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PREPARATION OF VANADIUM-TITANIUM SILICALITE-1



Miss Rattanawalee Sunphloi

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จุฬาลงกรณ์มหาวิทยาลัย
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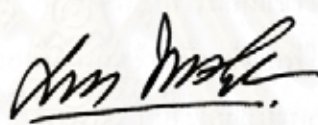
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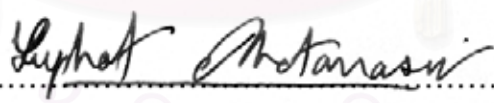
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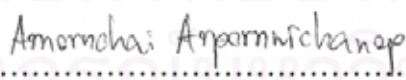

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งานวิจัยนี้ได้ทำการศึกษาคูณสมบัติที่เปลี่ยนแปลงของตัวเร่งปฏิกิริยาไททาเนียมซิลิกาไลต์-1 ที่มีคาร์บอนเติมโลหะวานาเดียมลงไปในตัวเร่งปฏิกิริยา การศึกษาการเปลี่ยนแปลงคุณสมบัติของตัวเร่งปฏิกิริยาในทางเคมีและฟิสิกส์ได้ทำการทดสอบโดยใช้เครื่องมือวิเคราะห์หลายประเภทในการทดสอบ นอกจากนี้งานวิจัยนี้ยังได้ทำการศึกษาคูณสมบัติในการทำปฏิกิริยาของตัวเร่งปฏิกิริยาที่ถูกเตรียมขึ้น โดยใช้ปฏิกิริยาออกซิเดชันของ 2-โพรพานอลที่ปริมาณความเข้มข้นของออกซิเจนในสายป้อน 8 % 2-โพรพานอล 5% โดยปริมาตร ในการทดสอบ การทดลองจะใช้ตัวเร่งปฏิกิริยาวานาเดียม-ไททาเนียมซิลิกาไลต์-1 ในปริมาณ 0.1 กรัม บรรจุอยู่ในเครื่องปฏิกรณ์ขนาดเล็กโดยทำปฏิกิริยาในช่วงอุณหภูมิระหว่าง 100-500 องศาเซลเซียส ที่ความดันบรรยากาศ พบว่าวานาเดียมที่เติมเข้าไปในตัวเร่งปฏิกิริยาไททาเนียมซิลิกาไลต์-1 ส่งผลให้เกิดการเปลี่ยนแปลงคุณสมบัติของตัวเร่งปฏิกิริยา ปริมาณวานาเดียมสูงที่สุดที่สามารถเติมเข้าไปในตัวเร่งปฏิกิริยาไททาเนียมซิลิกาไลต์-1 แล้วยังคงทำให้ตัวเร่งปฏิกิริยามีโครงสร้างเป็นเอ็มเอฟไอเช่นเดิมอยู่ที่ประมาณ 0.3% โดยโมล และพื้นที่ผิวของตัวเร่งปฏิกิริยาจะลดลงโดยแปรผกผันกับปริมาณวานาเดียมที่ถูกเติม สำหรับหาคูณสมบัติการทำปฏิกิริยาของตัวเร่งปฏิกิริยาวานาเดียม-ไททาเนียมซิลิกาไลต์-1 พบว่าปริมาณวานาเดียมที่เติมเข้าไปมีส่วนสำคัญต่อการเกิดปฏิกิริยาคีไฮเดรชัน นอกจากนี้ปริมาณวานาเดียมที่อยู่บนพื้นผิวของตัวเร่งปฏิกิริยาวานาเดียม-ไททาเนียมซิลิกาไลต์-1 ส่งผลต่อความสามารถในการเกิดปฏิกิริยาออกซิเดชันและปฏิกิริยาคีไฮเดรชัน

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จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี..... ถายมือชื่อนิสิต..... รัตนวลี ศูนย์พลอย.....
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KEY WORD: VANADIUM-TITANIUM SILICALITE-1/ OXIDATION

RATTANAWALEE SUNPHLOI: PREPARATION OF VANADIUM-TITANIUM SILICALITE-1. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 87 pp. ISBN: 974-17-6283-6

This research explores the changing catalytic behavior of titanium silicalite-1 incorporated with vanadium. In this research, the changing catalytic behavior of the prepared catalysts, physically and chemically were tested by using several techniques. The catalytic activity of the catalysts were tested using 2-propanol oxidation reaction at the concentration of oxygen 8% vol, 2-propanol 5% vol with argon balance in feed gas. The catalytic test reaction was carried out with 0.1 gram of catalyst packed in a microreactor at temperature ranging from 100-500°C at atmosphere pressure. This research found that the vanadium incorporated into titanium silicalite-1 causes the changing of the catalytic behavior of the vanadium-titanium silicalite-1. The highest quantity of vanadium can be incorporated into titanium silicalite-1 before the collapse MFI structure is about 0.3% mol. The surface area of the prepared catalysts decrease inversely with the amount of vanadium incorporated into titanium silicalite-1. For catalytic activity of titanium silicalite-1 incorporated with vanadium, it is found that the vanadium added into catalyst improves the dehydration reaction. In addition, the vanadium existing on the surface of the catalyst has some influence on the oxidation and dehydration reactions.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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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

The discovery of Titanium silicalite-1 (TS-1) in 1983 by Taramasso and co-worker was a great impact on catalyst study. TS-1 arises from substitution of titanium in the framework of a molecular sieve resulting in a new material with remarkable catalyst properties. The structure of TS-1 which is a zeolite of the pentasil family is MFI structure [see the detail of TS-1 in Appendix A]. TS-1 has become an interesting topic in the field of catalysis, owing to its excellent shape selectivity and reactivity. Many researches have tried to apply TS-1 to catalytic oxidation of many organic compounds, for example, epoxidation of olefins, hydroxylation of aromatic, oxidation of cyclohexanol and oxidation of alcohols with aqueous hydrogen peroxide as the oxidant under mild condition. The examples of applications of TS-1 as catalyst have been summarized in Table 1.1.

The success of TS-1 in numerous catalytic processes has stimulated the search for foreign atom containing in TS-1. Some authors have claimed the possibility of incorporating a large number of elements in framework position. Therefore, the idea of introducing the second metal ion into TS-1 to change catalytic properties is one of the interest in heterogeneous catalytic research. Vanadium have been largely studied in modifying many zeolites including zeolite in pentasil family (Centi et al.,1996). Since the vanadium is a key component of several catalytic selective in oxidation, therefore, interest lies also in exploring its catalytic behavior. Some reactions using vanadium containing zeolite catalyst are shown in Table 1.2.

Since vanadium is an interesting metal ion considered as a tool for modifying the acidic and catalytic behavior. In recent year, however, the research about adding vanadium in TS-1 to change catalytic properties has yet to be explored. The previous researches had not yet investigated the effect of amount of vanadium on the catalytic activity and structure of TS-1. Therefore, this research is established to study the

catalytic behavior that result from various vanadium content in TS-1. The gas phase oxidation of 2- propanol in used as test reaction.

The advantage of the reaction in gas phase is there in problem about mixing of reactants with different polarity which tends to exist in different phase. Likewise, the V-TS-1 catalyst has not been studied in 2- propanol oxidation in gas phase while the properties of vanadium containing zeolite catalysts in the oxidation reaction in gas phase had been studied less than in liquid phase.

The existing of only one reactive group, the –OH group, in the 2-propanol molecule assists in tracing the reaction pathway. This –OH group may be dehydrated to produced C=C bond or oxidized to produced C=O bond. The oxidation product may be an aldehyde or a ketone depends on the location of the –OH group. For 2-propanol, the ordination product should be acetone [see in Appendix B].

The main objective of this research is to study the properties of V-TS-1 in 2-propanol oxidation in gas phase to open the new route to determine catalytic behavior. This research has been scoped as follows

- 1) Preparation of V-TS-1 by hydrothermal method.
- 2) Characterization of V-TS-1 catalysts using the techniques following
 - Determine the bulk composition of Si, Ti and V by X-ray Ffluorescence 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).

Table 1.1 List of some researches using TS-1 as catalyst.

Year	Worker	Phase	Reaction	Object
1998	Hulea et al.	Liquid	cyclopentene oxidation	Reaction over TS-1 and Ti-beta. The research examine, the effect of zeolite structure on activity and selectivity of this reaction.
1999	Mantegazza et al.	Liquid	propylene epoxidation cyclohexanone mmoximation ammonia oxidation	To provide new information on the catalytic behavior of the active site. The samples have been tested in different reaction.
2001	Schuster et al.	Gas	oxidative dehydrogenation of propane	In th is study, various vanadium and titanium based materials are compared in a catalyst screening for their activity in the oxidative dehydrogenation of propane.
2002	Wang et al.	Liquid	epoxidation of propylene	In this paper, the synthesis of TS-1 by using TPABr as the template is presented. The catalytic properties were investigated in detail over the synthesized TS-1.
2002	Sooknoi et al.	Liquid	cyclohexane oxidation	Worker have proposed acetic acid to be a good solvent for the oxidation, and suggest that acetic acid does not only act as a solvent, but also serves as a good oxidizing agent when it reacts with hydrogen peroxide.

Table 1.1 List of some researches using TS-1 as catalyst.(continue)

Year	Worker	Phase	Reaction	Object
2004	Liu et al.	Liquid	Propylene epoxidation	The purpose of the research was to investigate, the influence of the nature of solvents on the catalytic properties of TS-1 in the epoxidation of propylene of zeolite.

Table 1.2 List of some researches relate to incorporating vanadium into zeolites.

Year	Worker	Type of zeolite	Phase	Reaction	Object
1996	Centi et al.	VS-1 VS-2 V-ZSM-5 and V-boralite	Gas	Oxidative dehydrogenation of propane	The catalytic behavior of various V-containing silicalites were tested in propane oxidative dehydrogenation.
1999	Lim et al.	V-MCM-41	Liquid	Methanol oxidation	In this study, the desired product of methanol oxidation was formaldehyde. Highly ordered V-MCM-41 to be used as a methanol oxidation catalyst was prepared on this structure sensitive reaction.

Table 1.2 List of some researches relate to incorporating vanadium into zeolites. (continue)

Year	Worker	Type of zeolite	Phase	Reaction	Object
2000	Lee et al.	V-MCM-41 and V-MCM-48	Liquid	benzene hydroxylation	In this work, various v-containing molecular sieve was synthesized, characterized and investigated their catalytic activity for benzene hydroxylation.
2001	Pirutko et al.	Al V Cr Fe Co and Ru modify TS-1	Liquid	benzene oxidation	The potential for producing active catalysts using TS-1 as matrix with some metal introduced at stage hydrothermal synthesis. The catalytic behavior was tested in benzene oxidation.
2003	Parvulescu et al.	V-MCM-41	Liquid	alcohol and aromatic oxidation	To explore different synthesis of V-MCM-41, These catalyst were investigate in alcohol and aromatic oxidation.

- 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).
 - Determine the metal species within framework of catalyst by electron spin resonance (ESR).
- 3) Catalytic reaction (2-propanol) in gas phase oxidation between 100-500°C and atmospheric 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 V-TS-1 catalysts, and the 2-propanol oxidation reactions over these catalysts including an expanded discussion.

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

CHAPTER II

CRITERIA FOR CATALYST PERFORMANCE EVALUATION METHODS

Chapter II presents criteria for the characterization method to test catalytic behavior. TS-1 was analyzed by several techniques to comprehend its catalytic properties.

2.1 Basic techniques.

The techniques employed to measure physical and chemical properties of the prepared catalysts are listed in Table 2.1 below.

Table 2.1 The basic techniques for characterization TS-1.

Techniques	measurement
BET	surface area and pore volume
Temperature Programmed Desorption (TPD)	strength and amount of acid site
Infrared spectroscopy (IR)	elements in the lattice
X-ray photoelectron spectroscopy (XPS)	chemical valence stage of metal.
X-ray diffraction (XRD)	structure and crystallinity
Ultraviolet-visible (UV-Visible)	oxidation stage
X-ray fluorescence spectroscopy (XRF)	chemical position
Atomic adsorption spectroscopy (AAS)	
Scanning electron microscopy (SEM)	morphology
Transmission electron microscopy (TEM)	
Electron spin resonance (ESR)	metal species within framework

In practice, we need not to use all available techniques to characterize a catalyst. In this study, the techniques employed are XRD, XRF, FT-IR, XPS, BET, ESR and TPD.

2.1 Criteria for test reaction selection

1. The reactant must not too inert because the tested catalyst may behave as an inactive catalyst. If the reactant is too reactive in testing, the conduct comparison between other catalyst will be difficult.
2. The reactant should have only one active functional group to help in determination the reaction pathway.
3. The reactant should not create catalyst deactivation, for example, poisoning coking and fouling etc.
4. The homogenous reaction of the reactant should be kept as minimum as possible in order to prevent the interference of the undesired reaction on result interpretation.

It should be noted here that in practice we may not have a reaction that satisfy all the listed criteria above.

From criteria, we resolve selecting alcohol as reactant because it have only one active group,(-OH group) in 2-propanol. The -OH group may be hydrolyzed to produce alkene in dehydration reaction. For oxidation reaction, The -OH group may be oxidized to produce ketone and aldehyde. We can follow reaction pathway easy if we choose alcohol as reactant to test catalytic activity. If we understand behavior of catalyst from reaction pathway we can choose the suitable reaction with catalyst. So we should study catalytic behavior to increase efficiency in catalyst application.

CHAPTER III

EXPERIMENTS

This chapter which explained the experiment procedures is divided into three sections. Firstly, the preparation flow chart of TS-1 having various vanadium contents using hydrothermal method is shown in Figure 3.1, while reagents used are listed in Table 3.2. The details of catalyst preparation are described in section 3.1 Secondly, the measurement conditions for chemical and physical properties of the prepared catalyst characterized by various techniques such as XRF, XRD, BET, SEM, XPS, TPD, ESR and FT-IR are listed in section 3.2. Finally, the tested condition by the oxidation reaction of 2-propanol are reported in section 3.3

3.1 Preparation of TS-1 and V-TS-1

3.1.1 Chemicals for the preparation of catalysts

The list of chemicals used to prepare TS-1 and V-TS-1 catalysts are shown in Table 3.1 below.

Table 3.1 List of chemicals for catalyst preparation.

Chemical	Grade	Supplier
Titanium (IV) butoxide 97%		Aldrich
Tetrapropylammonium bromine 98%		Aldrich
Vanadium (III) chloride 6.6%		Fuka
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merk

3.1.2 Preparation Procedures

The preparation of TS-1 and V-TS-1 by hydrothermal method has steps as shown in Figure 3.1, while the reagent used are report in Table 3.2

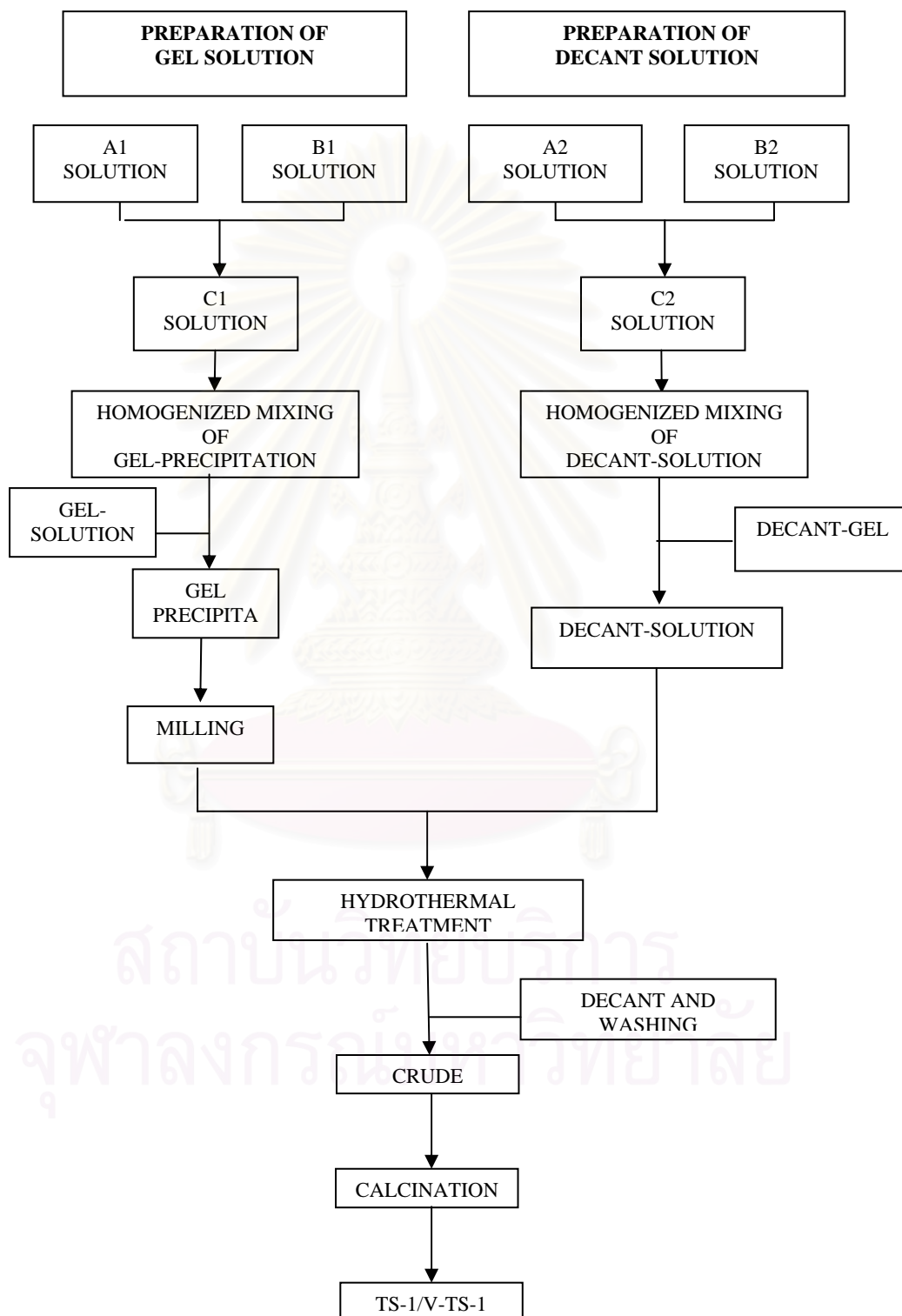


Figure 3.1 The preparation procedure of TS-1 or V-TS-1 by hydrothermal method.

Table 3.2 The reagents used to prepared TS-1 and V-TS-1 (see the detail calculation in Appendix C)

Solution for gel preparation		Solution for decant-solution preparation	
A1 Solution		A2 Solution	
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g	Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g	TPABr	7.530 g
VCl ₃	x g	VCl ₃	x g
NaCl	11.930 g	De-ionized water	60.00 ml
De-ionized water	60.00 ml	H ₂ SO ₄ (conc.)	3.40 ml
H ₂ SO ₄ (conc.)	3.40 ml		
B1 Solution		B2 Solution	
Sodium Silicate	69.000 g	Sodium Silicate	69.000 g
De-ionized water	45.000 g	De-ionized water	45.000 g
C1 Solution		C2 Solution	
TPABr	2.160 g	NaCl	26.270 g
NaCl	40.590 g	De-ionized water	104.00 ml
NaOH	2.390 g		
De-ionized water	208.00 ml		
H ₂ SO ₄ (conc.)	1.55 ml		

3.1.2.1 Preparation of decantation solution and gel solution

The synthesized catalyst uses Ti[O(CH₂)₃CH₃]₄ for Ti, Na₂O.SiO₂.H₂O for Si and VCl₃ for V, respectively as the sources of cations for preparation of gel and decantation solution. Tetrapropylammonium bromide (CH₃CH₂CH₂)₄NBr) was used as the organic template. The atomic ratio of silicon/titanium was set at 50. The detailed procedures are as follows: firstly, a gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise (NaOH solution was used to replace solution B-1 if solution B-1 was all used before solution A-1), while stirring with a magnetic stirrer at room temperature. The pH of the mixed solution was

controlled in the range 9-11, since it was expected that this pH value was suitable for precipitation. The gel mixing was stirred for 1-2 hours. This gel mixing was separated from the supernatant liquid by centrifugation. The precipitation gel mixing was thus milled and centrifuged in the following order: centrifuge (to remove the liquid out) → milled 15 min → centrifuge 15 min → milled 15 min → centrifuge 15 min → milled 15 min → centrifuge 15 min.

Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2. The method and condition of mixing were similar to the preparation of decantation solution. The precipitation from solution was separated by centrifuge about 15 min.

3.1.2.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution were mixed together in a glass vessel in an autoclave. The mixture was heated for crystallization in an autoclave from room temperature to 160 °C in 90 min and from 160 °C to 210 °C in 4.2 h. under pressure of 3 kg/cm²(gauge) of nitrogen gas. The hot mixture was allowed to cool down to room temperature in the autoclave. The product crystals were washed with distilled water to remove Cl⁻ out of the crystals, until the washed solution has pH about 7, by using the centrifuge separator (about 15-20 min per each batch) and dry in an oven at 110 °C over night.

3.1.2.3 Calcination

The dry crystal was milled before heated in a furnace under air (ambient) from room temperature to 550 °C with the heating rate about 8.6 °C /min and then kept at this temperature for 7 h.

3.2 Characterization of TS-1 and V-TS-1 catalysts

The TS-1 and V-TS-1 catalysts were characterized by using the following techniques.

3.2.1 X-ray fluorescence spectroscopy (XRF)

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

3.2.2 X-ray diffraction (XRD)

The XRD patterns (CuK α radiation) were recorded on a SIEMENS D5000. Each catalyst was scanned in the range of $2\theta = 6-40^\circ$ with a step size of $2\theta = 0.02^\circ$ and number of scan = 10.

3.2.3 Fourier-transform infrared spectroscopy (FT-IR)

The functional group in the catalysts were determined by using a Nicolet 6700 FT-IR. The catalyst was mixed formed into block before measurement. Infrared spectra were recorded between 400 and 1300 cm^{-1} on a microcomputer.

3.2.4 Scanning electron microscopy (SEM)

The morphology of catalyst was examined using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 10 kV.

3.2.5 X-ray photoelectron spectroscopy (XPS)

The chemical valence states of metals in the catalyst were examined using XPS AMICUS. The binding energy shift was calculated using the C 1s peak at 285 eV as reference.

3.2.6 BET

The surface area and pore volume of catalyst were measured by using BET Micromeritics ASAP 2020.

3.2.7 Temperature Programmed Desorption (TPD)

The strong acid and weak acid sites of the catalyst were determined by measuring the amount of adsorbed ammonia on the surface using Micromeritics Chemisorb 2750

3.2.8 Electron spin resonance (ESR)

The metal species within framework of catalyst were determined by using JEOL, model JES – RE2X.



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3.3 The catalytic activity.

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. 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 a 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 CO₂ 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 (°C)	100	70
- Final (°C)	100	120
- Heating rate (°C/min)	-	4
Detector temperature (°C)	130	120
Injector temperature (°C)	130	120
Analyzed gas	CO, CO ₂ , H ₂ O	Oxygenates

3.3.2 Oxidation procedure

The oxidation procedures are as follows:

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 nitrogen (or argon in case of no O₂ in the feed gas).
3. The reaction temperature was between 100-500°C. The effluent gases were analyzed by using the FID and TCD gas chromatographs. The chromatograph data were changed into mole of 2-propanol, propylene, isopropyl ether, acetone CO and CO₂ by calibration curves in Appendix D.

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

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

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

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

Where, A is reactant
 B is product



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CHAPTER IV

RESULTS AND DISCUSSIONS

In Chapter IV, results and discussion are divided into two sections. The first section is the result of characterization of V/TS-1 and TS-1 samples using XRF, XPS, BET, XRD, FT-IR, TPD and ESR techniques. The second section is the results of catalytic activity testing of TS-1 incorporated vanadium in 2-propanol oxidation reaction.

4.1 Catalyst characterization

The physical and chemical properties of TS-1 having containing vanadium were determined by several techniques to study the effects of vanadium on catalytic behavior.

4.1.1 Determine of composition by X-ray Fluorescence spectroscopy (XRF)

Table 4.1 summarizes the elemental composition and surface area of the synthesized V/TS-1 and TS-1 samples by X-ray Fluorescence spectroscopy and BET, respectively. It is found that too high vanadium compound in the synthesis mixture may inhibit the corporation of Ti^{4+} in to the framework. As can be seen from the case of V/TS-1(0.33) and V/TS-1(0.32) which the amount of vanadium compounds added during the synthesis of V/TS-1(0.32) is more than that was added during the synthesis of V/TS-1(0.32) but (the top two highest amount in this work) the amount of Ti^{4+} in the synthesized V/TS-1(0.32) reduced to 0.2370 %. The V/TS-1(0.69) is not considered as TS-1, because the structure is no longer MFI structure will be discussed in section 4.1.3(as seen in Figure 4.1).

It should be noted here that the corporation of each cation (Si, Ti and V) into the MFI structure is in random form. Therefore, it is impossible to fixed the ratio of Si/Ti of the synthesized catalyst for each sample. In addition, since the amount of

titanium is very low compared with the amount of Si, the ratio Si/Ti can a much when the amount of titanium only a little bit change.

4.1.2 Determine of surface area by BET

The surface areas of V/TS-1 and TS-1 samples are presented in Table 4.1 All V/TS-1 samples have surface areas less than that of TS-1. The TS-1 with higher amount of vanadium incorporation has lower surface area. When the amount of vanadium increases from 0% to 0.33%, the catalyst surface areas decreased markedly from around 320 m²/g to 245 m²/g (or about 20% reduction). It is assumed that the vanadium added into TS-1 may exist in the framework and extraframework, (such as pore and surface of V/TS-1). Therefore, the surface area of all V/TS-1 samples decrease.



Table 4.1 The composition and surface area of V/TS-1 and TS-1 samples.

Sample	%Si	%Ti	%V	Si/V	Si/Ti	A_{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size(A°)
TS-1	32.1521	0.4416	-	-	72.8049	323.01	0.1950	24.1239
V/TS-1(0.69)	31.1403	0.3399	0.6997	44.5046	91.6037	27.12	0.1885	27.7986
V/TS-1(0.33)	31.4542	0.5932	0.3273	96.0953	53.0258	246.35	0.2416	29.9541
V/TS-1(0.32)	31.9019	0.2376	0.3201	99.6761	134.2676	274.36	0.1561	22.7673
V/TS-1(0.30)	31.6470	0.5043	0.2938	107.7042	62.7533	272.19	0.1691	24.8494
V/TS-1(0.23)	31.6266	0.5085	0.2267	139.5305	62.1951	299.71	0.1931	25.7754
V/TS-1(0.10)	32.0326	0.4464	0.0964	332.4014	71.7566	329.58	0.2448	29.7108

4.1.3 X-ray diffraction (XRD)

The XRD diffraction patterns of each sample are shown in Figure 4.2. The crystal of each type of zeolite has different characteristic peaks. Hence, the XRD pattern can be used to identify the structure of the zeolite. The characteristic peaks describing the MFI structure appear at 2θ as 8, 8.8, 14.8, 23.1, 24 and 29.5 respectively (Zhao et al., 2000). From Figure 4.1, the XRD pattern of the V/TS-1 samples with 0.33%, 0.32%, 0.30% and 0.23% vanadium have the same characteristic peak as of the MFI structure of the TS-1. The discrepancy is the sample with 0.69% vanadium which shows a different XRD pattern suggesting the formation of other structure not the MFI form. Therefore, it can be concluded that too much vanadium compounds in the synthesis mixture will not result in the formation of TS-1. The maximum quantity of vanadium can be incorporated in the TS-1 using the preparation technique used in this work is about 0.33% mol.

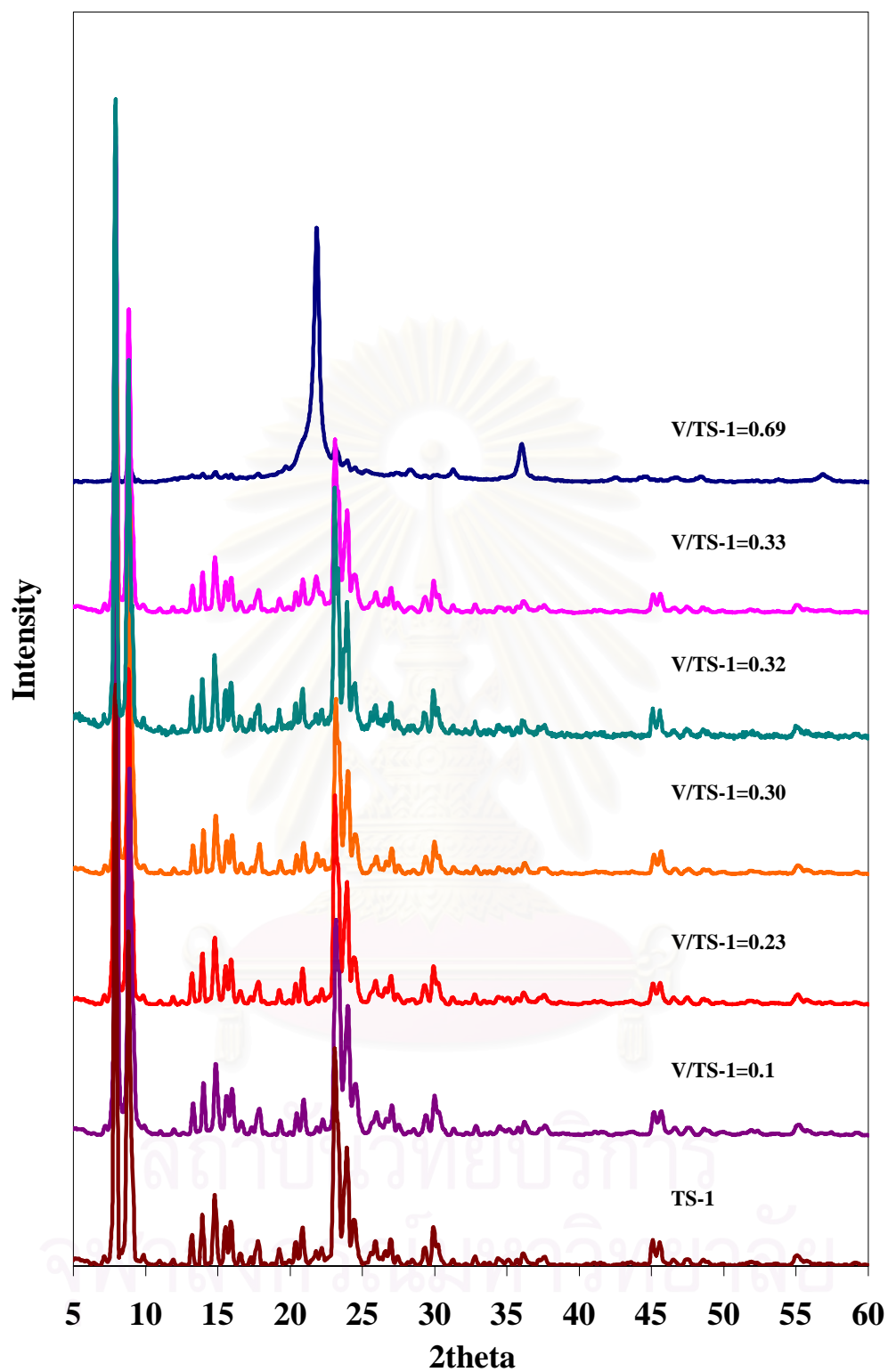


Figure 4.1 The XRD patterns of TS-1 and V/TS-1.

4.1.4 Fourier-transform infrared spectroscopy (FT-IR)

The IR spectroscopy was performed to obtain information concerning the existence of framework titanium and vanadium. From Figure 4.2, the TS-1 sample shows an absorption band at about 972 cm^{-1} and the absorption bands of V/TS-1 sample about $966\text{-}968\text{ cm}^{-1}$. It is well known that the absorption band around $960\text{-}975\text{ cm}^{-1}$ is the characteristic of metal-oxygen stretching vibrations (Sen et al., 1996). This band has been attributed to Si-O vibrations and is believed to be a proof for the presence of the metal ion in the framework. Obviously, the absorption band about $966\text{-}968\text{ cm}^{-1}$ should be ascribed to the stretching vibration of the Ti-O-Si bond and V-O-Si bond. This also suggests that titanium ion and vanadium ion are incorporated into framework lattice of the zeolite.



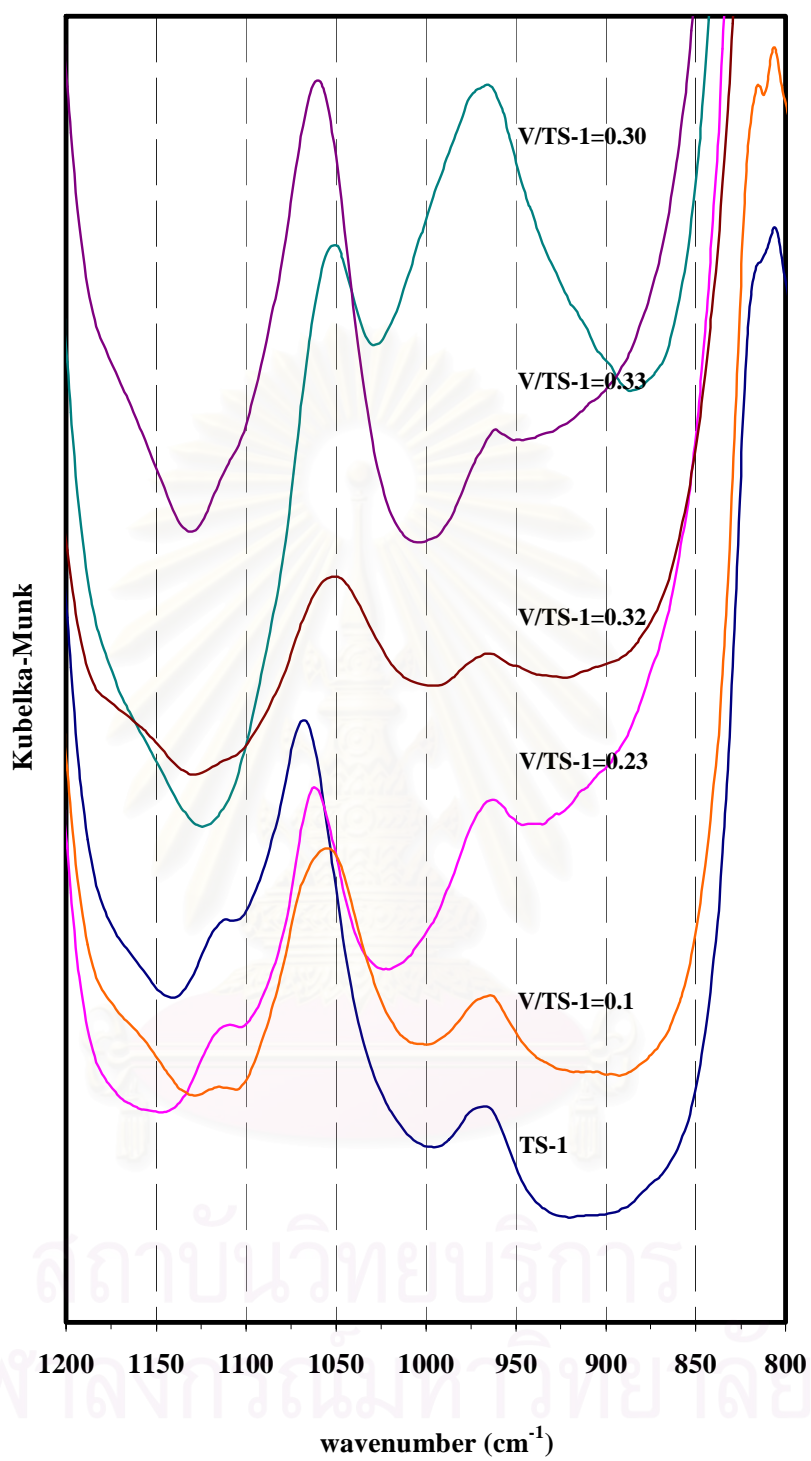


Figure 4.2 IR spectra of V/TS-1 and TS-1 samples.

4.15 X-ray photoelectron spectroscopy (XPS)

The XPS measurements can provide valuable information about the oxidation state and chemical environment of atoms due to the shift in binding energies of the vanadium contain catalysts. The correction of binding energy was performed by using the C1s peak of carbon at 285 eV as reference. The V 2p_{3/2} binding energy reported for V₂O₅ (V⁵⁺ oxidation state) ranges between 516.4 and 517.4 eV, while V⁴⁺ showed values in the range of 515.4 to 515.7 eV (George et al., 2005). The oxidation state of vanadium in V/TS-1, as determined from the corrected binding energy shown in Table 4.2, vary from V⁵⁺ in V/TS-1(0.33), V/TS-1(0.32), V/TS-1(0.30), and V/TS-1(0.23) down to V⁴⁺ in V/TS-1(0.1).

However, in the present case, an exact determination of the V2p binding energy is difficult due to the possibility of the presence of more than one type of V species with different chemical characteristics, which makes the XPS results more complicate. Since XPS is a surface technique, the intensity decrease may also arise from the lower percentage of vanadium on the TS-1 surface, as a large amount of the added metal species may be incorporated deep inside the silica framework for TS-1 materials, while for the V/TS-1 catalyst, low vanadium concentration plus the high disparity of the vanadium species on the surface may contribute to its weak signal intensity.

Table 4.2 The binding energy of TS-1 and V/TS-1

Sample	Binding Energy (eV)
V 2p _{3/2} (ref)	513.5
V/TS-1(0.33)	516.4
V/TS-1(0.32)	516.3
V/TS-1(0.30)	516.7
V/TS-1(0.23)	516.3
V/TS-1(0.1)	515.7

4.1.6 Electron spins resonance (ESR)

The ESR technique was applied to investigate the vanadium species presented within zeolite framework. As seen Figure 4.3, the ESR spectra of all V/TS-1 samples show no vanadium signal.

It can be explained that the vanadium species existing in the framework is likely to be V^{+5} species since V^{+5} has no signal when detected by the ESR technique (Whittington and Anderson, 1991). In the preparation procedure, all V/TS-1 samples were calcined in air to eliminate impurity. Hence, in this step the V^{4+} species may be oxidized completely to V^{+5} . Therefore, the result of ESR signal of vanadium species in TS-1 framework is V^{+5} species (Julbe et al., 2000).

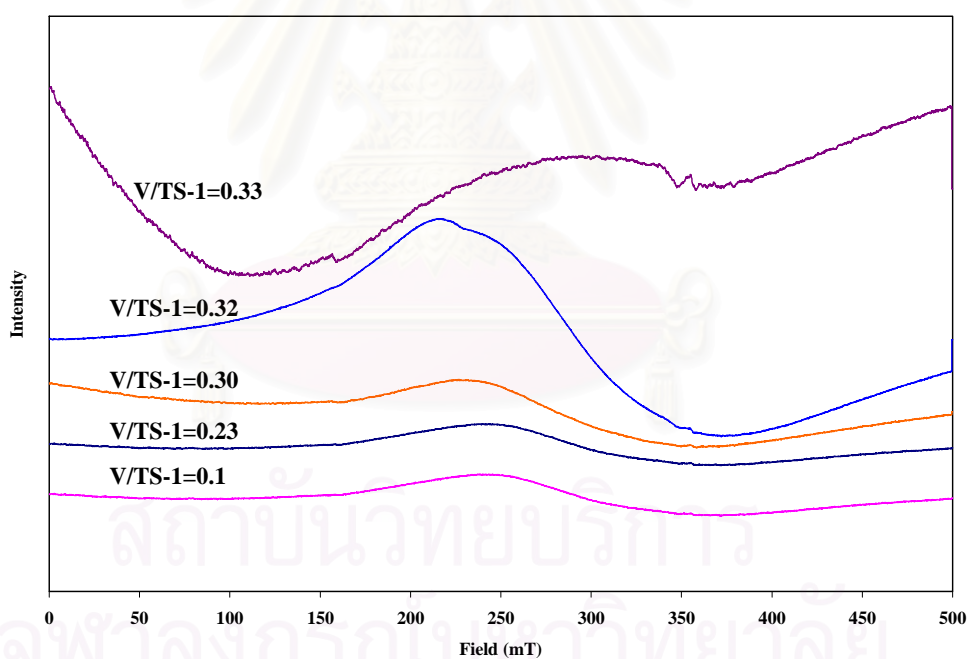


Figure 4.3 ESR spectra

4.1.7 Temperature Programmed Desorption (TPD)

The acid properties of the synthesized V/TS-1 and TS-1 samples were investigated by NH₃-TPD. The NH₃-TPD curve of the TS-1 and V/TS-1 show a large desorption peaks which can be deconvoluted into the sum of two peaks. The first peak is around 132-145°C represent a group of acidic sites weaker than another group which shows NH₃-TPD peak around 210-240°C. From Table 4.3, all V/TS-1 samples have the amount of have weak and strong acid site less than that of TS-1. Therefore, it can be assumed that the decrease of weak and strong acid site may be attributed to the incorporated vanadium in the samples.

Table 4.3 NH₃-TPD results

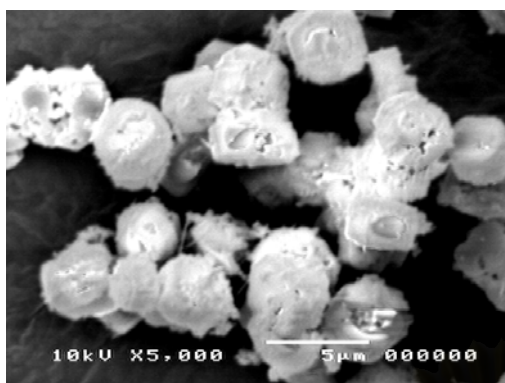
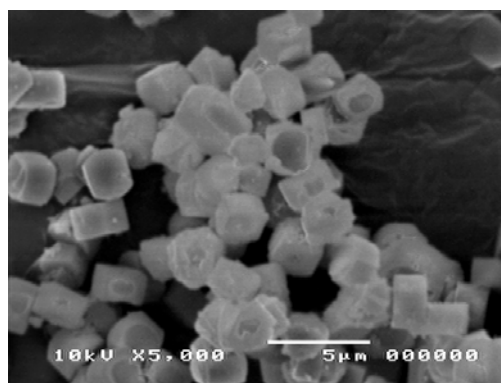
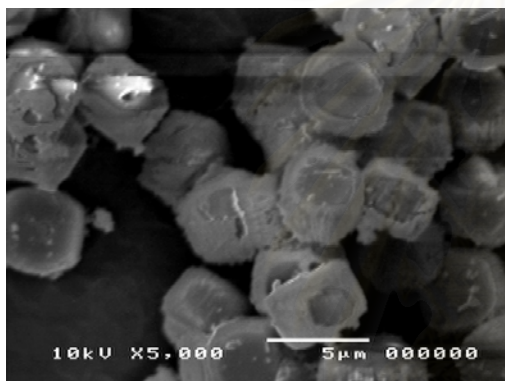
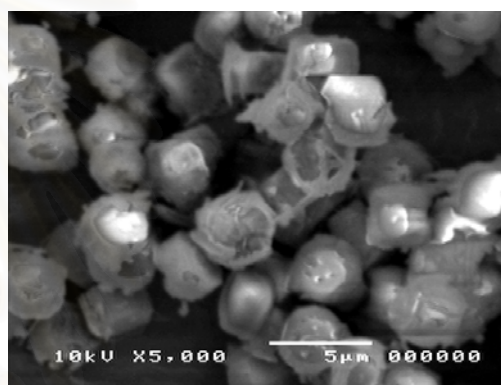
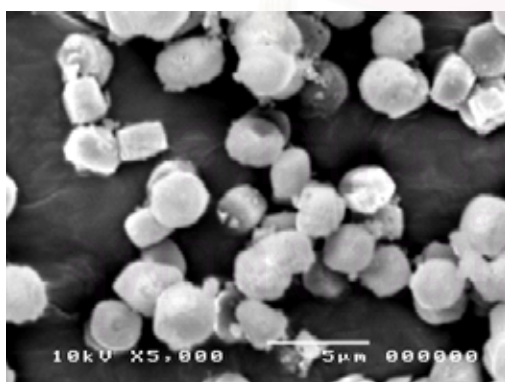
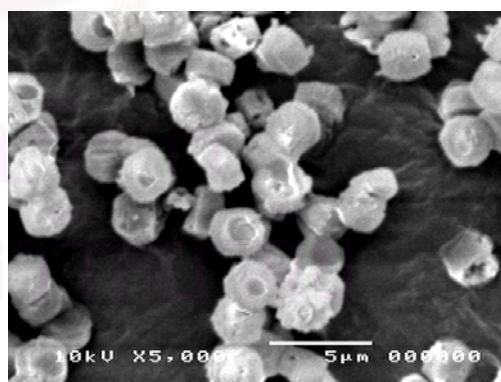
Sample	Weak acid site		Strong acid site		Total acid Site (μmol/g)
	Temp (°C)	Site (μmol/g)	Temp (°C)	Site (μmol/g)	
TS-1	138.5	180.9707	232	53.7235	234.6942
V/TS-1(0.33)	132	77.7026	212	13.7716	91.4742
V/TS-1(0.32)	136	122.7754	222	13.5227	136.2981
V/TS-1(0.30)	133	70.3945	212	55.7482	126.1427
V/TS-1(0.23)	145	118.7782	242	51.7237	170.5019
V/TS-1(0.1)	144	148.5704	232	40.3081	188.8785

4.1.8 Scanning electron microscopy (SEM)

Scanning Electron microscopy was used to determine the changing morphology of TS-1 incorporated vanadium and all samples have the crystal size range 3-5 μm . From Figure 4.4, when compare the crystal size of TS-1 with V/TS-1, it is found that the crystal size of TS-1 incorporated with vanadium was larger than TS-1. Likewise, the crystal size of V/TS-1 increases when the amount of vanadium incorporated increases.



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**V/TS-1 (0.33)****V/TS-1(0.32)****V/TS-1 (0.30)****V/TS-1(0.23)****V/TS-1 (0.1)****TS-1****Figure 4.4** The morphology of V/TS-1 and TS-1

4.2 The catalytic activity

Previously, it has been shown that when vanadium is incorporated into the TS-1, the obtained samples, V/TS-1, have different physical and surface properties from the pattern TS-1. This section reports the effect of vanadium on the catalytic behavior by using the oxidation of 2-propanol as test reaction.

4.2.1 2-propanol oxidation

Two C₃ products, acetone and propylene, are observed during the reaction. The formation of propylene should be owing to the dehydration of 2-propanol. Acetone is likely be produced by the oxidation reactions rather than the dehydration reaction. The catalytic activity and products selectivities of 2-propanol over TS-1 and V/TS-1 with various amount vanadium containing catalyst for 8% vol of oxygen concentration in feed gas as shown in Figures 4.5 to 4.11.

The results of conversion of 2-propanol oxidation of all the catalysts quickly reaches 100 % at a reaction temperature about 350°C and steadily at this conversion when the temperature is higher than 350°C. For all of these samples, acetone was the product in initial temperature at 100°C while carbondioxide become significant at the reaction temperature above 300°C. The maximum selectivities towards carbondioxide were obtained at the reaction temperature about 400–500°C. Carbondioxide was the product produced via further oxidation of acetone. It is believed that acetone was the primary oxidation product, which is produced directly from 2-propanol oxidation. The propylene was produced at 100°C by dehydration reaction and highest at the reaction temperature about 300°C. The reaction pathway over all the samples is likely to be the same as of TS-1 reported before (Chairat, 2004). The presence of vanadium does not create a new pathway to a new product. But alter the amount of reactants react in each route.

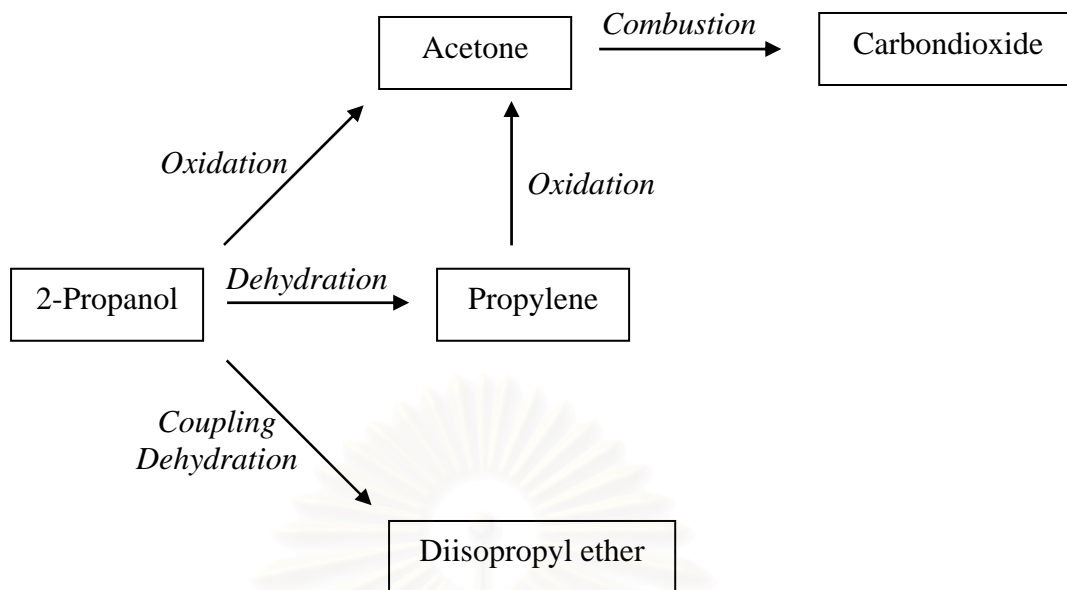


Figure 4.5 The pathway reaction of 2-propanol reaction

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4.2.2 Effect of vanadium on catalytic activity

The V/TS-1(0.1) have vanadium containing about 0.1% mol was compared with TS-1 that have similar amount of titanium incorporated.

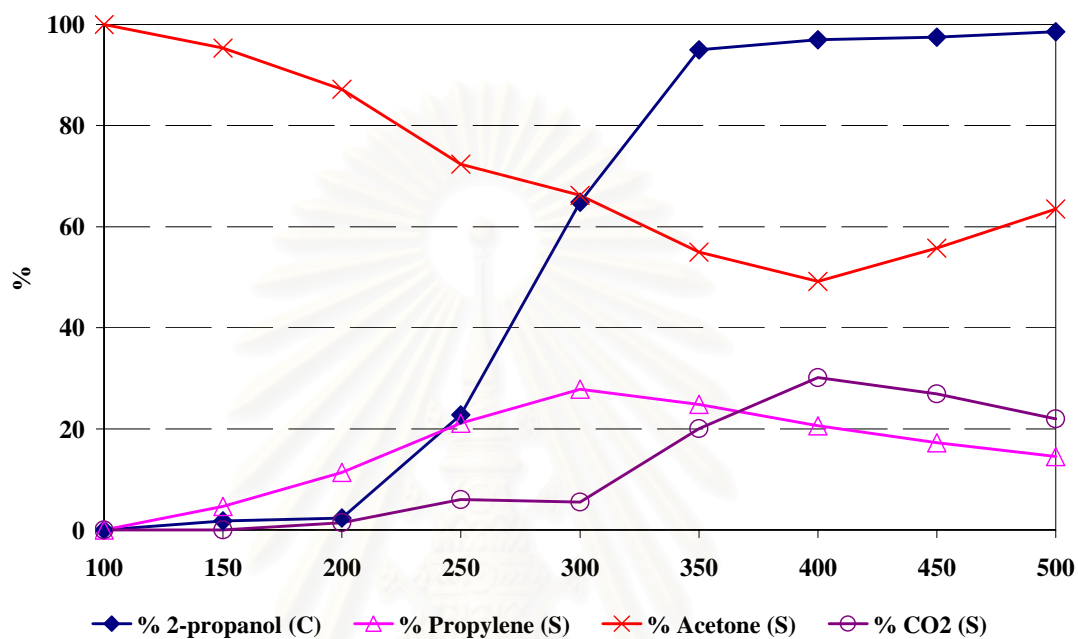


Figure 4.6 Product selectivity of 2-propanol over V/TS-1(0.1) for 8 vol % O₂ system (C-Conversion, S-Selectivity)

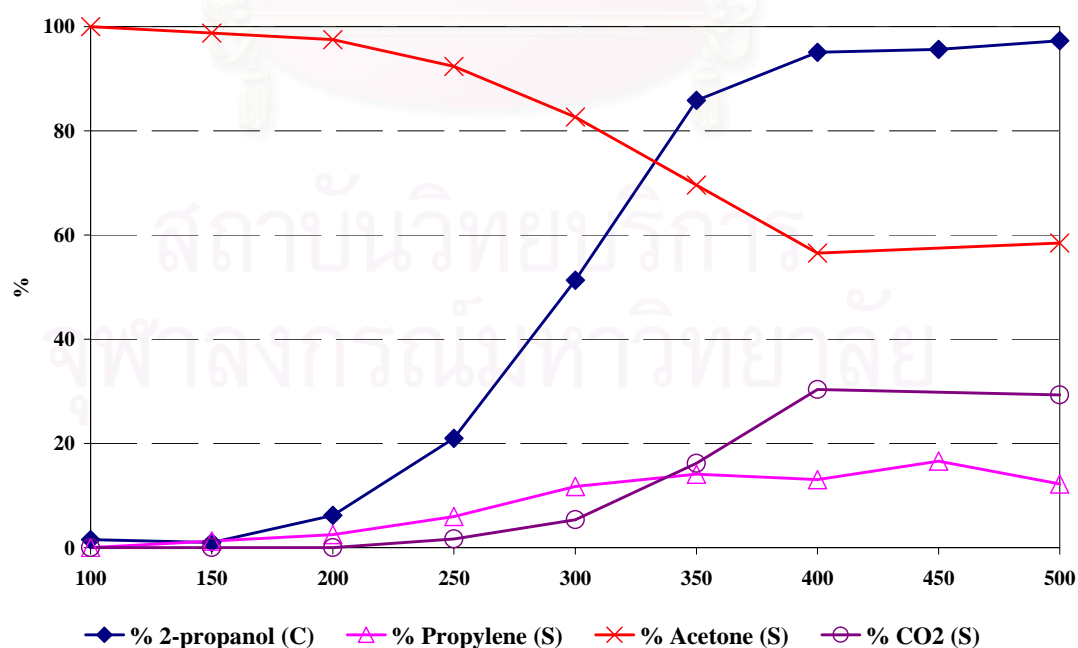


Figure 4.7 Product selectivity of 2-propanol over TS-1 for 8 vol % O₂ system (C-Conversion, S-Selectivity)

As seen in Figures 4.6 and 4.7, which compare the results obtained from V/TS-1(0.1) and TS-1, it is found that the oxidation arising from two catalysts is similar. But the formation of propylene over V/TS-1(0.1) is higher than TS-1. Therefore, it can be concluded that the dehydration over V/TS-1(0.1) is well occurs than on the TS-1. The higher selectivity to propylene of V/TS-1 is resulted from the vanadium incorporated in the catalyst. This conclusion is reached because both samples have the same amount of titanium but different amount of vanadium.



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4.2.3 Effect of surface vanadium on catalytic activity

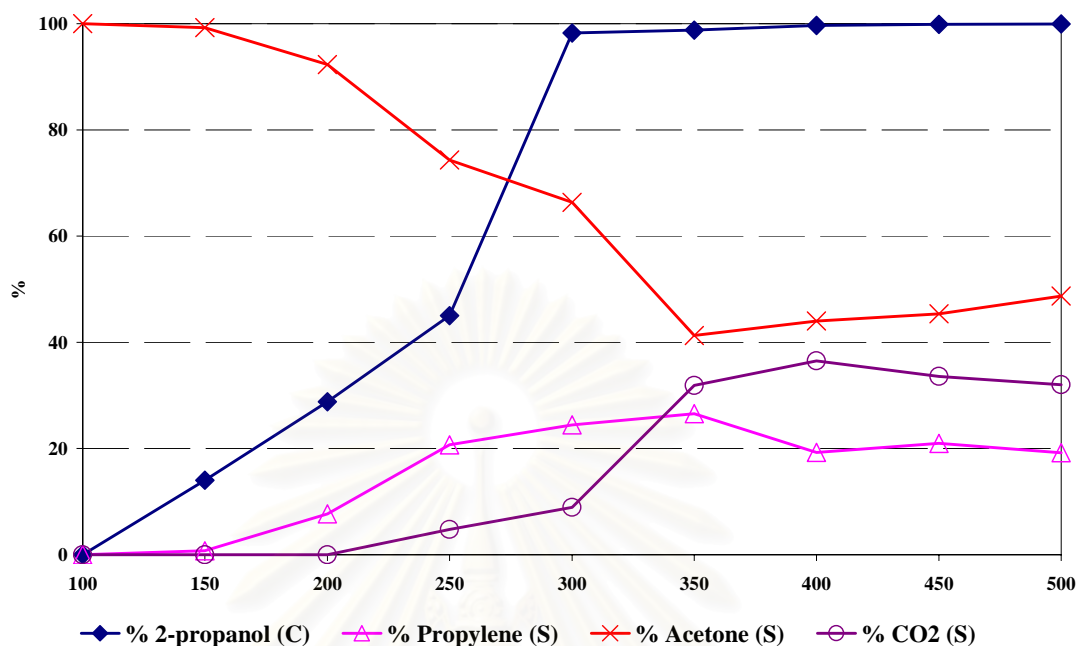


Figure 4.8 Product selectivity of 2-propanol over V/TS-1(0.32) for 8 vol % O₂ system (C-Conversion, S-Selectivity)

In this case taking V/TS-1(0.32) is compared with TS-1. The formation of acetone and propylene, from the oxidation and dehydration respectively, of V/TS-1(0.32) is much higher than that of TS-1. It result show that V/TS-1(0.32) is more active than TS-1 for both oxidation and dehydration reactions. We found that the amount of strong and weak acid sites of V/TS-1 (0.32) are less than TS-1(as detected by NH₃-TPD) but the catalytic activity of V/TS-1(0.32) is higher than that of TS-1.

A major difference between the two catalysts is V/TS-1(0.32) has vanadium on surface (as detected by XPS) while TS-1 is no. Thus vanadium ion is likely to be more active for both the dehydration and oxidation reactions than titanium ion.

4.2.4 Effect of weak acid site

In case of V/TS-1(0.30) and V/TS-1(0.33), both catalysts have about the same amount of weak acid site. But the amount of strong acid site of V/TS-1(0.30) is higher than that of V/TS-1(0.33) about 4 times. From Figures 4.9 and 4.10, the formation of acetone of these two catalysts shows that the oxidation of V/TS-1(0.30) is well occur than V/TS-1(0.33). For the dehydration reaction, V/TS-1(0.33) is more active than V/TS-1(0.30) in the formation propylene. These phenomena can be explained using the model shown in Figure 4.11 below.

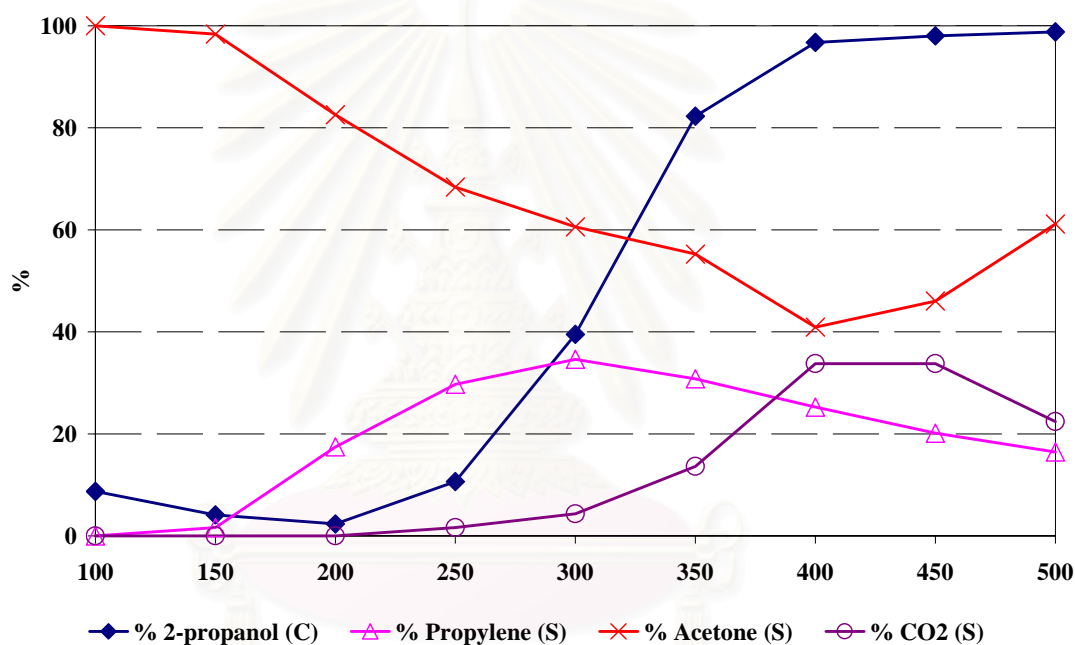


Figure 4.9 Product selectivity of 2-propanol over V/TS-1(0.33) for 8 vol % O₂ system (C-Conversion, S-Selectivity)

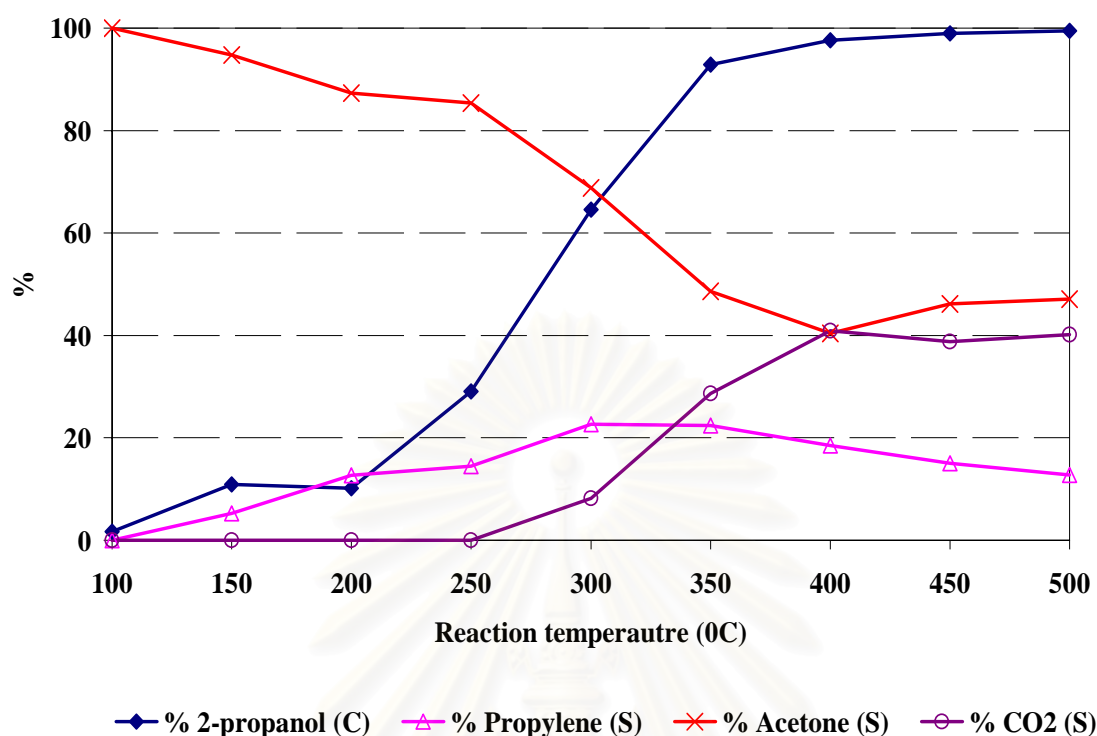
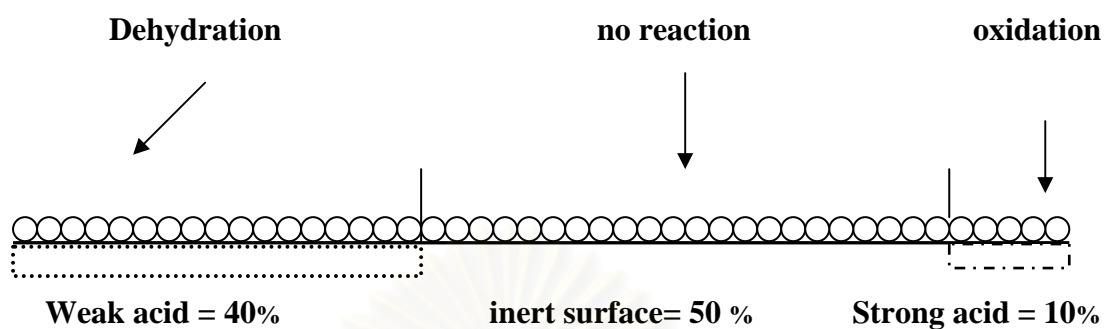


Figure 4.10 Product selectivity of 2-propanol over V/TS-1(0.30) for 8 vol % O₂ system (C-Conversion, S-Selectivity)

In case V/TS-1(0.33) suppose, initially we have 1000 reactant molecule uniformly distributed over the surface. In the first hit, 40% of the total molecule hit the weak acid site and transformed into dehydration product. Another 10 % hit the strong acid site and transformed into oxidation product. The remaining 50 % (500 molecules) does not react. When this portion is uniformly distributed again and hit the surface for the second time, 40 % is transformed into dehydration, 10% to oxidation product and 50% (250 molecules) does not react. When we repeat this sequence again and again the product distribution can be calculated as shown in Table 4.4.

V/TS-1(0.33)



V/TS-1(0.30)

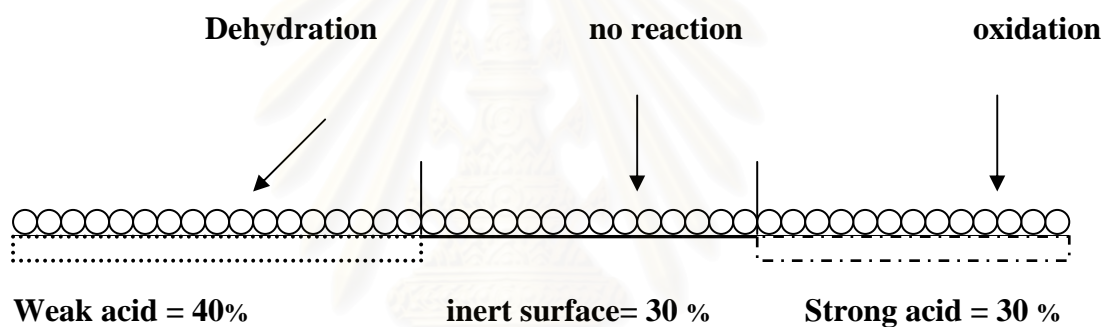


Figure 4.11 Model of reaction occurs on two catalysts with the same amount of weak acid site but different amount of the percentage of each type of surface area all assumed for the clarity of explanation only.

Table 4.4 The calculation of molecule react on surface of V/TS-1(0.33)

Number of hit	Weak acid	Strong acid	Remain	Total
1	400	100	500	1000
2	200	50	250	500
3	100	25	125	250
4	50	13	62	125
Total	750	188	62	

For the case of V/TS-1(0.30), which has the same number of weak acid site but higher amount of strong acid site (40 % weak acid site area, 30 % strong acid site area and , 30 % inert surface area). When we repeat the calculation shown above, the product distribution will be shown in Table 4.5

Table 4.5 The calculation of molecule react on surface of V/TS-1(0.30)

Number of hit	Weak acid	Strong acid	Remain	Total
1	400	300	300	1000
2	120	90	90	300
3	36	27	27	90
4	11	8	8	27
Total	667	425	425	

From the model, there is possibility that not all molecules collide with the surface meet the active site. It can be seen that the case of the same amount of weak acid site but different amount of strong acid site, the catalyst with higher number of strong acid site produce less dehydration product than the catalyst with less number of strong acid site.

It should be emphasized here that the active site is the cation species exist on the surface, which can be quantified by NH₃-TPD. The total amount of metal ion (cation) as determined from XRF is the sum of cation exist on the catalyst surface and beneath the surface, The first group has chance to react with a reactant, while the latter group has no chance. Thus, the total amount of cations (as determined from XRF) does not directly represent the total amount of available active sites.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions of this research are following as:

1. The formation of TS-1 structure is collapsed when the amount of the vanadium compound in the synthesis mixture is too high
2. The highest amount of vanadium that does not change the structure of TS-1 is about 0.3 % mol
3. The vanadium existing on surface is an influence on catalytic activity of catalyst more than vanadium exiting in framework.
4. For the dehydration reaction, the vanadium incorporated in TS-1 improves the selectivity to propylene.

5.2 Recommendation for future studies

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

1. Because the synthesis procedure influence the crystal size, therefore the synthesis parameters affecting the formation of crystal should be further identified.
2. Owing to vanadium has influence on the catalytic activity, the effect of the different vanadium source on the catalyst behavior should be further studied.

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APPENDICES

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APPENDIX A

BASIC INFORMATION OF TS-1

1. ISOMORPHOUS SUBSTITUTION

In recent years the isomorphous substitution in zeolite and aluminophosphate materials by other elements has been extensively studied. The isomorphous substitution of elements in these materials is carried out in order to modify their catalytic and shape selective properties. Different ways to perform such substitutions are well established, either during hydrothermal synthesis or by post-synthesis method in liquid and vapor phase. Generally, hydrothermal synthesis is preferred over post synthesis because it leads to better incorporation of a wide variety of metal ions. The post synthesis method of Fe^{3+} and Ti^{4+} incorporation in the liquid phase into the framework of various zeolites is reported using corresponding metal salts. In the vapor phase method the zeolite is subjected to dealumination and then treated with vapors of a volatile compound of the metal to be incorporated. It has been found that the di-, tri-, tetra- and pentavalent metal ions can all replace the framework tetrahedral sites in molecular sieves. They can also occupy one or more of the following positions in the zeolite, such as, defect sites, cation exchange sites, inside the pores or on the external surface as finely dispersed metal oxides and as bulk oxide on external surface. This results in different catalytic properties and may even lead to bifunctional catalysis. In the case of zeolites, the isomorphous substitution is mainly for Al but in aluminophosphates, it can happen in three different ways.

1. Substitution for only Al atoms (SM1),
2. Substitution for only P atoms (SM2) and
3. Substitution for a pair of Al and P atoms (SM3)

The partial substitution of P^{5+} with Si^{4+} by SM2 mechanism results in the formation of Al-(OH)-Si type linkages wherein the bridging hydroxyl groups are formed generating Brønsted acidity in the resulting aluminophosphate. The SM3 type of substitution is observed in silicoaluminophosphates (SAPO-n), wherein two Si atoms replace the isolated pair of adjacent Al and P atoms. This type of substitution results in the formation of Si(1Si 3Al) and Si(1Si 3P) environments. SM1 mechanism is unlikely to form, as it involves the formation of Si-O-P linkages, which is unstable in hydrothermal conditions.

Titanium silicalite-1

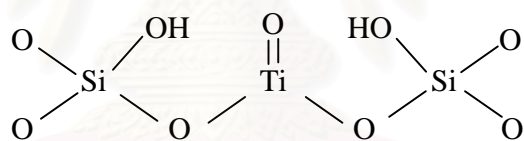
Crystalline titanium-silicate molecular sieves have titanium incorporated into the crystal lattice. Examples of titanium-silicate molecular sieves are TS-1 with MFI-type structure and TS-2 with MEL-type structure, both of which are in the pentasil family of zeolite structures. Other examples are Ti-beta, Ti-ZSM48, Ti-ZSM12, Ti-MCM22, Ti-UTD1, and the like.

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^{4+} compounds immediately shows that Ti^{4+} 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^{4+} 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^{4+} , 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^{4+} with Ti^{4+} it seems justified to represent TS-1 as a silicalite in which few Ti^{4+} have taken the place of Si^{4+} . The interpretation of the catalytic activity of TS-1 must take into consideration the role played

by these few Ti^{4+} : in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-1 crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{4+} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most Ti^{4+} must be isolated from each other by long sequences of $-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-$. If Ti^{4+} replaces a Si^{4+} 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 $\text{Ti}=\text{O}$ group, whose stretching frequency is 975 cm^{-1} with bond distances of $1.66 - 1.79\text{ \AA}$; 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^{4+} are occupied by Si^{4+} 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



The amount of Ti positioned within the framework of the molecular sieve is believed to be important and beneficial in many reactions. However, it is also widely believed that non-framework Ti-species, on the exterior or interior surfaces of crystals, may decrease the catalytic effectiveness of titanium-silicate molecular sieves. Similar deleterious effects may be caused by other contaminants such as aluminum and alkali elements. In particular, extraframework massive Ti-oxides, as well as other contaminants, cause undesirable side reactions, and, as a consequence, losses of activity and selectivity of the catalyst.

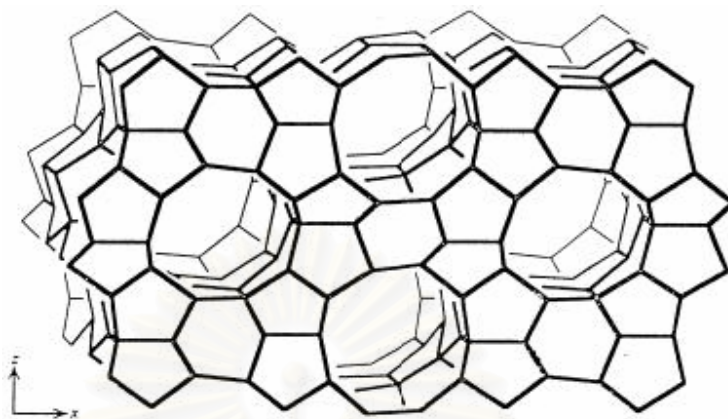


Figure A1 The MFI framework topology in three dimensional

SYNTHESIS OF TS-1

The synthesis and catalytic properties of TS-1 catalyst are being studied extensively in the recent years because of its interesting catalytic properties in various oxidation reactions using aqueous H_2O_2 as oxidant. The catalytic properties of TS-1 are strongly affected by the Si/Ti ratio, crystallite size and the amount of framework and extraframework titanium content. The various silicon and titanium sources are used to synthesize TS-1 with the intention to incorporate more amount of titanium in the framework

It is believed that the silicon source plays an important role in controlling the crystallization rate of the MFI-type zeolites. The different synthesis routes have been proposed, using different silicon and titanium sources and templating. In figure A2, some synthesis routes are exemplified (Perego et al., 2001).

The cost of TS-1 is mainly determined by the source of silica used and therefore it was desirable to find an alternate cheaper silicon source to prepare pure TS-1 for industrial use. In the present investigation, a new silicon source Ethyl silicate-40 (ES-40) was used for the synthesis of TS-1 for the first time.

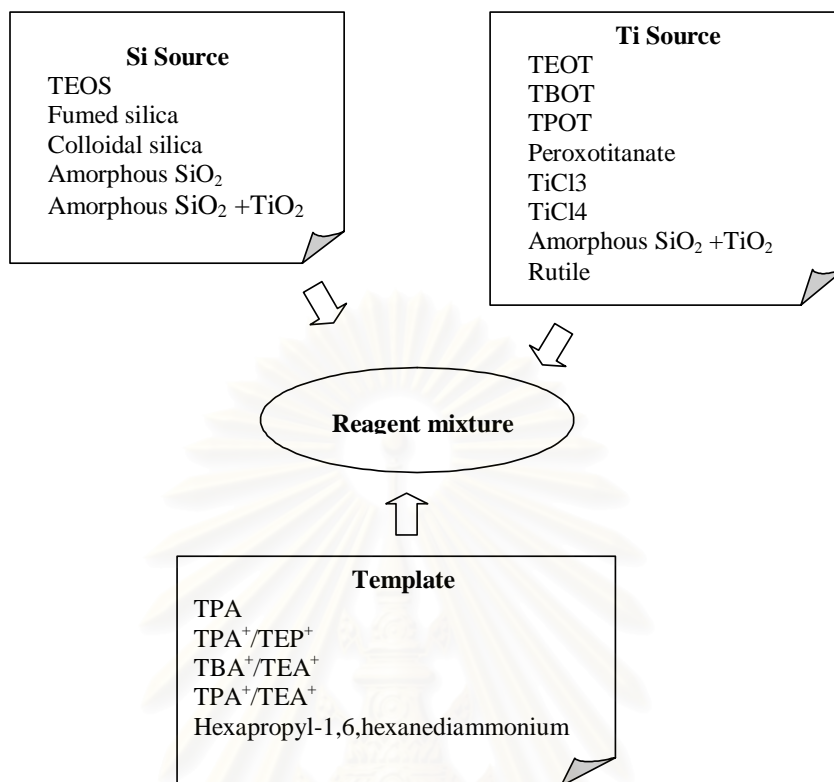


Figure A2 Some examples of reagent mixtures for TS-1 preparation.

APPLICATION OF TS-1

TS-1 is distinguished from their pure silica congeners by the substitution of small amounts of Ti for Si in the crystal lattice (the literature variously reports upper limits for Ti/(Si+Ti) mole ratios in Ti silicalites without non-framework admixture of from 0.01 to approximately 0.025 to 0.025 and even to 0.07, although the higher ratio is in some doubt due to the purported presence of non-framework Ti in the samples. Superior catalytic properties are attributed to a combination of the catalytic oxidation properties of Ti sites and shape selectivity effects of the sieve framework. Compared with the traditional commercial processes, oxidation reactions catalyzed by titanium silicates

The molecular sieves has been applied to catalytic oxidation of different organic substrates, for example, epoxidation of olefins, hydroxylation of aromatics, oxidation of cyclohexanol, and oxidation of alcohols, and exhibit excellent reactivity and selectivity in

such catalytic oxidations. These crystalline titanium-silicates, when used as catalysts and/or catalyst supports, are useful in some industrial processes. TS-1 molecular sieves, in particular, is synthetic, crystalline, medium-pore-microporous materials, which exhibit excellent catalytic reactivity and selectivity in various oxidation reactions.



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APPENDIX B

REACTION OF ALCOHOL

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.

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.

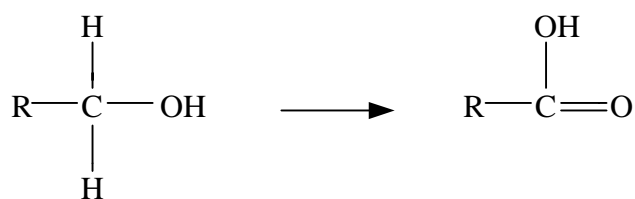
A primary alcohol contains two α -hydrogens, and can either lose one of them to form an aldehyde,



A 1° alcohol

An aldehyde

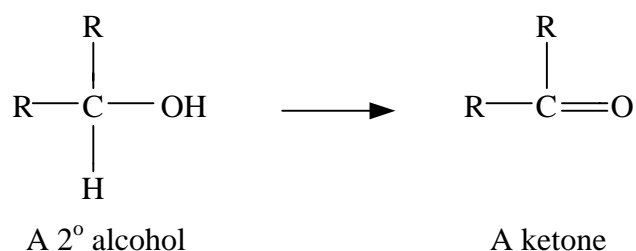
or both of them to form a carboxylic acid.



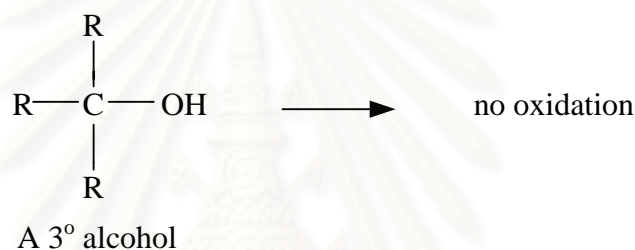
A 1° alcohol

A carboxylic acid

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

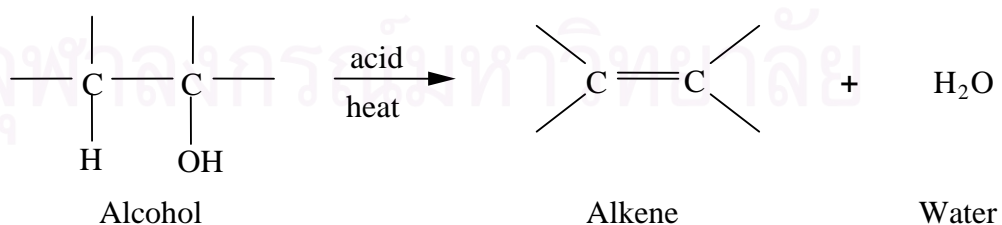


A tertiary alcohol contains no α -hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).



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 $3^\circ > 2^\circ > 1^\circ$

APPENDIX C

SAMPLE OF CALCULATIONS

The calculations is base on weight of Sodium Silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) in B1 and B2 solution.

$$\begin{aligned}\text{Molecular weight of Si} &= 28.0855 \\ \text{Molecular weight of SiO}_2 &= 60.0843 \\ \text{Weight present of SiO}_2 \text{ in Sodium Silicate} &= 28.5\end{aligned}$$

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

$$\begin{aligned}\text{Mole of Si used} &= \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)} \times \frac{(1\text{mole})}{(\text{M.W. of Si})} \\ &= 69 \times (28.5/100) \times (1/60.0843) \\ &= 0.3273 \text{ mole}\end{aligned}$$

MFI catalyst

For example , to prepare Si/Ti atomic ratio of 50 by using $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ for titanium source.

$$\begin{aligned}\text{Molecular weight of Ti} &= 47.88 \\ \text{Molecular weight of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= 340.36 \\ \text{Weight \% purities of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= 96\end{aligned}$$

Si/Ti atomic ratio = 50

$$\begin{aligned}\text{Mole of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 \text{ required} &= 0.3273/50 \\ &= 6.546 \times 10^{-3} \text{ mole} \\ \text{amount of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= (6.546 \times 10^{-3}) \times (340.36) \times (100/97) \\ &= 2.2970 \text{ g}\end{aligned}$$

For example, to prepare Si/V atomic ratio of 50 by using VCl_3 for vanadium source.

$$\text{Molecular weight of V} = 50.942$$

$$\text{Molecular weight of } \text{VCl}_3 = 157.30$$

Si/V atomic ratio = 50

$$\text{Mole of } \text{VCl}_3 \text{ required} = 0.3273/50$$

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

$$\text{amount of } \text{VCl}_3 = (6.546 \times 10^{-3}) \times (157.30) \times (100/96)$$

$$= 1.0726 \text{ g}$$



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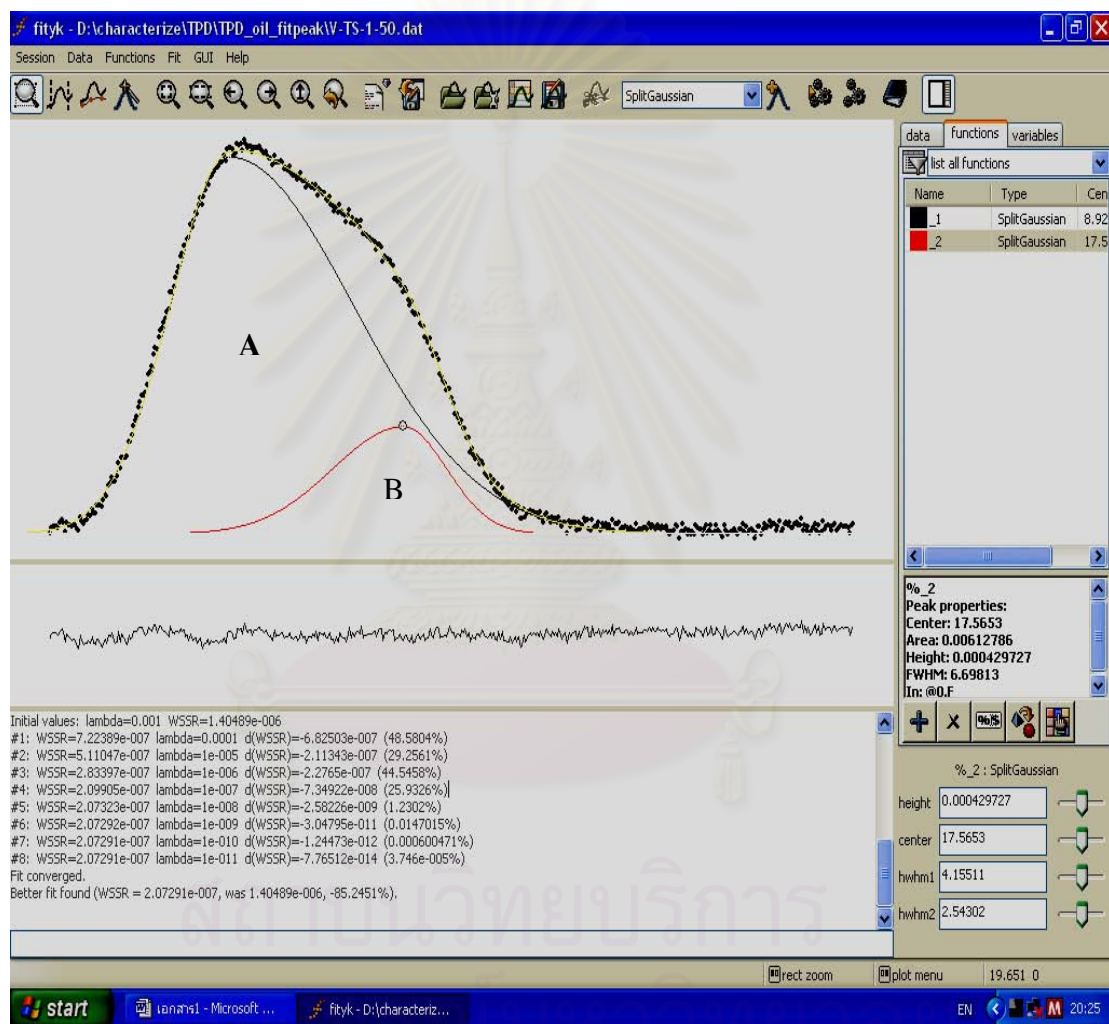
APPENDIX D

Deconvolution of NH₃-TPD peaks

Hence :

A = weak acid site

B= strong acid site



Peak A

Center: 8.92067

Area: 0.0345748

Height: 0.00151011

Temp: 132

Peak B

Center: 17.5653

Area: 0.00612786

Height: 0.000429727

Temp: 212

Figure D1 Peak fitting for V/TS-1(0.33)

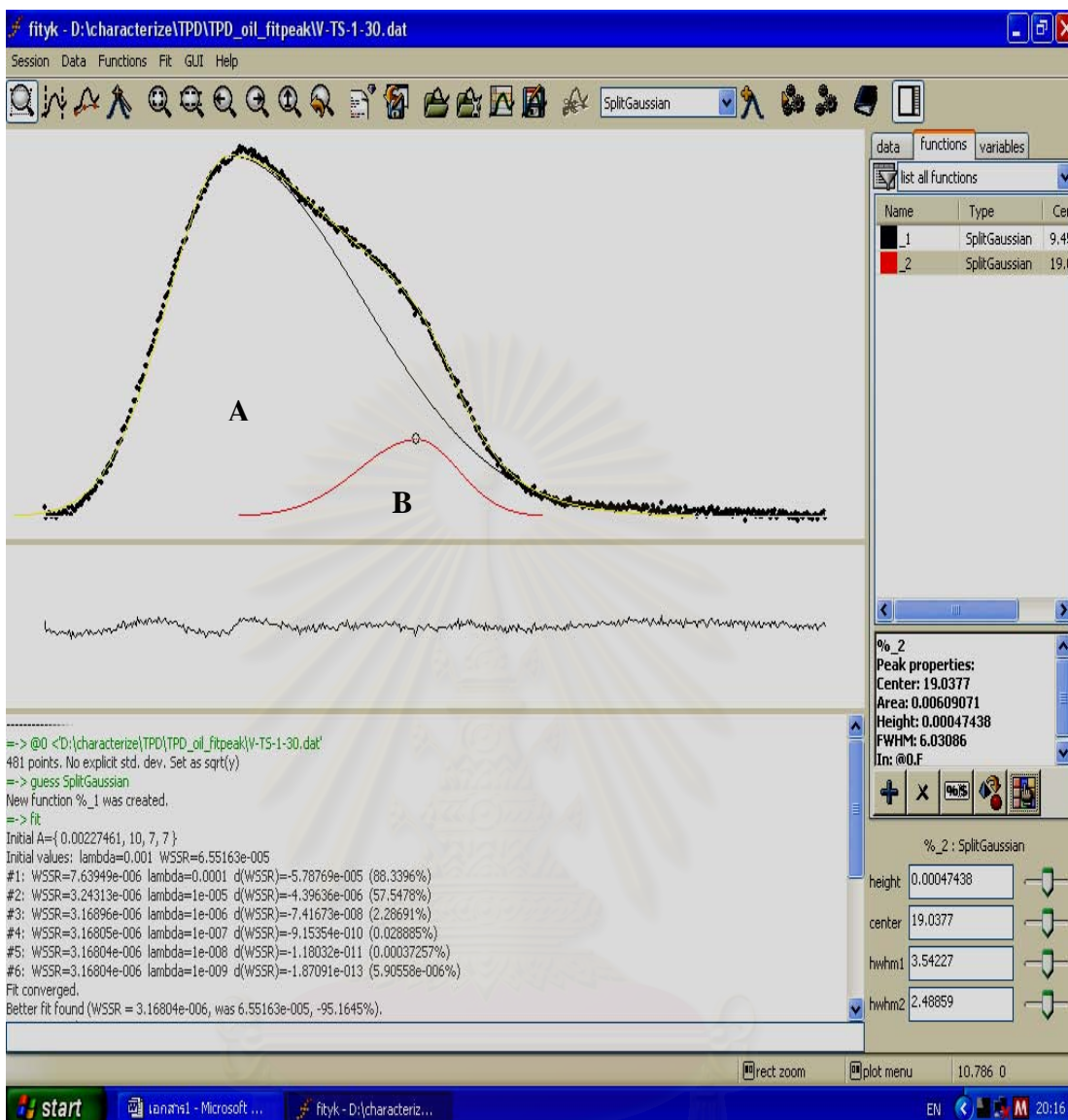
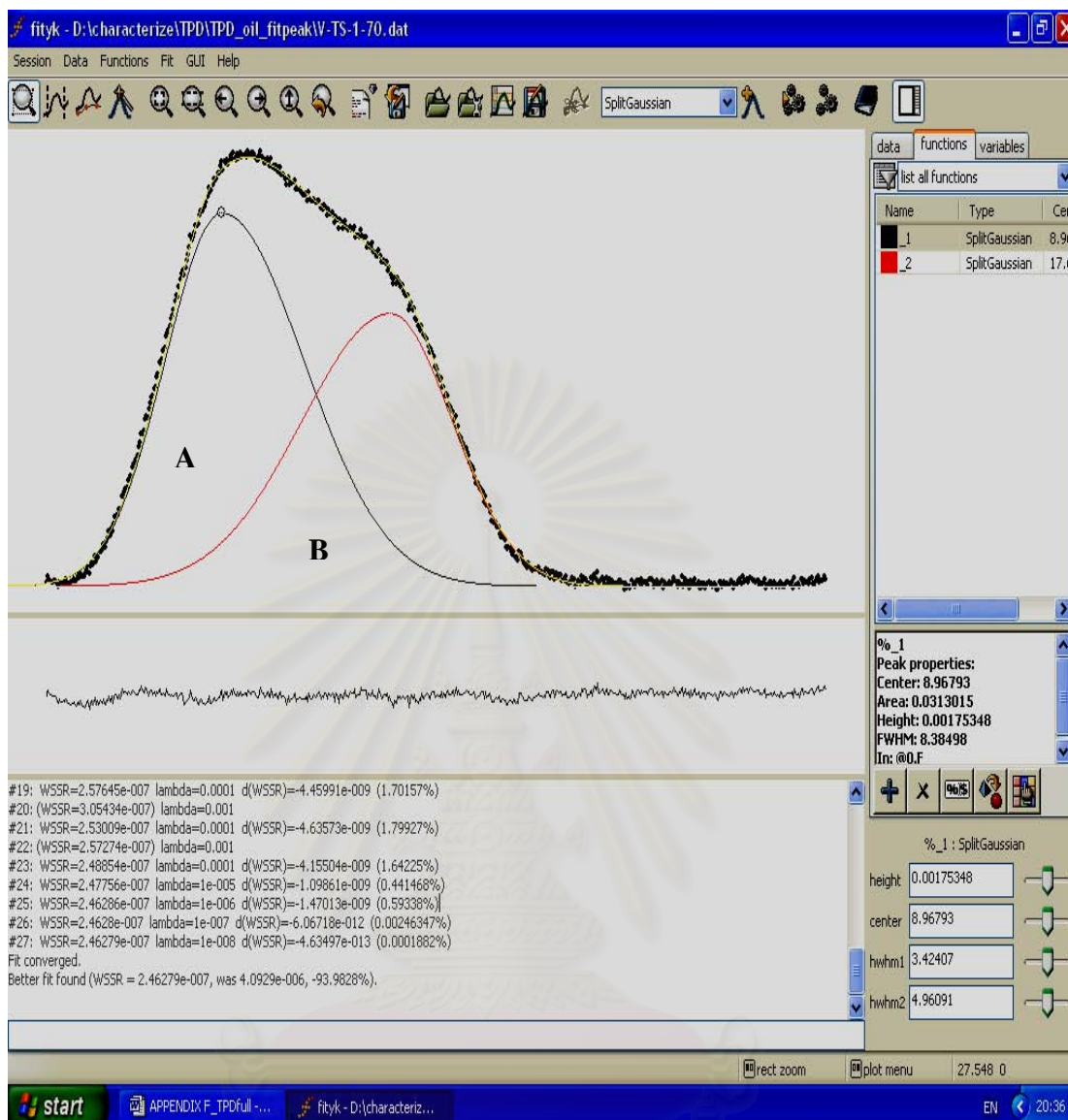
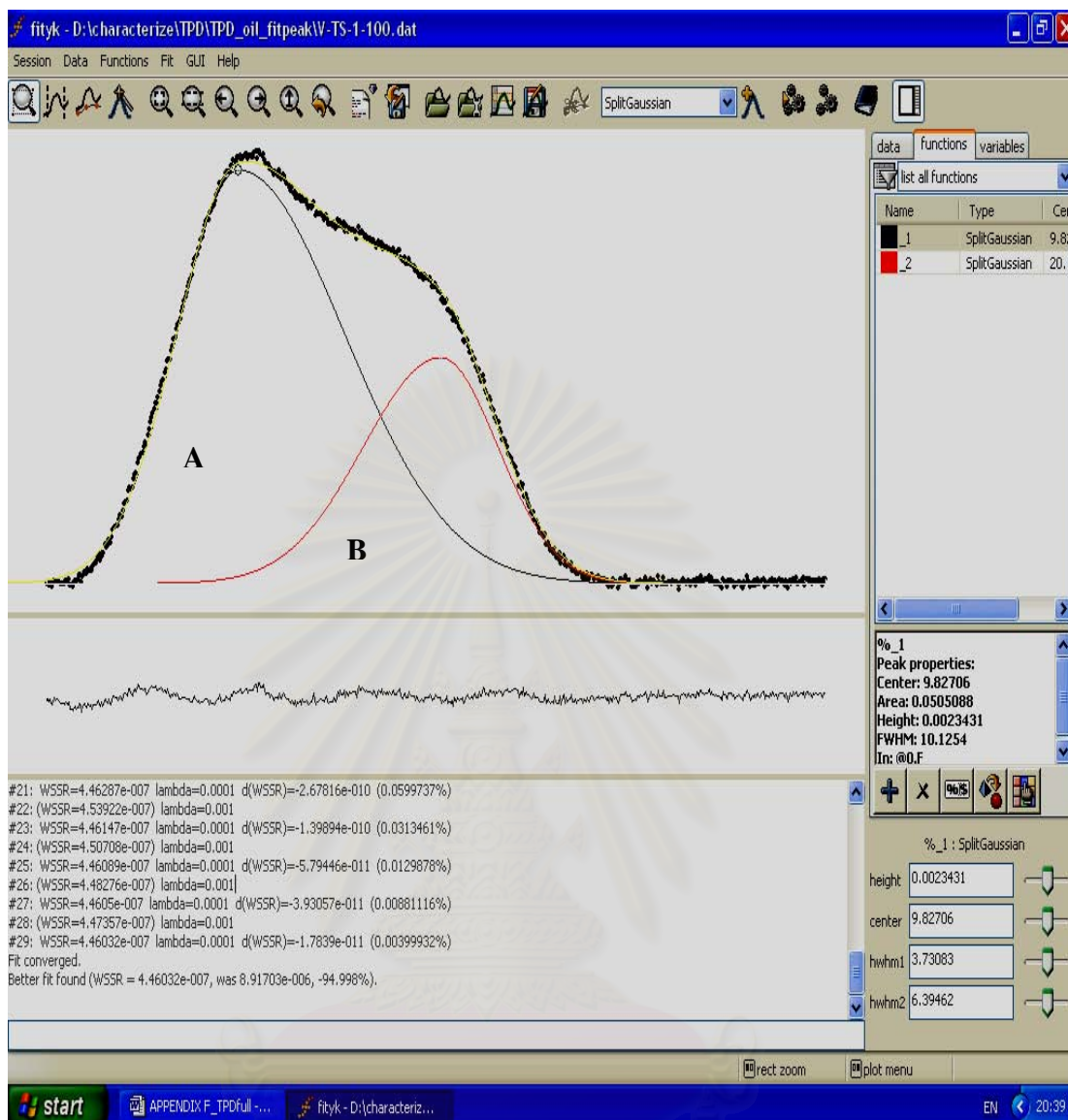
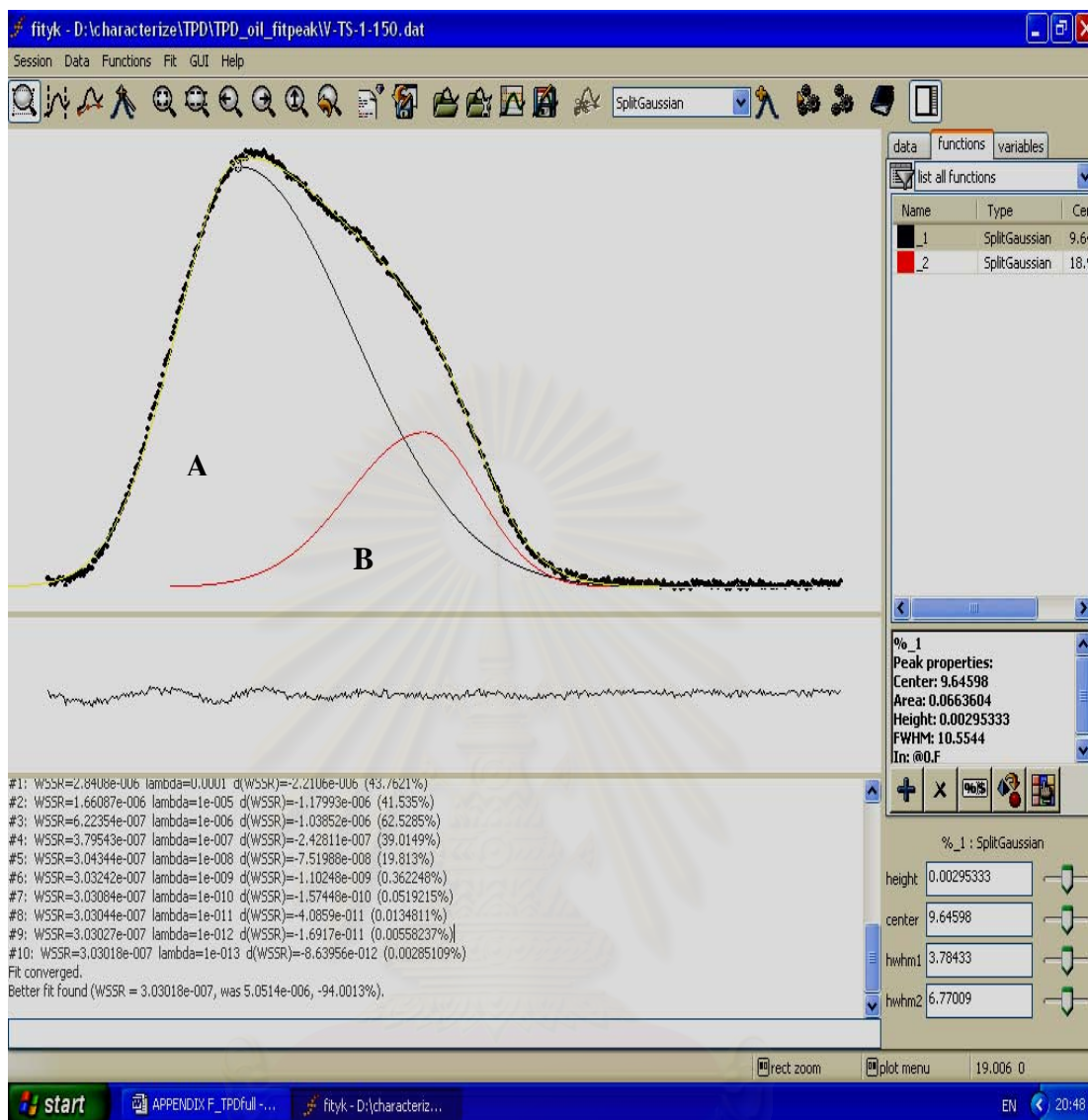


Figure D2 Peak fitting for V/TS-1(0.32)

**Peak A****Center: 8.96793****Area: 0.0313015****Height: 0.00175348****Temp: 133****Peak B****Center: 17.6136****Area: 0.0247889****Height: 0.00128158****Temp: 212****Figure D3** Peak fitting for V/TS-1(0.30)

**Peak A****Center: 9.82706****Area: 0.0505088****Height: 0.0023431****Temp: 145****Peak B****Center: 20.1888****Area: 0.022158****Height: 0.00128011****Temp: 242****Figure D4** Peak fitting for V/TS-1(0.23)



Peak A

Center: 9.64598

Area: 0.0663604

Height: 0.00295333

Temp: 144

Peak A

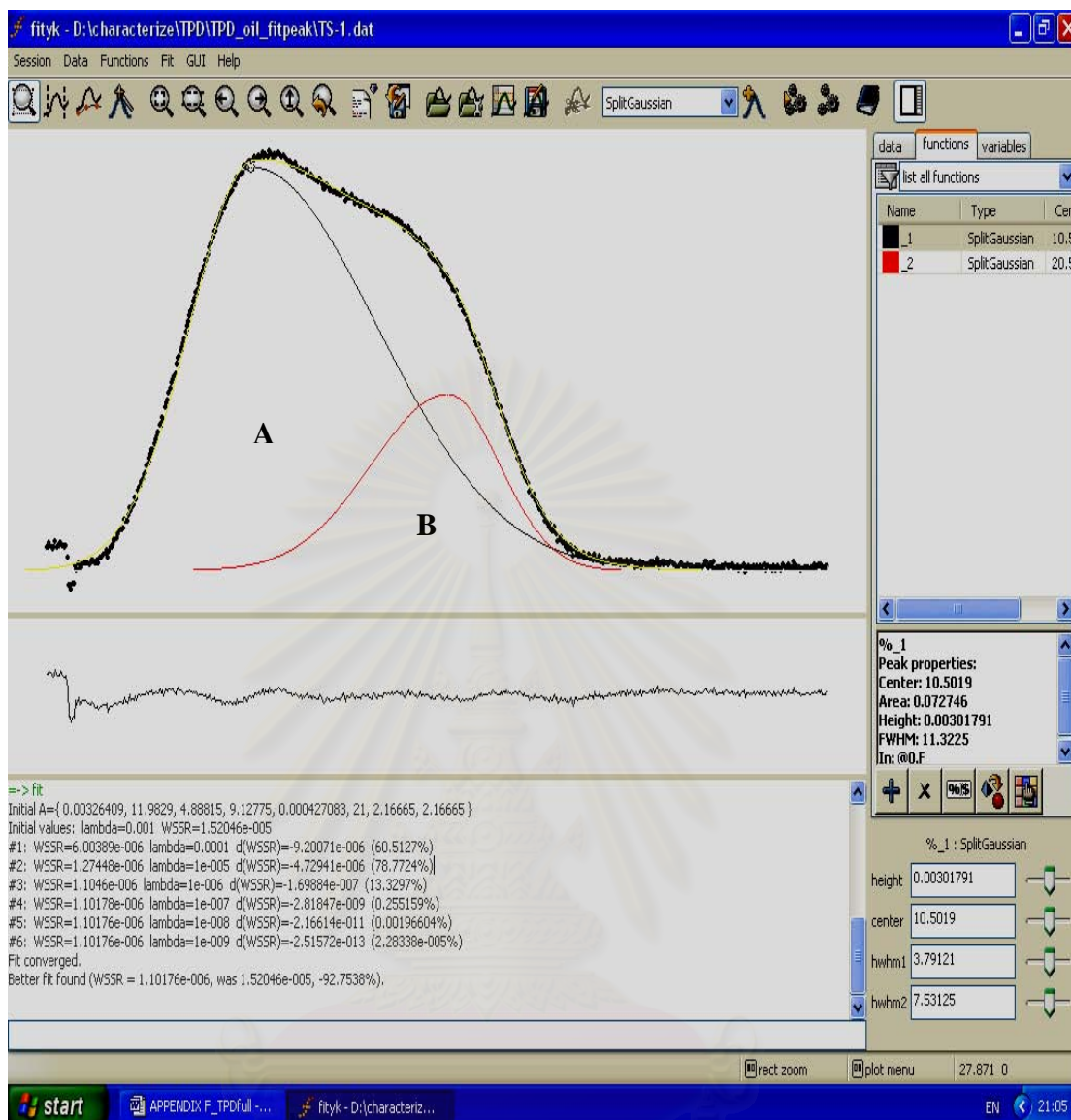
Center: 18.9269

Area: 0.0178612

Height: 0.00108684

Temp: 232

Figure D5 Peak fitting for V/TS-1(0.10)

**Peak A****Center: 10.5019****Area: 0.072746****Height: 0.00301791****Temp: 138.5****Peak B****Center: 20.5196****Area: 0.0215956****Height: 0.00132083****Temp: 232****Figure D6** Peak fitting for TS-1

APPENDIX E

CALIBRATION CURVE

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

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO, CO₂ by using Molecular Sieve 5A and Porapak-Q columns respectively.

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



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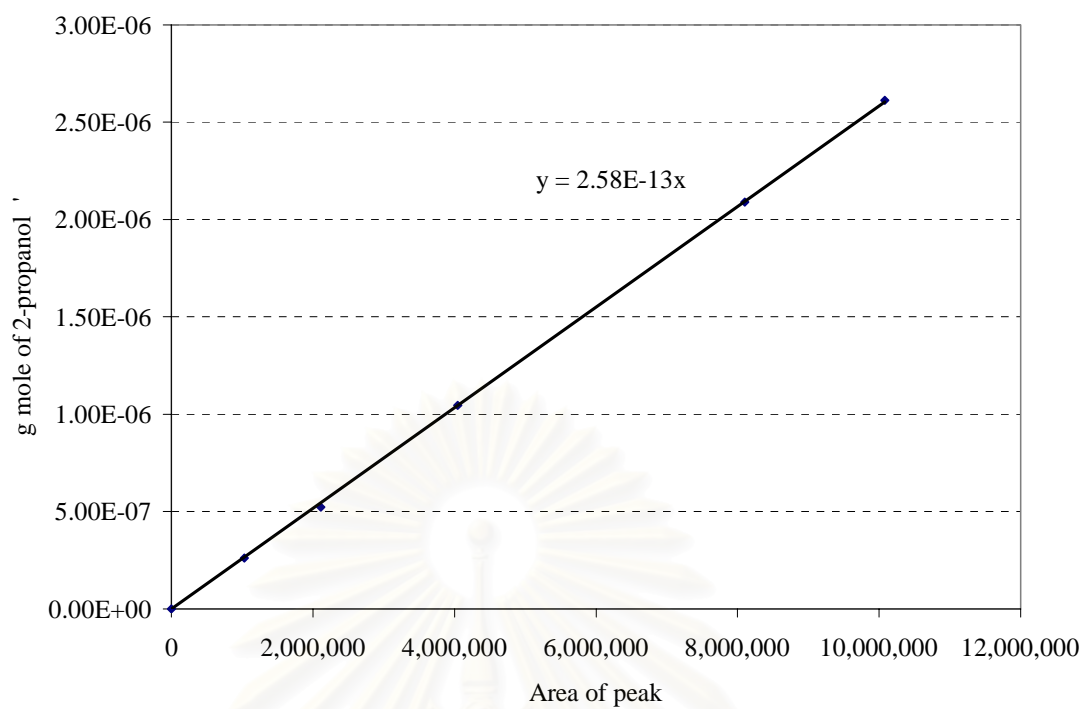


Figure E1 The calibration curves of 2-propanol

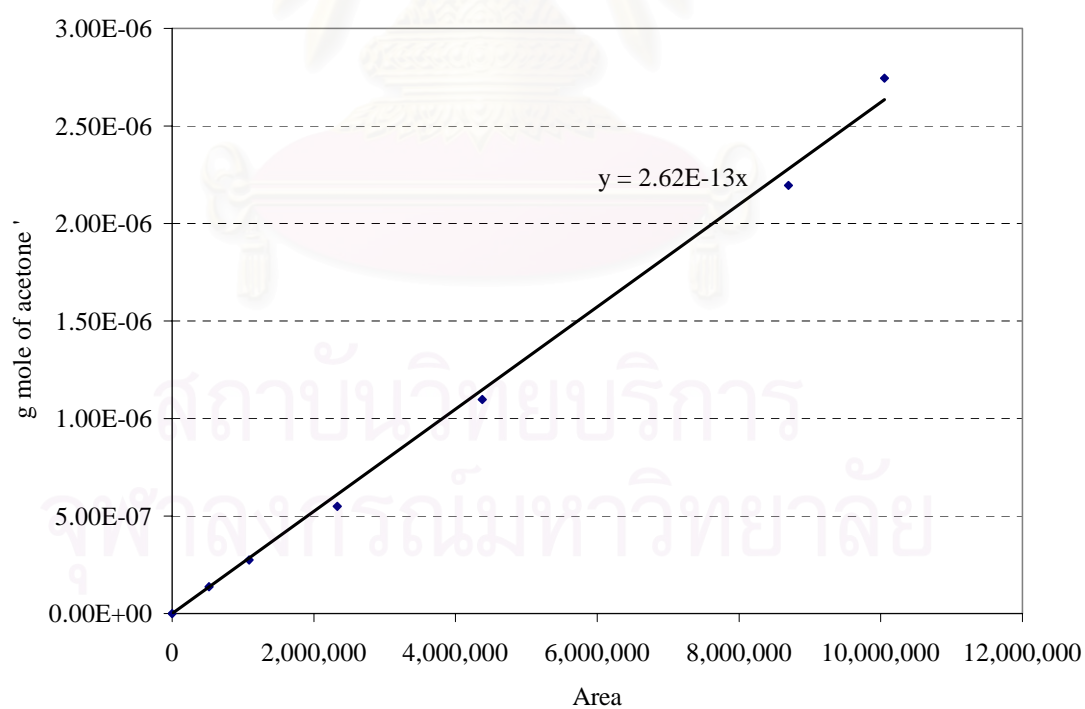


Figure E2 The calibration curve of acetone

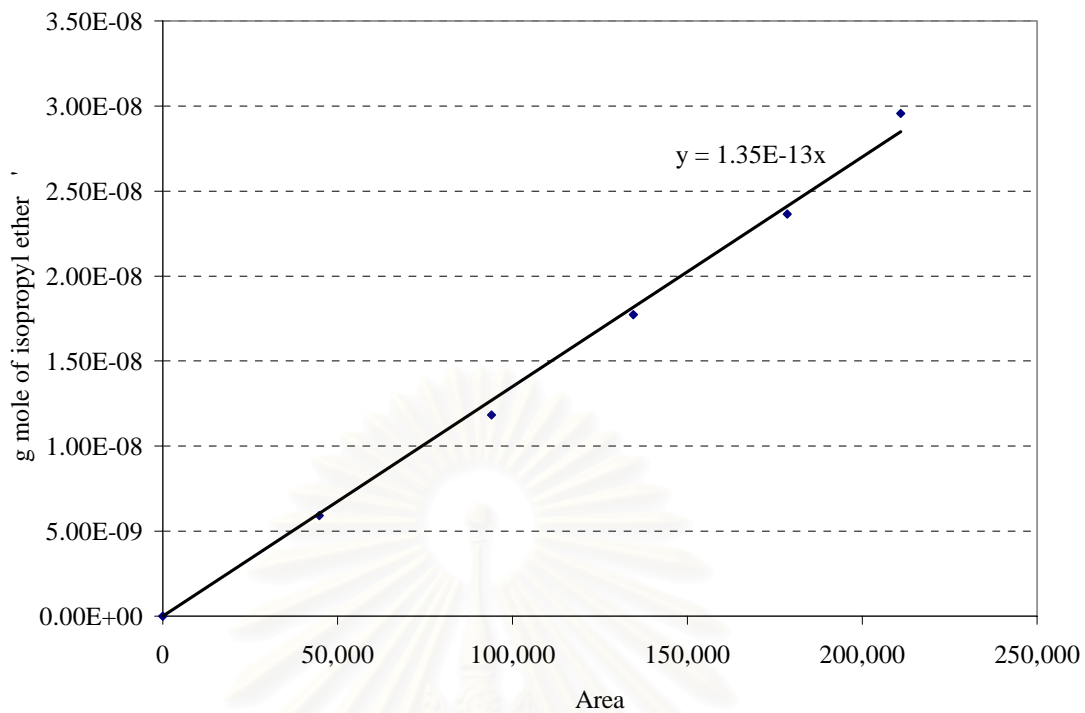


Figure E3 The calibration curve of isopropyl ether

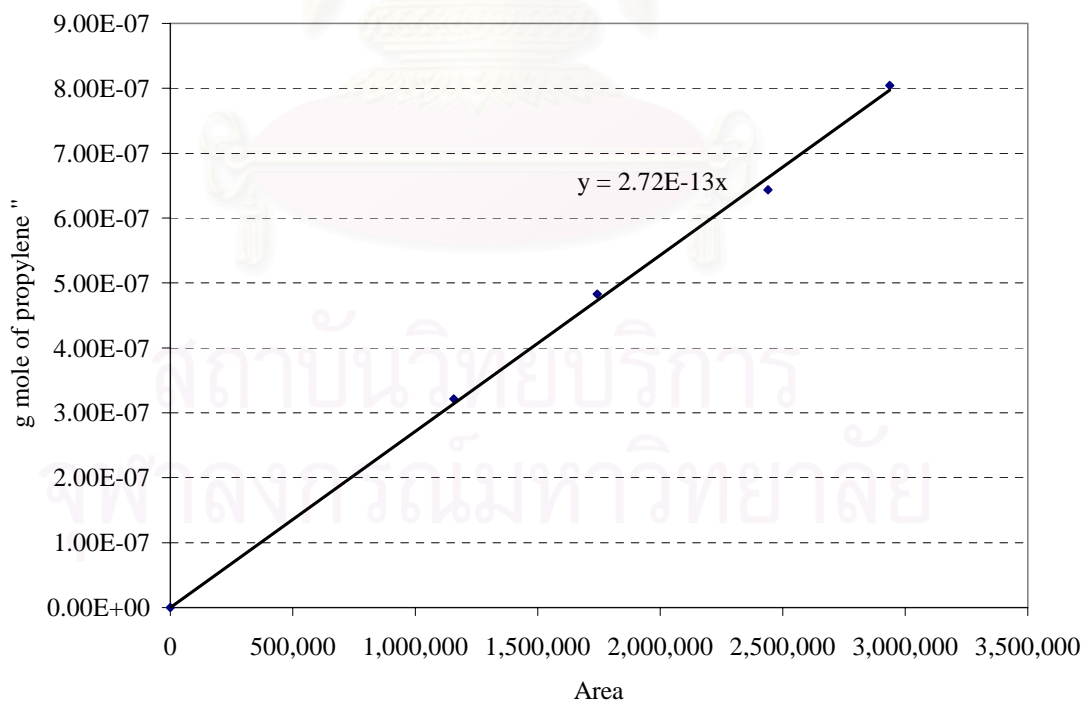


Figure E4 The calibration curve of propylene

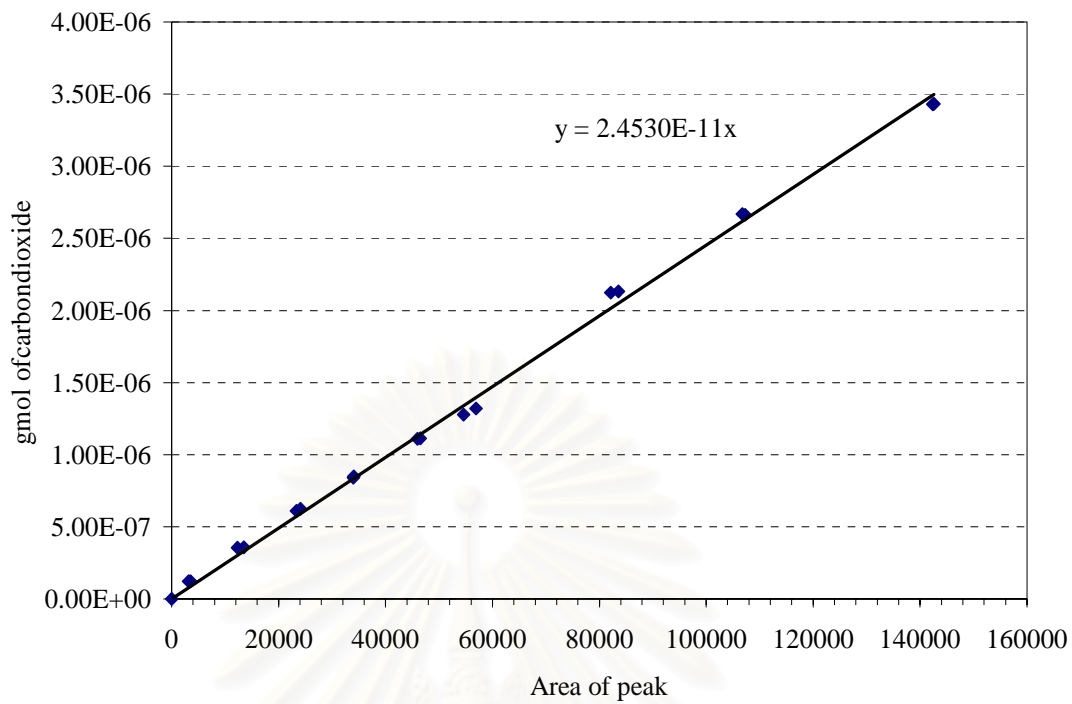


Figure E5 The calibration curve of carbon dioxide.

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APPENDIX F

DATA OF EXPERIMENTS

Table F1 Data of figure 4.6

Reaction temperature (°C)	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	1.82	4.66	0.00	95.34	0.00
200	2.33	11.35	0.00	87.19	1.46
250	22.79	21.10	0.55	72.36	5.99
300	64.83	27.85	0.42	66.19	5.54
350	95.01	24.82	0.16	54.95	20.07
400	97.00	20.61	0.06	49.20	30.14
450	97.46	17.24	0.04	55.78	26.94
500	98.59	14.50	0.00	63.49	22.01

Table F2 Data of figure 4.7

Reaction temperature (°C)	Component				
	% 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
450	95.63	16.57	0.05	76.51	6.88
500	97.29	12.23	0.00	58.46	29.31

Table F3 Data of figure 4.8

Reaction temperature (°C)	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	14.03	0.77	0.00	99.23	0.00
200	28.81	7.72	0.00	92.28	0.00
250	45.05	20.73	0.18	74.30	4.79
300	98.25	24.47	0.19	66.38	8.96
350	98.76	26.58	0.22	41.29	31.91
400	99.68	19.26	0.23	44.02	36.49
450	99.86	20.95	0.14	45.35	33.56
500	99.96	19.22	0.06	48.72	32.00

Table F4 Data of figure 4.9

Reaction temperature (°C)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO ₂ (S)
100	8.76	0.00	0.00	100.00	0.00
150	4.12	1.66	0.00	98.34	0.00
200	2.37	17.43	0.00	82.57	0.00
250	10.62	29.73	0.32	68.35	1.60
300	39.47	34.58	0.53	60.59	4.29
350	82.26	30.79	0.38	55.24	13.59
400	96.73	25.25	0.13	40.89	33.73
450	98.02	20.14	0.05	46.01	33.79
500	98.77	16.46	0.00	61.15	22.39

Table F5 Data of figure 4.10

Reaction temperature (°C)	Component				
	% 2-propanol (C)	% propylene (S)	% isopropyl ether (S)	% acetone (S)	% CO ₂ (S)
100	1.68	0.00	0.00	100.00	0.00
150	10.88	5.26	0.00	94.74	0.00
200	10.13	12.69	0.00	87.31	0.00
250	29.11	14.42	0.19	85.39	0.00
300	64.62	22.66	0.30	68.82	8.22
350	92.90	22.42	0.33	48.63	28.62
400	97.66	18.55	0.13	40.39	40.93
450	98.97	15.02	0.05	46.15	38.78
500	99.49	12.79	0.00	47.08	40.13

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APPENDIX G

MATERIAL SAFETY DATA SHEET

Vanadium (III) chloride

Safety data for Vanadium (III) chloride

General

Synonyms: Vanadium (III) chloride

Molecular formula: VCl_3

Chemical formula: VCl_3

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

Harmful if swallowed

Causes burn

Personal protection

Avoid contact with eyes.

Wear suitable protective clothing, gloves and eye/face protection

In case of accident or if you feel unwell, seek medical advice diately (show the label where possible)

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-utoxytitanium(IV)~Tetra-n-butylorthotitanate; 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/cm³

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 : colorless crystals or white powder

Melting point : 804 °C

Boiling point : 1413 °C

Vapor pressure : 1 mm Hg at 865°C

Specific gravity : 2.16 g cm⁻³

Solubility in water : 35.7 g/100g at °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 : colorless white solid (often sold as pellets)

Melting point : 318 °C

Boiling point : 1390 °C

Vapor pressure : 1 mm Hg at 739 °C

Specific gravity : 2.12 g cm⁻³

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.



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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: $\text{Na}_4\text{O}_4\text{Si}$

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 : colorless oily liquid

Melting point : $-2\text{ }^\circ\text{C}$

Boiling point : $327\text{ }^\circ\text{C}$

Specific gravity : 1.84 g cm^{-3}

Vapor pressure : $<0.3\text{ mm Hg}$ at $20\text{ }^\circ\text{C}$ (vapor 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.



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2-Propanol

Safety data for 2-Propanol

General

Synonyms: Isopropanol, Isopropyl alcohol

Molecular formula: C₃H₈O

Chemical formula: CH₃CH(OH)CH₃

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/ml (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 H

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.



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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 were 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 be 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 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 that have to be considered are the amount of the second cation to be loaded and the loading procedure.

In a published research, an attempt has been made to load 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 contained 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 the 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, respectively. 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 an 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 ((CoNO₃)₂.6H₂O, Cu(NO₃)₂, VCl₃, or Cr(NO₃)₃.9H₂O) 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 K α 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.

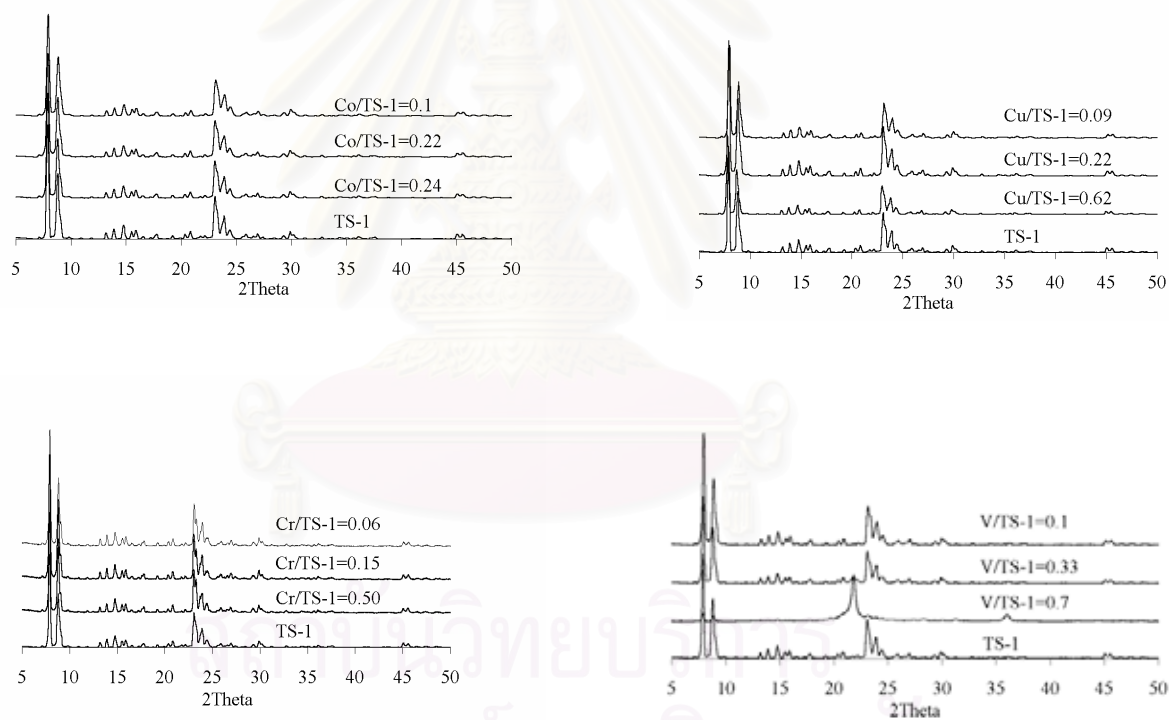
Chemical valence states of metals in the catalysts were measured by XPS technique using an AMICUS instrument with Mg K α radiation as excitation source. The binding energy shift was calculated using the C 1s peak at 286.7 eV as reference.

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 2 θ 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 possess surface area around 300 m²/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

**Figure 1** XRD Patterns of Top left : Co/TS-1, Top right : Cu/TS-1, Bottom left : Cr/TS-1 and Bottom right : 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 .

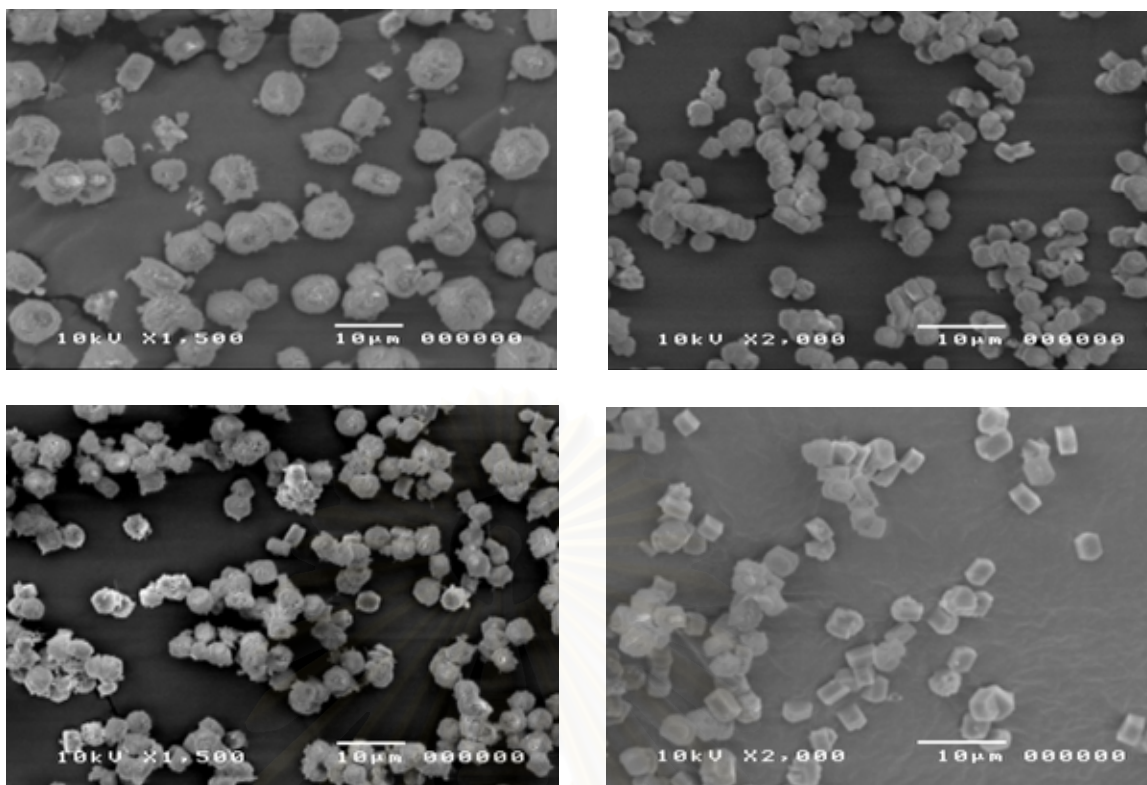


Figure 2 SEM photo of Top left : Co/TS-1, Top right : Cu/TS-1, Bottom left : Cr/TS-1 and Bottom right : V/TS-1

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 exist 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 exist 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 due to Cr^{6+} while the lower binding shifts of Cr/TS-1(0.15) and Cr/TS-1(0.06) suggest the presence 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)	779.50		Cu 2p _{3/2} (ref)	934.40	
Co/TS-1(0.24)	784.04	4.54	Cu/TS-1(0.62)	935.15	0.75
Co/TS-1(0.22)	784.80	5.30	Cu/TS-1(0.22)	935.35	0.95
Co/TS-1(0.1)	785.40	5.90	Cu/TS-1(0.09)	934.25	-0.15
Cr 2p _{3/2} (ref)	575.70		V 2p _{3/2} (ref)	513.55	
Cr/TS-1(0.5)	579.80	4.10	V/TS-1(0.7)	518.80	5.25
Cr/TS-1(0.15)	578.60	2.90	V/TS-1(0.33)	518.30	4.75
Cr/TS-1(0.06)	577.00	1.30	V/TS-1(0.1)	517.40	3.85

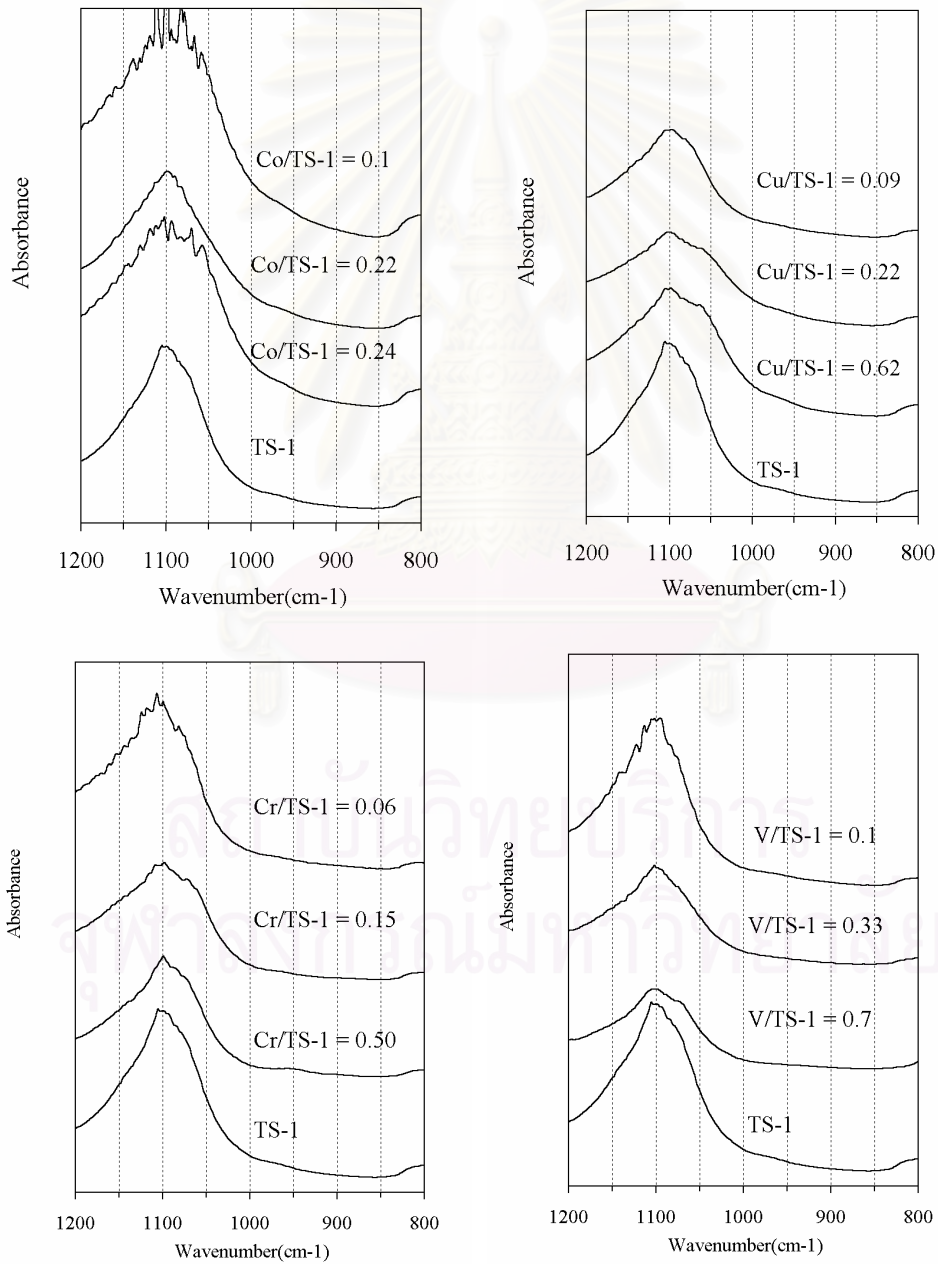


Figure 3 IR absorption spectra of modified and unmodified TS-1 samples.

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].

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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