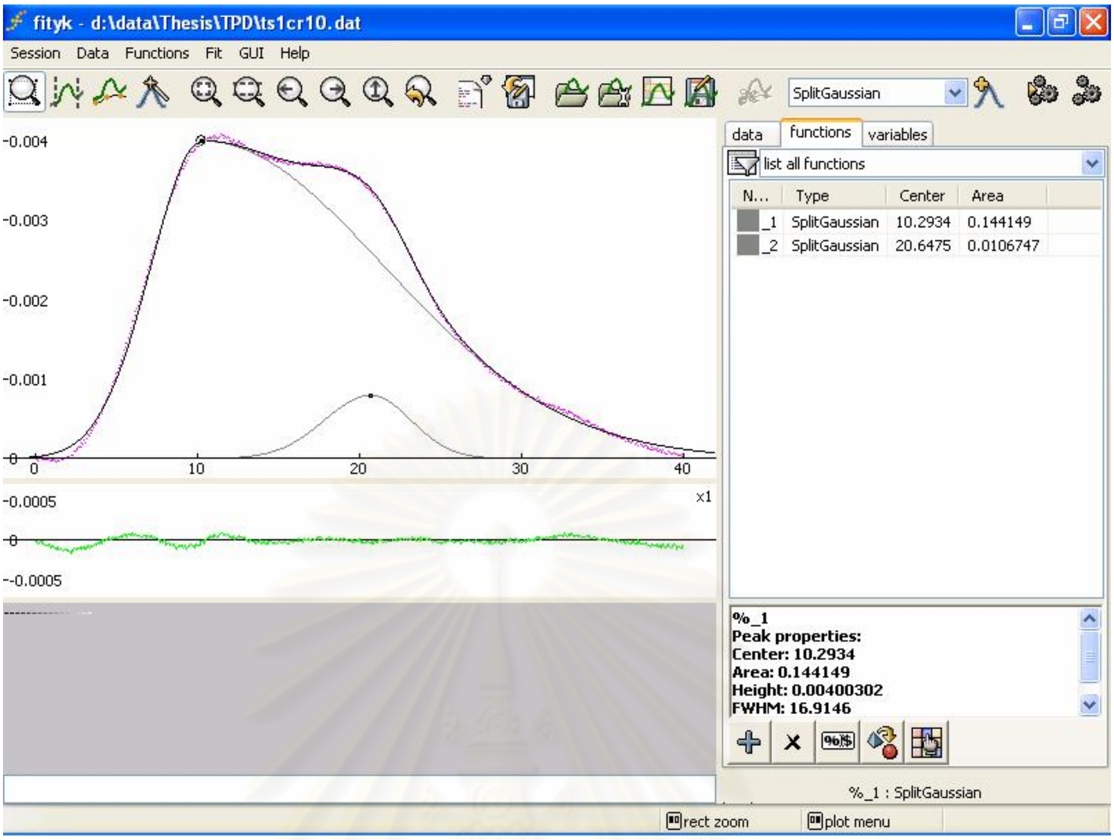


Name	Type	Center	Area
_1	SplitGaussian	10.1795	0.0880703
_2	SplitGaussian	20.3736	0.014847

%_2
Peak properties:
Center: 20.3736
Area: 0.014847
Height: 0.00100122
FWHM: 6.9654

%_2 : SplitGaussian

Figure E5. Data for calculating of acid site ratio of Cr(0.40 %)-TS-1 from peak fitting program



N...	Type	Center	Area
_1	SplitGaussian	10.2934	0.144149
_2	SplitGaussian	20.6475	0.0106747

```
%_1
Peak properties:
Center: 10.2934
Area: 0.144149
Height: 0.00400302
FWHM: 16.9146
```

Figure E6. Data for calculating of acid site ratio of Cr(0.50 %)-TS-1 from peak fitting program

Calculation of acid site ratio

To calculate acid site ratio, experiment data from Micromeritrics Chemisorb 2750 are transferred to peak fitting program to separate peak. As known, the first peak of desorption process is indicated as weak acid, relative with another peak, and the second one is strong acid. Ratio of each acid site on the catalyst surface is calculated from peak areas reported by peak fitting program as shown above.

For example, Cr(0.50 %)-TS-1, the ratio of each acid site on catalyst surface is calculated from the following equation.

$$\text{The ratio of weak acid} \quad = \frac{1^{\text{st}} \text{ peak area}}{\text{summation of both peak areas}} \times 100\ \%$$

from figure E6, 1st peak area and 2nd peak area are equal to 0.144149 and 0.0106747, respectively.

$$\text{The ratio of weak acid} = \frac{0.144149}{0.144149 + 0.0106747} \times 100\ \%$$

$$= 93.11\ \%$$

$$\text{therefore, the ratio of strong acid} = 100 - 93.11\ \%$$

$$= 6.89\ \%$$

Note. Reported center values of both peaks from peak fitting program reveal times at the maximum of both peaks occur. Since, we know the relationship between time and temperature during desorption process from Micromeritrics Chemisorb 2750, hence, the temperature at the maximum of both peaks as we state as desorption temperature of both acid sites can be located.

APPENDIX F

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 °C (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 °C
Boiling point: 1413 °C
Vapour pressure: 1 mm Hg at 865 °C
Specific gravity: 2.16 g cm^{-3}
Solubility in water: 35.7 g/100g at 0 °C

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 °C
Boiling point: 1390 °C
Vapour pressure: 1 mm Hg at 739 °C
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, oxidizing 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.

Chromium nitrate nanohydrate

Safety data for Chromium nitrate nanohydrate

General

Synonyms: chromic nitrate, chromic nitrate nonahydrate, chromium nitrate
Molecular formula: $Cr(NO_3)_3 \cdot 9H_2O$

Physical data

Appearance: blue or purple crystals
Melting point: 60 °C

Stability

Stable at room temperature, but may explode when heated. Incompatible with organic materials, reducing agents. Use polyethylene tools.

Toxicology

Harmful if inhaled or swallowed. Irritant. May cause allergic skin reaction. [Note that there is evidence that certain chromium compounds may cause cancer in humans, though it is not known whether trivalent chromium can cause cancer.]

Personal protection

Safety glasses, adequate ventilation, gloves. Treat as a possible carcinogen.

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 G

LIST OF PUBLICATION

Eakawut Poompichate, Darunee Sookhom, Rattanawalee Sunphloi, Nitiporn Sangngen and Tharathorn Mongkhonsi, "Synthesis and Characterisation of Metal Modified TS-1", Proceedings of Thai Institute of Chemical Engineering and Applied Chemical Conference 15th, Chonburi, Thailand, Oct, 2005, Ref. No.CA09.

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 synthesised catalysts was characterised 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. There are many uses of catalyst with MFI structure in various applications, *e.g.* production of catechol and hydroquinone from phenol oxidation, and production of phenol from benzene oxidation. 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 synthesised 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.

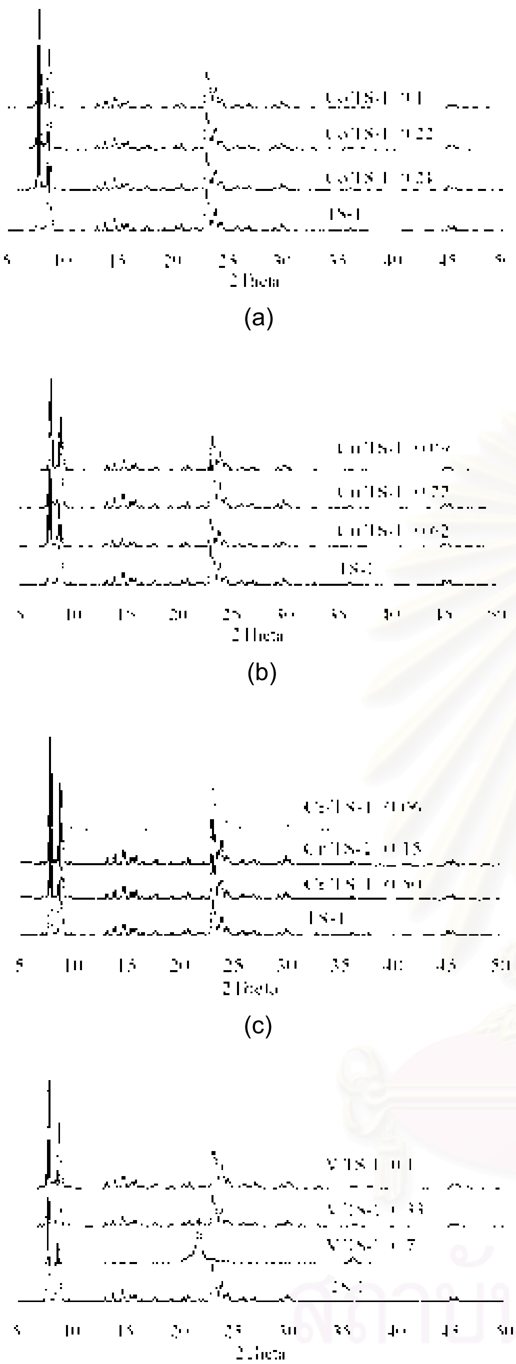
Chemical valence states of metals in the catalysts were measured by XPS technique using an AMICUS instrument with Mg Kα radiation as excitation source. The binding energy shift was calculated using the C 1s peak at 286.7 eV as reference.

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



(a)

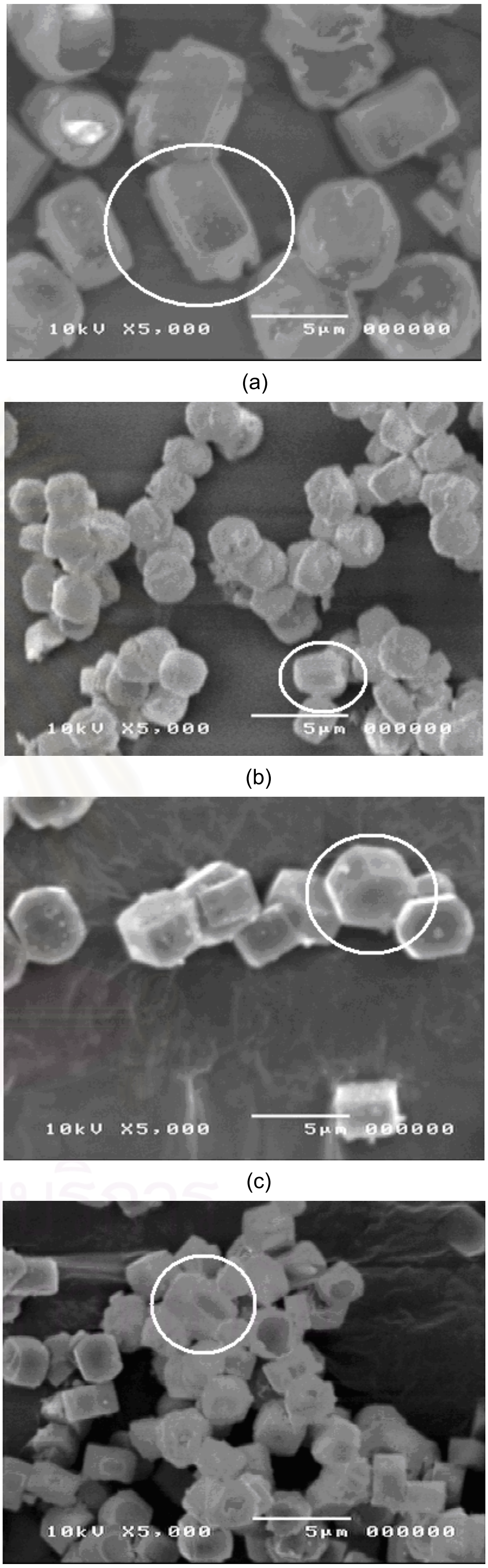
(b)

(c)

(d)

Figure 1 XRD Patterns of (a) : Co/TS-1, (b) : Cu/TS-1, (c) : Cr/TS-1 and (d) : V/TS-1

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.



(a)

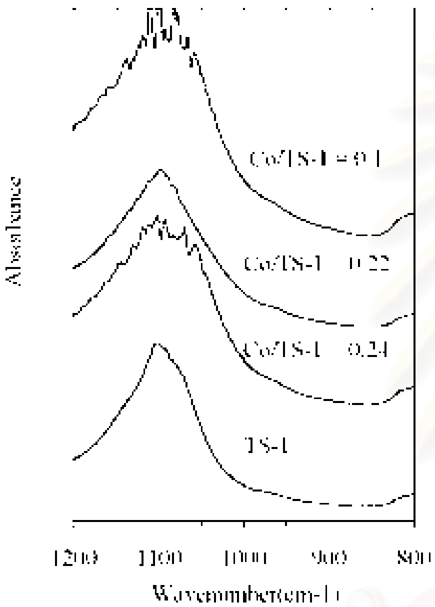
(b)

(c)

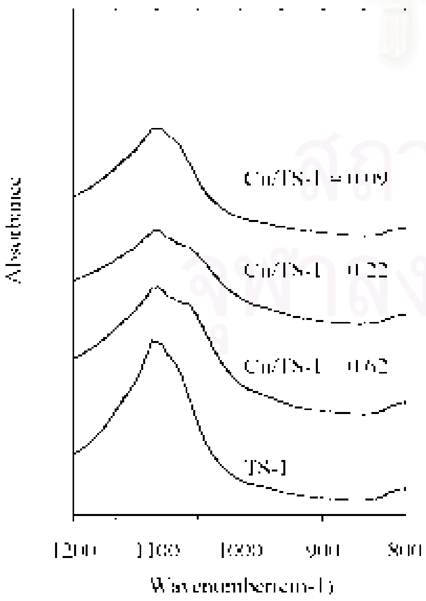
(d)

Figure 2 SEM photo of (a) : Co/TS-1, (b) : Cu/TS-1, (c) : Cr/TS-1 and (d) : V/TS-1

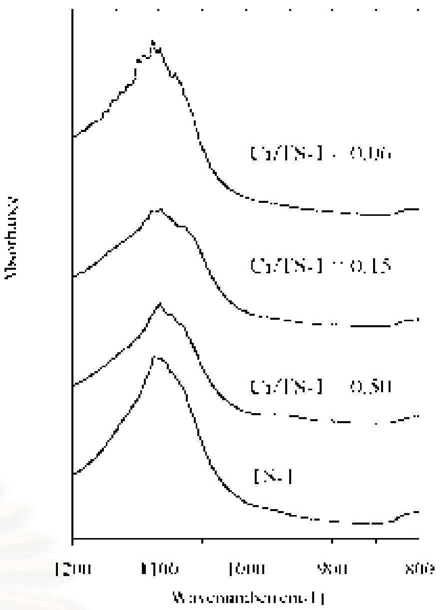
IR spectroscopy (figure 3) of the unmodified TS-1 shows a shoulder around 960-975 cm^{-1}, characteristic of Ti^{4+} in silicalite lattice [2]. This absorption band less appears for the modified TS-1 samples. These results indicate that the second metals may be in TS-1 framework; as a result, lower quantities of Ti^{4+} can be in silicate lattice. 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].



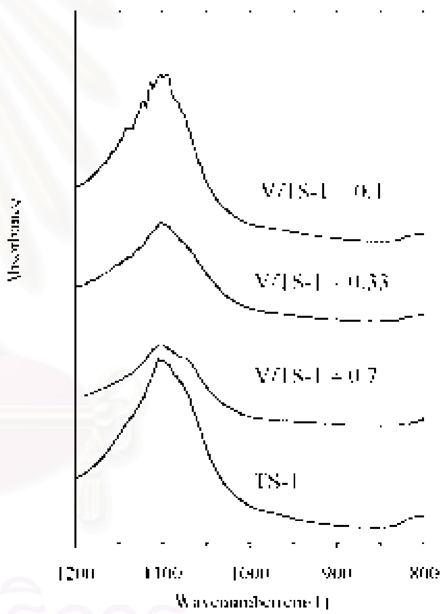
(a)



(b)



(c)



(d)

Figure 3 IR absorption spectra of (a) : Co/TS-1, (b) : Cu/TS-1, (c) : Cr/TS-1 and (d) : V/TS-1

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)
Co $2p_{3/2}$ (ref)	779.50	
Co/TS-1(0.24)	784.04	4.54
Co/TS-1(0.22)	784.80	5.30
Co/TS-1(0.1)	785.40	5.90
Cu $2p_{3/2}$ (ref)	934.40	
Cu/TS-1(0.62)	935.15	0.75
Cu/TS-1(0.22)	935.35	0.95
Cu/TS-1(0.09)	934.25	-0.15
Cr $2p_{3/2}$ (ref)	575.70	
Cr/TS-1(0.5)	579.80	4.10
Cr/TS-1(0.15)	578.60	2.90
Cr/TS-1(0.06)	577.00	1.30
V $2p_{3/2}$ (ref)	513.55	
V/TS-1(0.7)	518.80	5.25
V/TS-1(0.33)	518.30	4.75
V/TS-1(0.1)	517.40	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.

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VITA

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