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PREPARATION OF COPPER-TITANIUM SILICALITE-1

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งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลของการเติมโลหะทองแดง โดยการเติมเข้าไปในโครงสร้างของ TS-1 ระหว่างการก่อตัวเป็นผลึก TS-1 โดยใช้ปฏิกิริยาออกซิเดชันแบบเลือกเกิด ของ 2-โพรพานอลเป็นปฏิกิริยาทดสอบ โดยมีความเข้มข้นของ 2-โพรพานอลร้อยละ 5 โดยปริมาตรและออกซิเจนร้อยละ 8 โดยปริมาตร ทำปฏิกิริยาในช่วงอุณหภูมิ 100 ถึง 500 องศาเซลเซียส จากการศึกษาพบว่าโลหะทองแดงสามารถรวมตัวในโครงสร้างของ TS- 1 ได้สำเร็จและได้แสดงให้เห็นว่าไอออนทองแดงอยู่ใน 3 บริเวณในสารตัวอย่าง ได้แก่ เกิดเป็นไอออนทองแดงชนิด 2+ ซึ่งรวมเข้ากับโครงสร้างของไทเทเนียซึ่งวัดโดยใช้ ESR กระจายตัวอยู่ที่พื้นผิวของไทเทเนีย และก่อตัวในรูปออกไซด์ของโลหะทองแดง ซึ่งสามารถวัดโดย ESR และ XPS เทคนิคการดูดซับแอมโมเนียถูกนำมาใช้เพื่อวัดปริมาณและความแรงของกรด เพื่อศึกษาความสัมพันธ์ระหว่างพฤติกรรมในการเกิดปฏิกิริยาและคุณสมบัติของตัวเร่งปฏิกิริยา (คุณสมบัติความเป็นกรดและความแรงของกรด) ผลของการทดลองแสดงให้เห็นว่า ปฏิกิริยาออกซิเดชันของตัวเร่งปฏิกิริยา Cu-TS-1 ให้ค่ายีลด์ของอะซิโตนที่สูงเมื่อเทียบกับตัวเร่งปฏิกิริยา TS-1 การเติมโลหะทองแดงในตัวเร่งปฏิกิริยา TS-1 ส่งผลถึงค่าการเปลี่ยนของ 2-โพรพานอลและค่าการเลือกเกิดของคาร์บอนไดออกไซด์ นอกจากนี้ค่าการเลือกเกิดของโพรพีลีนไม่ได้เพิ่มขึ้นเป็นสัดส่วนกับปริมาณโลหะทองแดงที่เติมเข้าไป นอกจากนั้นยังพบว่าการเติมโลหะทองแดงในโครงสร้าง TS-1 นั้นมีโครงสร้าง คุณสมบัติ และความสามารถในการเป็นตัวเร่งปฏิกิริยาเหมือนกับ TS-1 งานวิจัยชี้ให้เห็นว่าถ้าความเข้มข้นของโลหะทองแดงน้อยความแรงของกรดจะมาก ดังนั้นปริมาณตำแหน่งกรดและความแรงของกรดควรมีสัดส่วนที่เหมาะสมเพื่อทำให้ความว่องไวและค่าการเลือกเกิดในการเกิดปฏิกิริยาดีขึ้น

ภาควิชา.............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต.......ดรุณี สุขหอม.............
สาขาวิชา...........วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา..........................
ปีการศึกษา..........2548.....................

##477029821: MAJOR CHEMICAL ENGINEERING
KEY WORD: TITANIUM SILICALITE-1/ COPPER/ INCORPORATION

DARUNEE SOOKHOM: PREPATION OF COPPER-TITANIUM SILICALITE-1. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D. 93 pp. ISBN: 974-17-4522-2

The effects of incorporating Cu atom directly into the TS-1 framework during the formation of TS-1 crystalline for the gas phase selective oxidation of 2-propanol were investigated under inlets conditions of 8 vol% of O_2 and 5 vol% of 2-propanol in the reaction temperature range of 100-500 °C. The research found that TS-1 can be successfully modified by copper incorporation. Three forms of copper (II) ions exist in three different environments in the catalysts. Isolated copper (II) ions incorporated into the titania network were detected by ESR spectroscopy, exists on CuO phase (from the ESR results) and surface complexes of Cu ions with titania (from the XPS results). Temperature programmed desorption of ammonia (NH_3–TPD) are used to determine the amount and strength of acid site to find the relationship between catalytic behavior and catalyst properties. From the catalytic reaction, it can be indicated that the catalyst oxidation over Cu-TS-1 catalyst yields acetone more than TS-1 catalyst. The addition of Cu to TS-1 catalyst slightly affects the over all conversion of 2-propanol, but significantly increases the selectivity toward CO_2. Nevertheless, there is no direct relationship between the content of Cu and the selectivity of propylene. Similarities between structure, properties and catalytic activity of TS-1 and Cu-TS-1 catalysts exists. This research indicated that lower copper concentration, higher acid strength. In addition, an appropriate combination of acid sites should exist to improve the catalytic activity and selectivity.

Department……Chemical Engineering… Student's signature……ดารุณี สุขหอม……
Field of study….Chemical Engineering… Advisor's signature……………………
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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 hydrothermal synthesis of the titanium-containing derivatives of high-silica ZSM-5 was first reported by Taramasso et al. (1983). The new material was named titanium silicalite-1 or TS-1 that is a zeolite with a MFI structure that has received much attention over the past years due to its noticeable catalytic properties. The titanium atoms located in the zeolite framework behave as active sites for oxidation of many organic substrates under mild reaction conditions (liquid phase, H_2O_2 as oxidant and low temperature). TS-1 has been found to catalyze aromatic hydroxylation, alkene epoxidation, ketone ammoximation, alcohol and alkane oxidation, etc. [Hayashibara et al. (1994)] In all cases, high activities, selectivities and efficiency of H_2O_2 are obtained. As a consequence, several reactions catalyzed by TS-1 (phenol hydroxilation, cyclohexanone ammoximation, and propylene epoxidation) are at present in different stages of industrial application. [Boccuti et al. (1989)]

Historically, TS-1 has been widely investigated over various metal loading such as simple metal ions, and metal complexes, some of these works are summarized in Table 1.1. Some of these catalysts have shown potential catalytic activities. In addition, copper (II) ions ions-exchanged in a zeolite have been reported to have a redox function and have been used as catalysts for various gas-phase catalytic oxidations. In the gas-phase oxidation of organic compound, it is usually difficult to control the selectivity of a partial and/or deep oxidation.

Landong et al. (2004) have applied Cu–TS-1/cordierite prepared from ion-exchange and impregnation methods. However, to the best of our knowledge, copper incorporated into the TS-1 framework has not been reported yet. This research, therefore, has been set up to investigate the possibility of incorporations Cu atom directly into the TS-1 framework during the formation of TS-1 crystalline. The prepared TS-1 with different Cu loading will then be characterized using different analytical techniques. The gas phase reaction of 2-propanol at different temperature is used to evaluate the catalytic activity of the prepared catalyst.

Table 1.1 The metal modified TS-1

Auther	Year	Catalyst	Method	Process
Petrov et al.	1996	Cu-TS-1	ion-exchange	Carbon monoxide oxidation and nitric oxide reduction reactions.
Pirutko et al.	2001	Al-TS-1 V-TS-1 Cr-TS-1 Fe-TS-1	incoporation	Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by NO_2
Jenzer et al.	2001	Pd–Pt/TS-1	incoporation	Epoxidation of propylene with oxygen and hydrogen.
Guo et al.	2004	Ag/TS-1	deposition–precipitation and impregnation methods	Effects of preparation method and precipitator on the propylene epoxidation
Li et al.	2004	Cu-TS-1	ion-exchange and impregnation	Selective catalytic reduction (SCR) of nitrogen oxides (NOx).
Grieken et al.	2004	Al-TS-1	wetness impregnated	Role of solvent nature in the liquid phase rearrangement of 1,2-epoxyoctane.
Taylor et al.	2005	Au-TS-1	deposition–precipitation	Gas-phase epoxidation of propylene.
Ma et al.	2005	Sn-TS-1	impregnation	Transesterification of dimethyl oxalate.

The scope of this research is as follows:

1) Preparation of Cu-TS-1 catalysts by using the hydrothermal method.
2) Characterization of Cu-TS-1 catalysts by using the following techniques.
    - Determination of bulk composition of Cu, Si and Ti by X-ray fluorescence Spectrometer (XRF)
    - Determination of specific area by N_2 adsorption based on BET method (BET).
    - Determination of structure and crystallinity of the prepared catalysts by X-ray diffractrometer (XRD).
    - Determination of incorporation of Ti atoms as a framework element by IR Spectra (IR).
    - Determination of the Cu (II) species in the catalysts by electron spin resonance (ESR).
    - Determination of state of Cu atom by X-ray photoelectron Spectroscopy (XPS)
    - Determination of catalyst granule morphology by scanning electron microscopy (SEM)
    - Determination of acid properties by temperature programmed desorption (TPD)
3) Catalytic study using the gas phase oxidation of 2-propanol between 100 - 500°C and atmospheric pressure to determine catalytic activity.

This present thesis is organized as follows:

Chapter I presents the background and scopes of the research.

Chapter II presents literatures relate to TS-1 catalysts and oxidation of alcohols on various reaction in the past and comments on previous work.

Chapter III presents the theory of this research, studies about the introduction of TS-1 and the oxidation reaction and its possible mechanism

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

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

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

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

CHAPTER II

LITERATURE REVIEWS

2.1 Literature reviews

In 1983, Taramasso, and co-worker reported the synthesis of a titanium-substituted analogue of silicalite, given the name titanium silicalite or TS-1. The new material synthesized in a tetrapropylammonium hydroxide (TPAOH) system substantially free of metal cations. TS-1 contains low levels (up to about 2.5 atom %) of titanium substituted into tetrahedral positions in the silicalite lattice. The product has proved to be an extremely useful oxidation catalyst, particularly in conjunction with a peroxide. In epoxidations and related reactions, TS-1 is an active and selective catalyst.

Since its discovery in early 80's TS-1 has been studied, mainly, as oxidation catalyst for a variety of reactions in the presence of aqueous H_2O_2 as oxidant. Examples of TS-1 as oxidation catalysts are manifested in the following reactions,

- Oxyfunctionalization of alkanes [Huybrechts et al. (1991)].
- Ammoximation of carbonyl compounds [Thangaraj et al (1991)]
- Oxidation of ethers [Reddy et al. (1992)]
- Oxidation of alcohols [Maspero et al. (1994)]
- Oxidation of amines [Joseph et al. (1995)]
- In Bayer-Villiger oxidation to from lactones [Kumar et al. (1998)]
- Hydroxylation of aromatics [Wu et al. (1998)]
- Epoxidation of alkenes [Laufer et al. (1999)]

Other than its use as oxidation catalyst, it is also used in C-C bond formation and also used in diastereo-selective epoxidation of allylic alcohols [Adam et al. (1996)].

The investigation of preparation TS-1 was undertaken in a lot of laboratory. Some of the more prominent studies and the modified TS-1 for several reactions are summarized below.

TS-1 samples of different particle size were synthesized and investigated by van der Pol et al. (1992). They found that smaller particles were more active than larger particles. The calculation of the Weisz modulus revealed that large zeolite particle were not fully utilized because of pore diffusion limitations. They also observed that the product distribution was also influenced by particle size.

Petrov et al. (1995) prepared a surface coated with TS-1 mullite fibre. From this material, a copper containing zeolite catalyst was produced by ion exchange. The Cu containing TS-1 was found to be more active for carbon monoxide oxidation reaction than the noble metal containing supported catalysts. By combining the copper containing catalyst with rhodium and ceria, a catalyst for carbon monoxide oxidation and nitric oxide reduction reactions, superior in activity to noble metals supported catalysts were prepared.

They concluded that the similarities between structure, properties and catalytic activity of Cu-TS-M and ZSM-5 catalysts exists, but suggested that one should be careful in drawing general conclusions. It was also reported that the chemical composition of the zeolite framework played a decisive role in determining the catalytic properties of the Cu containing catalysts.

Weitkamp et al. (1997) investigated samples of TS-1 which had different mole ratios of Si/Ti. They observed that samples prepared according to two different synthesis procedures could differ significantly in their hydrophobic/hydrophilic surface properties For Si/Ti ratio above ca. 40, the hydrophobicity of the surface decreased with increasing titanium content which had been attributed to the increased formation of polar Si-O-Ti bridges in the zeolite framework. For TS-1 samples with higher titanium content, the hydrophobicityicity strongly depended on the method of preparation and was considerably influenced by the formation of additional titanium-containing species in extra-framework positions. From the results of the catalytic characterization in the hydroxylation of phenol they concluded that, in particular, TS-1 samples with high titanium content were the more active.

Pestryakov and Lunin (2000) studied the active electronic states of supported metal catalysts (Ag, Cu, Au) in the processes of alcohol partial oxidation by physicochemical methods. Comparison of the obtained catalytic and spectroscopic data revealed that one-charged cations M^+ were the active sites of the local interaction on the metal catalyst surface in the processes of alcohol oxidation. The catalyst selectivity strongly depends on the effect charge of the surface active sites.

Schuster et al. (2001) investigated the activity of titanium and vanadium containing zeolitic and non-zeolitic materials in the oxidative dehydrogenation of propane to propene. Using TS-1 as the catalyst showed the optimum performance. The propane and oxygen partial pressure had no influence on the selectivity, and the mass transport limitation in the macro- and mesopores could be neglected. The addition of water caused a decrease in the conversion, but increased the selectivity, probably due to a competitive adsorption of the water molecules and the reactant molecules on the active site. They assumed that the reaction probably took place on the outer surface of the TS-1 crystallites on Lewis acid sites, the exact reaction mechanism nor the exact active site were not clear. In addition, increasing the Lewis acidity by a sulfation of TS-1 in both the gas phase and the liquid phase prior to the reaction resulted in an increase of the conversion of up to 17% with a selectivity about 74%.

Wang et al. (2003) investigated the effect of preparation, treatment method of the Ag/TS-1 catalyst and the reaction conditions on propylene epoxidation using oxygen as the oxidant in a fixed-bed quartz glass reactor. The result of the effect of preparation condition was summarized into three parts. The first one was the effect of Ag loading showed that the amount of Ag loading had an important effect on the catalytic properties. With an increase in Ag loading, the propylene conversion increased significantly, and then leveled off, but the selectivity to propylene oxide decreased significantly with an excessive increase of Ag loading. The second one was the effect of support showed that the different supports (TiO_2, SiO_2, silicalite-1, HZSM-5, TS-1). Their catalytic activities for the epoxidation of propylene differently. Only TS-1 was the suitable support, the third one was the effect of Si/Ti ratio of TS-1. They found that the Si/Ti ratio of TS-1 had a great effect on the propylene epoxidaton. With an increase in the Si/TI ratio of TS-1, both the propylene conversion and the selectivity to propylene oxide increased. The Si/Ti ratio was 64, the catalyst exhibited optimum performance, 0.92% propylene conversion and 91.21% propylene oxide selectivity.

Moreover, they also studied the effect of pretreatment condition of Ag/TS-1 catalysts. The results showed that an increase in the calcination temperature, both the propylene conversion and the selectivity to propylene oxide increased. The catalyst calcined at 450 ºC, exhibited the optimum performance. In case of the effect of calcinations methods of Ag/TS-1 catalysts, they also presented that calcinations methods also had an important effect on the reaction. The optimum activity showed when the catalyst was calcined in air at 450 ºC. The results of the characterization showed that the oxidized Ag species without single electrons played an important role in the epoxidation of propylene.

Yap et al. (2004) studied the direct vapor-phase epoxidation of propylene using hydrogen and oxygen over gold particles prepared by the deposition-precipitation (DP) method on various modified titanium silicalite supports (TS-1). The reaction was carried out over a reaction time of 24-36 hrs at a space velocity of 7000 $mlg_{cat}^{-1}h^{-1}$ and temperatures of 140, 170, and 200 ºC. Au/TS-1 catalysts achieved propylene conversions of 2.5-6.5% and propylene oxide selectivities of 60-85% at 170 ºC, with dilute Au and Ti catalysts exhibiting good stability. They explained that propylene oxide rates were not highly influenced by the TS-1 particle size and are thus not proportional to the specific external surface area of the support.

The conclusion that activity might reside in the channels of the TS-1 was supported by the finding that the observable gold particles decorating the TS-1 particle only account for about 30% of the total gold content of the catalyst. Increasing the gold loading up to 0.74 wt% did not increase the propylene oxide rates proportionally, suggesting that the active Au-Ti propylene oxide-forming centers were limited.

Li et al. (2004) investigated the effect of Cu–TS-1/cordierite prepared with ion-exchange and impregnation methods from TS-1/cordierite. The prepared catalysts were used in the purification of exhaust from lean burn engine. Main pollutants in the exhaust gas NO_x, hydrocarbons and CO were treated at one time and good conversions were gained. Copper ion-exchanged TS-1/cordierite had good duration and anti-poison properties while cooper impregnatedTS-1/crodierite not. Copper in the duct of TS-1 zeolite was reported to be the main active component of the catalyst and the existence of Cu(I) in the reaction was thought to be essential.

Guo et al. (2004) studied the effects of preparation method and precipitator on the catalytic properties of Ag/TS-1 in the gas-phase epoxidation of propylene in a fixed bed, quartz reactor. The Ag/TS-1 catalysts were characterized by XRD, UV–vis, FT-IR and TEM. The results showed that the catalysts prepared by both deposition-precipitation and impregnation methods exhibit catalytic activity and selectivity in the reaction. 0.48% propylene conversion with 57.88% selectivity to propylene oxide was obtained over Ag/TS-1 catalyst prepared by impregnation method. However, the deposition-precipitation method was optimum.

Wang et al. (2004) investigated the effect of calcinations atmosphere of the Ag/TS-1 catalyst and other Ti-containing supports on propylene epoxidation in the presence of hydrogen and oxygen. The results showed that the calcinations atmosphere had an important effect on the catalytic properties. The catalyst, which was calcined in air, exhibited the optimum catalytic activity. However, the catalyst, which was calcined in nitrogen or hydrogen, exhibited obviously activity decrease. The framework titanium species was reported to play an important role in the reaction, but the extra framework titanium species also had weak epoxidation activity. They concluded that excessive extra framework titanium species (hexahedral) could decrease the propylene oxide selectivity and the oxidized silver ions are the main active sites for the gas-phase epoxidation of propylene.

2.2 Comment on previous works

From the previous studies about the preparation of catalyst, there are many researches studied about different methods such as impregnation, co-precipitation, deposition-precipitation, ion exchange for preparing TS-1. The knowledge is gained through the project to select proper preparation methods for different systems. The main objectives of our work to study of the different way to prepare the catalyst, in order to synthesize well dispersed particles of metals on framework of TS-1.

Although, the preparation of Cu/TS-1 by using ion exchange and impregnation have been reported, but the previous studies showed no research study the preparation of Cu-TS-1 by using incorporation method. Thus, the preparation of Cu-TS-1 by using incorporation is chosen to studied in this research.

CHAPTER III

THEORY

3 INTRODUCTION OF TS-1 ZEOLITE

3.1 Definition and classification

Zeolites are crystalline solid made up of silicon (Si), aluminium (Al) and oxygen (O) as the essential elements. They are joined tetrahedrally in such a fashion that both the Si and Al occupy the center of the tetrahedron and O shares the corner position. The tetrahedra are joined together by an oxygen bridge such that no two adjacent tetrahedrons can have the Al atom in the center. The general formula of any zeolite can be represented as

$$Mx/n\ [(AlO_2)\ x\ (SiO_2)y]\ Z\ H_2O.$$

This represents the crystallographic unit cell formulae of any zeolite where M is the cation from group I or II of valence n. M can also be organic cations. The ratio y/x may have any value from one to infinity. Z is the number of water molecules. The presence of one Al atom in the lattice develops one unit negative charge in the framework. The presence of silicon could lead to no such residual charge, as it is tetrapostive in nature. The negative charge, imposed by the presence of aluminium atom, is either compensated by group I or group II metals cations or by organic cation molecule in case of as synthesized zeolite material. The trivalent Al ion in the zeolite can either partly or completely be replaced by trivalent other ions like Ga^{+3}, B^{+3} Fe^{+3}, etc or by tetravalent ions such as Ti^{+4}, Zr^{+4}, Sn^{+4}, etc. These metallo-silicate analogs of the zeolite are commonly referred as molecular sieves. There is no single classification by which all the properties of a particular zeolite can be explained. Therefore, various classifications of zeolites are there, like on the basis of pore opening, chemical composition, natural abundance etc. All zeolites can be classified by the number of T atoms, where T = Si or Al, that define the pore opening. Zeolites containing these pore openings may also be referred to as small pore with 8- member ring (MTN, NU-1 etc.), medium pore having

10- member ring opening (MFI, MEL, etc.), large pore with 12- member ring opening (FAU, BEA, MTW 2 etc.) and ultra large pore having 14- member ring opening (UTD-1). The ordered mesoporous materials (M41S) are also reported. Zeolites are also classified on the basis of chemical composition. Irrespective of its chemical composition and distribution of T- atoms, IUPAC and IZA assigned 3 letters code to describe a known framework topology like LTA, MFI, UTD-1, etc, are given in the following table.

Table 3.1 Framework topology of MFI structure

Type	**Si/Al Ratio**	**Example**
Low silica	1.5	LTA, FAU, LTL, etc
High silica	5-500	MFI, BEA, etc
All silica	∞	Silicalite-1, Si-NCL- 1, Si-UTD-1, etc

3.2 Metallo-silicates

Various metal ions have been successfully incorporated in framework structures of different morphologies and the resultant molecular sieves are termed as metallo-silicates. Various metal ions with varying charges have been used for the synthesis of metallo silicates. They are briefly summarized in the following table.

Table 3.2 Various metal ions with varying charges have been used for the synthesis of metallo silicate

Metal ion	Example
M^{+3}	B^{+3}, Al^{+3}, Fe^{+3}, Cr^{+3}, V^{+3}, Ga^{+3}, As^{+3}, etc
M^{+4}	Ti^{+4}, Sn^{+4}, Zr^{+4}, Ge^{+4}, V^{+4}, etc
M^{+5}	As^{+5}

Depending on the charge of the metal ion incorporated, the resultant framework may be cationic or neutral. When a tetravalent metal ion like Fe^{+3} is incorporated, the unit cell of the 3 incorporation of a tetravalent metal ion like Ti^{+4} does not create any charge imbalance in the framework. When a B^{+3} is introduced in the zeolite framework it is called boro-silicate, similarly for Ga^{+3}, it is called gallo-silicate and for Ti^{+4} it is called titano-silicate.

3.2.1 Titanosilicates:

Titanosilicate results when a Si^{+4} from silicate matrix is replaced tetrahedrally in the framework position by Ti^{+4} ion. When the substitution is carried out in the silicalite -1, pure siliceous analog of ZSM-5, the resultant titanosilicate is termed as TS-1. When the substitution is carried out on silicalite-2, pure siliceous analog of ZSM-11, the resultant titanosilicate is known as TS-2. Similarly titanosilicates from other morphologies such as ZSM-48, Beta, MCM-41, etc are also known. Among all the titanosilicates, TS-1 and TS-2 have been used extensively in the catalytic reactions because of their unique pore architecture and higher catalytic activity. They have MFI and MEL structure respectively and both of them are members of the pentasil family. Linking of chains of 5-membered ring secondary building units forms them. MFI topology are obtained when adjacent planes or sheets are related to one another by an inversion center and MEL types are obtained when the sheets are related by a mirror plane. This type of linking results in the formation of two intersecting channels in MFI with 10- membered ring openings. One is elliptical with cross section 0.51 nm ´ 0.53 nm and the other one is circular with a cross section of 0.55 nm. The cavities formed in ZSM-5 (MFI) by these intersecting channels are equivalent to a maximum diameter of 0.9 nm (shown in figure 3.1). The theoretical channel length in ZSM-5, obtained from crystallographic data, is 8.8 nm.

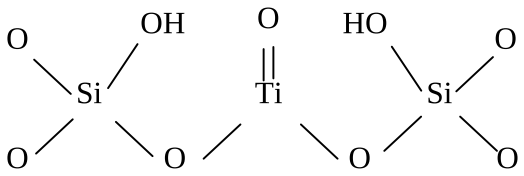


Figure 3.1 Framework of TS-1

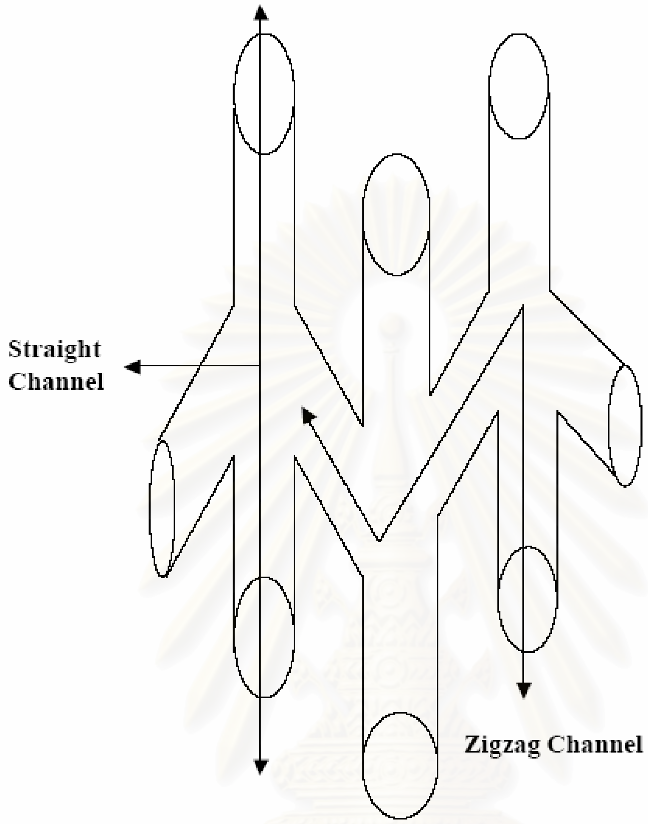


Figure 3.2 Pore and channel structure of TS-1

3.2.2 Synthesis of Titanosilicalite-1:

The difficulty in the synthesis of metallo-silicates arises because of the formation of stable insoluble metal oxide / hydroxide precipitate, either during preparation of gel or during the crystallization of the metallo silicate. The normal pHs of the gels for the synthesis of the metallo silicates are around 9-13. Under such alkaline conditions, Ti^{+4}

has a strong tendency to form insoluble amorphous TiO_2 species, unlike silicates or aluminates which dissolve under alkaline conditions.

The presence of extra-framework Ti-species has a strong influence in its catalytic activity. It may promote extensive homolytic side reactions including decomposition of hydrogen peroxide.

To overcome the above difficulties in the synthesis of TS-1, several routes are tried to synthesize TS-1 with no amorphous extra- framework titanium species.

Kumar et al. (1996) had tried the synthesis of metallosilicate in presence of complexing agent such as oxalic acid, acetyl acetone. The use of this complexing agent may prevent the formation of metal oxide / hydroxide precipitate by complexing with the metal ion used in the synthesis. TS-1 has been synthesized successfully using acetylacetone as the complexing agent without formation of extra-framework TiO_2 species.

Padovan et al. (1989) had tried synthesis of TS-1 by wetness impregnation method of SiO_2- TiO_2 co-precipitate. The dried SiO_2-TiO_2 co-precipitate is impregnated with a required quantity of TPAOH solution similar to the pore volume of the solid and the subsequent treatment leads to the formation of TS-1 without the formation of TiO_2 species.

Uguina et al. (1994) has successfully synthesized TS-1 from SiO_2-TiO_2 co gel using modified Padovan's method.

Atom planting method was introduced by Kraushaar et al. (1988) where highly siliceous zeolites are treated with titanium chloride vapor at high temperature. Ti-mordenite, which has not been synthesized under hydrothermal conditions, synthesized by this atom planting method.

Gao et al. (1995) synthesized TS-1 using aq. solution of TiC_{l3} as the titanium source and thereby avoiding the precipitation of TiO_2. After 2-5 days of autoclaving at 160 ^oC, TS -1 was obtained without any trace of extra-framework titanium species.

Van der Pol et al. (1993) has studied the effects of various reaction parameters on the synthesis of TS-1 and had shown that those smaller crystallites are much more active than the larger crystallites. So attempts have been made to synthesize TS-1 with smaller crystal sizes.

Recently Kumar, et al. has developed a new method for synthesizing TS -1 using phosphoric acid as promoter. This method gives particles in the size range 100 nm – 200 nm with almost uniform particle size distribution. G. Zhang et al. (1995) synthesized discrete colloidal crystals of TS-1. W. Honglin et al. (1998) synthesized nano structured TS -1 supported on TiO_2.

3.2.2.1 Effect of templates:

These are organic molecules, generally, organic amines or organic quaternary ammonium salts. They usually contain a hydrophobic part (hydrocarbon chain) and a hydrophilic part (amine or quaternary ammonium moiety). The hydrophobic part of the template molecule polarizes the hydrophilic water envelope around the various building units and reorganizes them in a particular orientation. These molecules are usually known as structure directing agents as well as void filler. Depending on the nature of the template, zeolites with different morphologies are obtained. Templates may help the formation of zeolite either by kinetically or thermodynamically or both. Chemically they help TO_4 units to pack around themselves in a preferred orientation and thereby providing it with nucleus on which further nucleation followed by crystallization can occur. Thermodynamically it may help by lowering the chemical potential of the lattice formed upon the inclusion of the templates during nucleation. Tetrapropylamonium cation in the form of hydroxide is the most commonly employed template for the synthesis of TS-1. Although tetrapropylamonium hydroxide is most commonly used, tetrapropylamonium bromide is also used in presence of different amines such as ammonia, hexane diamine, etc.

3.2.2.2 Alkalinity

Alkalinity of the solution plays a key role in the hydrothermal synthesis of zeolites. This is known as mineralizer or mobilizing agent. It solubilizes both silicon and aluminium sources and brings them in a homogeneous solution with sufficient number of soluble precursors for the zeolite synthesis. A supersaturated solution is reached which contains sufficient number of T-atoms in tetrahedral position with condensable ligands. Through condensation of these T atoms from the supersaturated solution, nucleus of the zeolite is formed which due to further nucleation leads to the formation of zeolite crystal. However, the alkalinity of the solution has a marked influence on the crystal size as well as the solid yield of the TS-1. At high OH^- concentration multiple nucleation takes place which leads to the formation of irregularly shaped crystals. The solubilization of different silicate precursors leads to a decrease in the yield of TS-1.

3.2.2.3 Temperature:

The rate of nucleation increases with increase in temperature helping crystallization in zeolite synthesis. It can again determine the type of products that will crystallize from the solution. At high temperature, the water molecules, which normally fill up the pores of the porous solids, will be evaporated and dense packed structure is expected. Similarly if the pores are filled up with the high boiling liquid, then even at high temperature open porous structure is formed. However, TS-1 synthesis is dependent on temperature. It has both a lower limit and an upper limit. Beyond these limiting values, formation of extra-framework titanium species is facilitated.

3.2.2.4 Time:

The crystallinity of a zeolitic material usually increases with time up to a certain extent, after that the phase transformation in zeolites follows the Ostwa ld rules of successive transformation. The least thermodynamic product will form first. This is then successively transformed to most stable product through meta-stable phase. TS-1 also follows the general rule that with time the crystallinity of the sample increases.

3.2.2.5 Dilution:

Dilution also has an effect in the nucleation and crystallization process in the synthesis of TS-1. Increase in the water content leads to the dilution of the reactive zeolite precursors. Therefore, increased dilution prevents supersaturation and retards nucleation. Besides, increase in dilution forms a thicker sphere of hydration around both the silicate / titano-silicate species. Before these reactive species condense, they have to strip off their hydration sphere. So increased dilution may lead to an increase in nucleation time and may retard crystallization.

3.2.2.6 Inorganic cation:

The presence of inorganic cations (Na^+, K^+, Cs^+, etc) has a tremendous role in the synthesis of TS-1. In general, inorganic cations (Na^+, K^+, Cs^+, etc) as well as organic strongly perturb the hydrogen bonding among the water molecules and orient them in a particular pattern around them. The smaller the size of the cation, greater is the charge density, greater the perturbation of the hydrogen bonded water molecules. Depending on whether these cations can organize the water molecules or not, they are defined as structure breaking and structure making. The small cations such as Li^+, Na^+, K^+, etc, are called structure making as they can reorganize the water molecules. Large cations like Cs^+, NH_4^+, etc are called structure breaking, as because of their low charge density they are not able to reorganize the water molecules. The silicate can replace these organized water molecules and aluminate species and cage like structure can be obtained. However, alkali and alkaline earth metals have a negative effect on the synthesis of TS-1. The presence of alkali cation prevents the incorporation of the Ti^{4+} in the silicalite lattice and favors the formation of extra-framework titanium species.

3.2.2.7 Promoter:

The addition of a small amount of certain oxyanions of group VA and VIIA (such as perchlorate, phosphate, arsenate, etc) to the synthesis mixture of zeolites significantly enhances the nucleation and crystallization process of silica based molecular sieves.

Various promoters reduce the synthesis time of different zeolites in a varying degree. A direct correlation was observed between the charge by radius ratio (Z/r) of the central cation of the promoter and the synthesis time of ZSM-5 prepared with that promoter. As the polarizing ability of the central cation increases, the synthesis time decreases. This is applicable not only to microporous aluminosilicates, but also to metallosilicates and also for mesoporous materials. In the synthesis of TS-1, phosphoric acid is used as promoter. Using phosphoric acid, TS-1 can be obtained within 6 h of the reaction at 160 ^{o}C.

3.3 Physico-Chemical Characterization:

There are several techniques for the characterization of different zeolites. Each technique is unique by itself and provides important information about the structure of a particular zeolite. The most commonly employed characterization techniques are power X-ray diffraction spectroscopy (PXRD), adsorption and surface area analysis, chemical analysis by energy dispersive X-ray (EDX), infrared spectroscopy (IR), ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM).

3.3.1 Powder X-ray diffraction (PXRD):

When a solid is isolated from a synthesis mixture, it is first analyzed by PXRD. The outcome of the PXRD of the material is the following,

- Uniqueness of structure
- Presence of single phase or mixture of phases
- Incorporation of other elements
- Level of crystallinity

From the unit cell volume expansion it is possible to predict about the incorporation of the metal in the framework. The incorporation of the larger titanium atoms will change the unit cell lattice parameter. Thus in TS-1, a, b and c values are 20.111Å, 19.997 Å and 13.385 Å compared to 20.101, 19.887 and 13.365 Å respectively for monoclinic silicalite-1.

3.3.2 Infrared Spectroscopy:

This is another experimental technique, which offers structural details of zeolite structure through different vibrational modes. Besides, it helps in measuring the acidity of the materials as well as for detection of isomorphous substitution in the framework. There are several techniques for recording IR spectra such as dilution with KBr, nujol mull, and selfsupported wafer40. The KBr dilution method is the most commonly employed method. The lattice vibrations of zeolites, normally, occur in the range 300-1300 cm^{-1}. The assignment that can be done from IR is given below,

Internal tetrahedra:	
Asymmetric Stretching:	1250 – 950 cm^{-1}
Symmetric stretching:	720 – 650 cm^{-1}
T-O Bending:	420 – 500 cm^{-1}
External linkages:	
Double ring:	650 – 550 cm^{-1}
Pore opening:	300 – 420 cm^{-1}
Symmetric Stretching:	750 – 820 cm^{-1}
Asymmetric Stretching:	1050 – 1150 cm^{-1}

Acid strength of zeolites can also be determined by FTIR spectroscopy in the absorption range 3600 – 3700 cm^{-1} (Brönstead acid sites) by using ammonia, pyridine, triphenyl phosphine, etc as probe molecules. Incorporation of metals also can be determined as an additional band at 960 cm^{-1} appears because of M-O-Si linkages (M = Metal). In the case of TS-1, it has two important regions in the IR spectrum. One the OH region and the other below 1000 cm^{-1}. In the region of OH vibrations it has got two major peaks. The first one at 3540 cm-1 is broad and the other one at 3728 cm^{-1} is sharp. However, these peaks can not be differentiated as to whether they are because of the titanol group or due to silanol group.

In the other region below 1000 cm^{-1}lattice structure bands appears at 805 and 555 cm^{-1}. All the titanium silicates exhibit one common feature in this region, a band at about 960- 970 cm $^{-1}$. Such a band is also found in the case of other metallo silicates where metal is in the framework position. Though there are lot of discrepancies regarding the assignment of this band, but it is generally accepted that this band is due to stretching vibration of Si-O bond perturbed by a neighboring Ti (IV) in the lattices position.

3.3.3 UV- Vis Spectroscopy:

This is particularly useful for metal incorporated zeolites i.e., metallosilicates. The absorption in the UV-Vis range arises because of the ligand to metal charge transfer. It helps to determine the co-ordination number of the metal in the zeolite. Thus for TS-1, the absorption at 215 nm is due to the transfer of charge from O^{-2} to tetrahedrally coordinated Ti^{+4}. With increase in co-ordination number, the charge-transfer band shifted to longer wave- length. TS-1 exhibits a charge transfer band at 205-220 nm due to the presence of isolated [TiO_4] or [TiO_3OH] moieties. This charge transfer occurs due to electron transfer from ligand oxygen to the vacant orbital of titanium ions in the framework. Therefore, it is directly related with the titanium incorporation in the framework position. So a change in the band position is directly related with the change in coordination state of Ti (IV) in the framework. Hence the presence of the band at ca. 210 nm is accepted as evidence for the presence of isolated Ti (IV) species whereas the band at 280-330nm, if present, is taken as the presence of extra-framework titanium species.

3.3.4 Scanning Electron Microscopy:

This is another important tool for characterization of the zeolite catalyst. The micrograph shows the morphology of the particle formed (e.g., cubic, circular, etc) as well as the presence of amorphous phase in the samples.

3.3.5 NMR Spectroscopy:

Nuclear magnetic resonance spectroscopy, both in the liquid state and in the solid state, is very important for determining the active species in the molecular level during synthesis of zeolites from aluminosilicate gels. Lippamaa et al. (1981) has shown that ^{29}Si MAS NMR is highly sensitive to the nature and chemical environments of the atoms. Considerable knowledge regarding the structure of the alumino-silicate has been gained through ^{27}Al and ^{29}MAS NMR.

3.3.6 Adsorption Measurement:

To determine the pore size distribution, pore volume and surface area, the adsorption of nitrogen is usually carried out over zeolites and related molecular sieves at low pressure (10 - 6 Torr) and low temperature (-196 ºC). The sieving property of a zeolite depends on its pore size, pore volume as well as surface area. The analysis of adsorption isotherm helps in determining the micropore volume and pore size distribution of the molecular sieves.

3.4. Catalysis:

The catalytic activity in zeolite and porous materials is governed, mainly, by diffusion process. The main processes governing the catalytic activity are,

- Transport of the reactant to the zeolite surface followed by diffusion of the reactant to an active site inside the pore / channel.
- Adsorption of the reactant to an active site.
- Chemical reaction of the adsorbed reactant to form adsorbed product(s).
- Desorption of the adsorbed product(s).
- Diffusion of the adsorbed products from interior active site to the outer surface of the catalyst.
- Transfer of the product(s) away from the zeolite surface.

3.4.1 Shape selectivity:

One of the interesting features of the heterogeneous solid catalysts is the shape selectivity of the reactions. Three types of shape selectivity are mainly observed in zeolite catalysis. The reactant shape selectivity, product shape selectivity and restricted transitionstate shape selectivity. The reactant shape selectivity arises because of the different dimensions of reactant molecules. When more than one reactant is involved in a reaction, that reactant, the molecular dimension of which fits the pore diameter/channel dimension of the zeolite, can enter and react. This is known as reactant shape selectivity. This type of shape selectivity is utilized in petrochemical chemistry where linear alkanes are cracked preferentially leaving aside the branched alkanes. When a number of products are formed inside the pores/channels of a zeolite, those products will diffuse out whose sizes are within the range of the pore diameter/channel dimension of the zeolite. The remaining heavyproducts will either break down to smaller molecules and will come out or they will deactivate the catalyst. This is known as product shape selectivity. Not all transition states are allowed to form inside the zeolite pore/channel. Only those transition states whose molecular dimension is within the dimension of the zeolite pore channel will be selectively formed. This is exhibited in the subsequent product distribution pattern. This is known as transition state shape selectivity.

3.4.2 Applications of TS-1:

Since its discovery in early 80’s TS-1 has been studied, mainly, as oxidation catalyst for a variety of reactions in presence of aqueous H_2O_2 as oxidant. Examples of TS-1 as oxidation catalysts are manifested in the following reactions,

- Oxyfunctionalization of alkanes.
- Hydroxylation of aromatics.
- Epoxidation of alkenes.
- Oxidation of alcohols.
- Oxidation of ethers.
- Ammoximation of carbonyl compounds.
- Oxidation of amines.
- In Bayer-Villiger oxidation to from lactones.

Other than its use as oxidation catalyst, it is also used in C-C bond formation and also used in diastereo-selective epoxidation of allylic alcohols.

Recently TS-1 has been used in presence of promoter like Pd to enhance its catalytic activity and selectivity. Sometimes TS-1 is used for N_2O decomposition. Selective oxidation of propylene to propylene oxide is done over Au supported on TS -1 in presence of H_2 and O_2.

3.4.3 Catalytic sites in TS-1:

TS-1 behaves as a unique oxidation catalyst in the presence of aqueous hydrogen peroxide in a variety of reactions. Therefore, naturally, the emphasis on is to find out the reactive species in variety of oxidation processes involving TS-1 and aqueous H_2O_2. By different characterization techniques it was proved that Ti- ion, in TS-1, was in +4 oxidation state and is in tetrahedral environment. There are several evidences that Ti^{+4} in the Td site in the framework is responsible for catalytic oxidation. But, however, the nature of the tetrahedral titanium species as well as the nature of the active species involved in the oxidation, still, has been the matter of discussion and debate. Recently Zecchina et al. have shown with the help of the EXAFS studies that there are at least two different kinds of tetrahedral framework titanium species in TS-1.

Several changes were observed when TS-1 is treated with aqueous H_2O_2.

- The white color of TS-1 turned yellow upon addition of aq. H_2O_2.
- There is a dramatic change in the UV-Vis absorption of the TS -1samples. The band at 212 nm decreases and 3 additional band appear at 305, 385 and 425 nm.
- A change in the IR spectrum is also observed. The intensity of the 960 cm^{-1} decreases and a new band at 870-800 cm^{-1} is formed. An anisotropic signal with gzz = 2.0238, gyy= 2.0099 and gxx=2.0030 is found in the E.S.R. spectra of the samples.

All these changes are completely reversible as heating or drying of the samples leads to the generation of the original samples. On the basis of all the above experimental results the following active species for TS-1 in presence of aq. H_2O_2 have been envisaged (Figure 3.3).

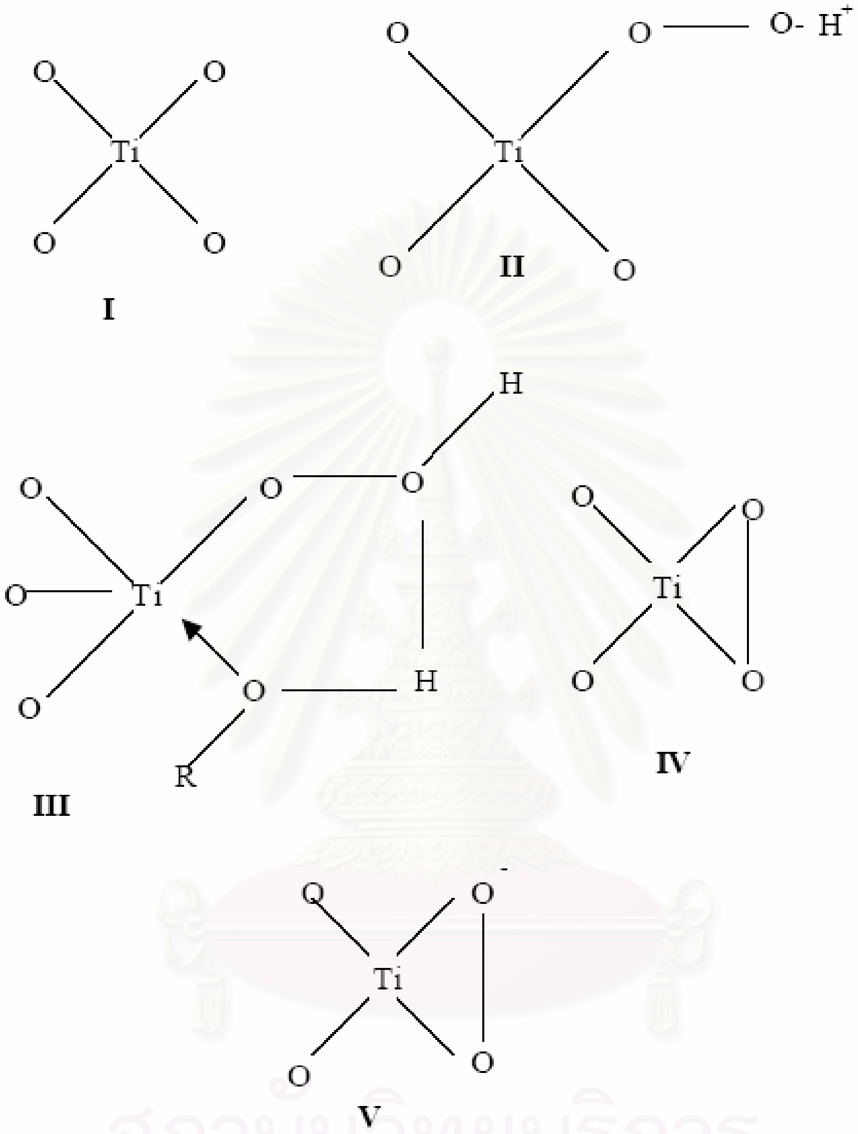


Figure 3.3 Different Potential Active Ti-Species

3.5 Reactions of alcohols

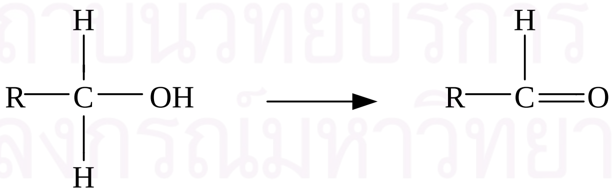
3.5.1 Oxidation States of Alcohols

- **Oxidation**: Reaction that causes a decrease in electron ownership at carbon bond formed between carbon and a more electronegative atom (Usually N, O, S or halogens). or bond broken between carbon and a less electronegative atom (Usually H).
- **Reduction**: Reaction that causes an increase in electron ownership at carbon bond broken between carbon and a more electronegative atom (Usually N, O, S or halogens) or bond formed between carbon and a less electronegative atom (Usually H).

3.5.2 Oxidation of Alcohols

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 can lead to aldehydes, ketones or carboxylic acids, depending upon the reaction conditions and the degree of substitution on the alcohol.

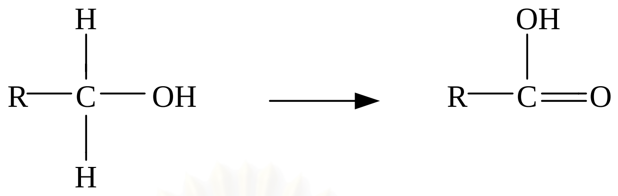
A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,



$$R-CH_2-OH \longrightarrow R-CH=O$$

A 1°alcohol An aldehyde

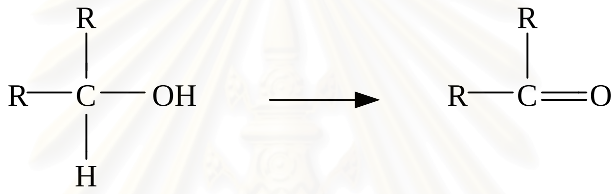
or both of them to form a carboxylic acid.



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

A 1° alcohol A carboxylic acid

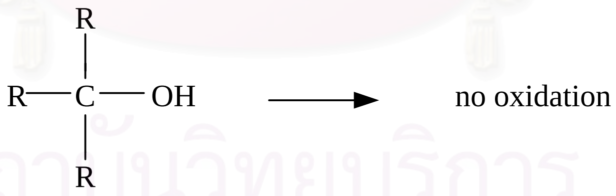
A secondary alcohol can lose its only α-hydrogen to form a ketone.



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

A 2° alcohol A ketone

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



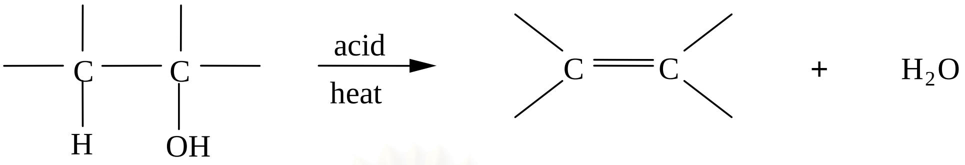
$$R-\overset{R}{\underset{R}{C}}-OH \longrightarrow \text{no oxidation}$$

A 3° alcohol

3.1.2 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).



Alcohol Alkene Water

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

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

CHAPTER IV

EXPERIMENTAL

The experimental in this chapter is divided into three major parts: (1) catalyst preparation, (2) catalyst characterization, and (3) reaction study in oxidation of 2-propanol. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure, surface properties, acidity of the catalyst characterised by various techniques such as XRD, BET, XRF, ESR, XPS, FT-IR, SEM, and NH_3-TPD are discussed in section 4.2. Finally, the details of the reaction study are illustrated in section 4.3.

4.1 Catalyst preparation

4.1.1 Chemicals

All chemicals used in this preparation procedure of Cu-TS-1 are following in Table 4.1.

Table 4.1 The chemicals used in the catalyst preparation

Chemical	Grade	Supplier
Titanium(IV) butoxide 97%	-	Aldrich
Tetrapropylammonium bromide 98%	-	Aldrich
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck
Cupric nitrate	Analytical	Aldrich

4.1.2 Preparation Procedures

The preparation procedure of Cu-TS-1 by rapid crystallization method is shown in Figure 4.1, while the reagents used are shown in Table 4.2.

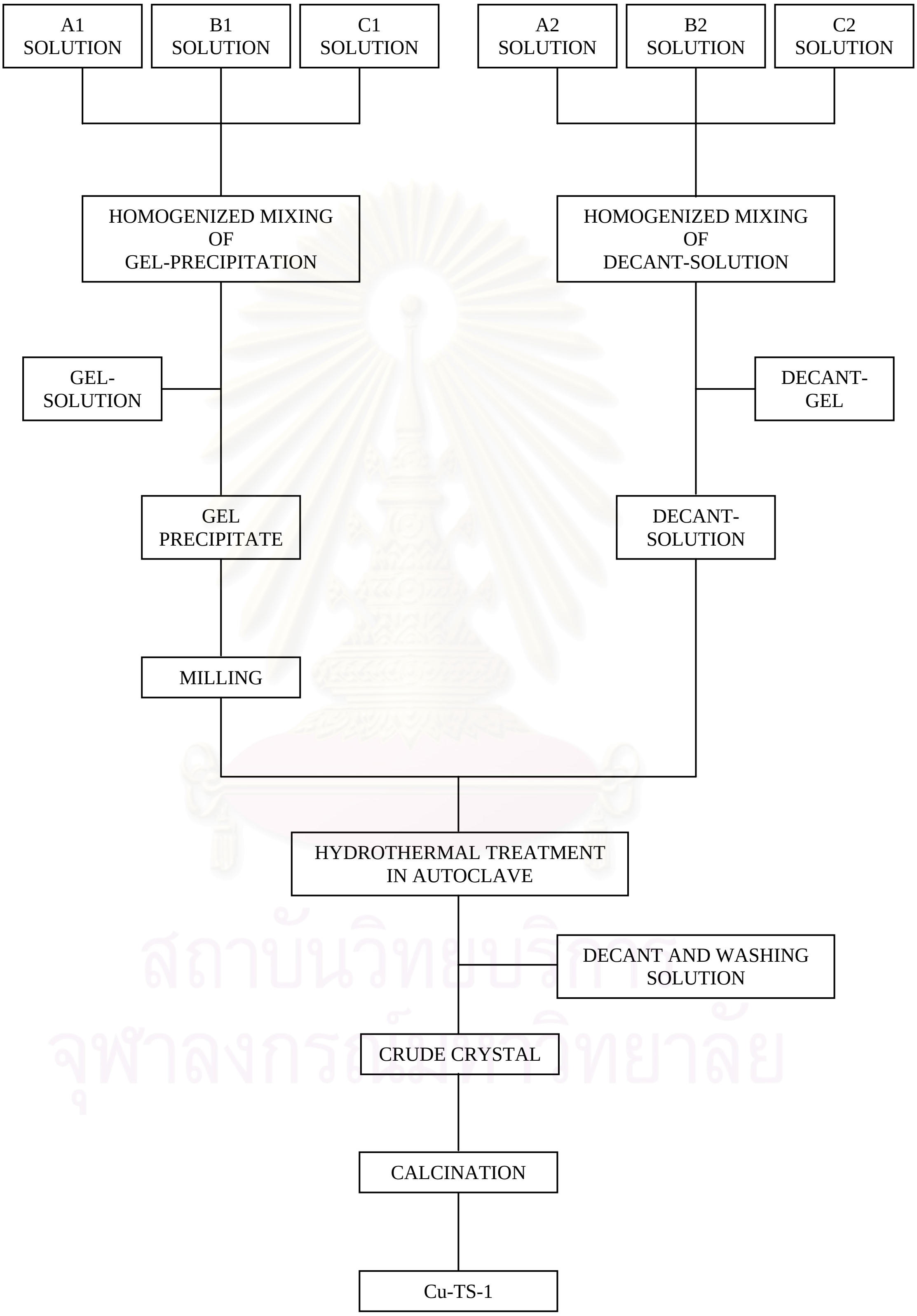


Figure 4.1 The preparation procedure of Cu-TS-1 by rapid crystallization method

Table 4.2 Reagents used for the preparation of Cu-TS-1 : Si/Ti = 52 (Appendix A)

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]_4$	2.2085	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Cu(NO_3)_2$	x	g	$Cu(NO_3)_2$	x	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
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			
H2SO4 (conc.)	1.55	ml			

4.1.2.1 Preparation of Gel Precipitation and Decantation Solution

The source of metals for preparation of decantation and gel solutions were $Cu(NO_3)_2$ for Cu , $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si, respectively.

TPABr (Tetra-n-Propyl Ammonium Bromide[$(CH_3CH_2CH_2)_4N$]Br) was used as organic template. The atomic ratio of Silicon/Titanium was set as 52. The preparation of supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. The detailed procedures were as follows: Firstly, a gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture was maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or NaOH solution were used to adjust pH of the gel mixture to an appropriate level if it was necessary. The gel mixture was separated from the supernatant liquid by a centrifuge. The precipitated gel mixture was milled for totally 1 hour. the milling was done for 15 min and then the supernatant solution was removed by centrifugal separation before the hydrothermal treatment in order to obtain the uniform, fine crystals. The milling procedure was as follows: milled 15 min → centrifuge (to remove liquid out) 15 min → milled 15 min → centrifuge 15 min → milled 30 min → centrifuge 15 min.

Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2, same as for the preparation of gel mixture. The supernatant liquids from A-2, B-2 and C-2 were mixed together with the milled gel mixture. However, before mixing, the pH of solution was maintained between 9-11. The colorless supernatant liquid was separated from the mixture by centrifugation.

4.1.2.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution was filled in a 500 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. Then, the autoclave was heated from room temperature to 160 ^oC with a heating rate of 2 $^oC/min$, and then heating up to 210 ^oC with a heating rate of 12 $^oC/h$ while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The product crystals were washed with de-ionized water by centrifugation in order to remove chloride out of the crystals. Then the crystals were dried in an oven at 110 ^{o}C for at least 24 h.

4.1.2.3 Calcination

The dry crystals were calcined in an air stream at 550 ^{o}C and held at that temperature for 7 h, by heating them from room temperature to 550 ^{o}C at heating rate of 8.6 ^{o}C/min, to burn off the organic template and leave the cavities and channels in the crystals. Then, the calcined crystals were finally cooled down to room temperature in a dessicator.

4.2 Catalyst characterization

4.2.1 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for fully control of XRD analyzer. The experiments were carried out by using Cu Kα radiation with Ni filter. Scans were performed over the 2θ ranges from 6^{o} to 40^{o}.

4.2.2 BET surface area measurement

Procedure

The carrier gas which mixed with 30 % nitrogen and 70% helium flowed through the system at the flow rate 15 mm/min. The sample 0.3 g was placed in the unit cell, which was heated up to 200 °C and held at this temperature for 1 hour to remove water in sample. Next step, the sample was cooled down at room temperature and ready to measure the surface area. There were two steps to measure the surface area.

(1) Adsorption step

The sample was dipped into a liquid nitrogen bath. Nitrogen was adsorbed on the surface of the sample until an equilibrium was reached. And then the equipment showed the adsorption peak area.

(2) Desorption step

A liquid nitrogen bath was moved away from the unit cell. In order to desorb nitrogen from the surface of sample, the nitrogen-adsorbed sample was blowed with fan. When this step was completed, the equipment showed the desorption peak area obtain from the Micromeritics Chemisorb 2750 analyzer.

(3) The BET surface area means the desorption peak area divided by weight of sample.

4.2.3 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst was performed by X-ray fluorescence (XRF) using Siemens SRS3400 at Scientific Intruments Service Centre, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang.

4.2.4 Electron spin resonance (ESR)

ESR measurements were made at room temperature on a JEOL, model JES-RE2X spectrometer operated at X-Band frequencies, 8.8-9.6 GHz Klystron frequencies, and 100 KHz magnetic field modulations. The simulation of the ESR spectra was performed with the program ES-IPRIT. The g and hyperfine splitting values use in this work are taken from the simulated spectra.

4.2.5 X-Ray photoelectron Spectra (XPS)

The chemical valence states of metals in the catalysts were measured by XPS technique using an AMICUS instrument with Mg Kα radiation as excitation source.

4.2.6 Fourier transform Infrared (FT-IR)

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 and then pressed into a thin wafer. Infrared spectra were recorded between 400 and 1300 cm^{-1} on a microcomputer

4.2.7 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to determine the catalyst granule morphology, using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 20 kV.

4.2.8 NH_3 Temperature Programmed Desorption (NH_3-TPD)

Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the acid properties of catalysts. NH_3-TPD were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550°C in helium flow for 1h and then saturated with 15 %NH_3/He mixture after cooling to 100 °C. After purging with helium at 100 °C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 °C at therate of 10 °C/min in a helium flow of 50 cm^3/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer

The deconvlution of NH_3-TPD peak was carried out with the “fityk” curve fitting programme. The peaks were assumed to be Gaussian with showness shape (using parameter ‘SplitGaussian’ in the programme).

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4.3 The catalytic activity measurements

4.3.1 Chemical and reagents

The reaction conditions are chosen as follows:

Catalyst : Copper/Titanium Silicalite-1
Catalyst weight : 0.1 g.
Reactant : 2-propanol
Feed composition : 2-propanol 5 vol%, Oxygen 8 vol%, Argon balance
Flow rate of reactant : 100 ml/min
Reaction temperature : 100-500°C
Space velocity : 60,000 $g^{-1}h^{-1}$

4.3.2 Instruments and Apparatus

4.3.2.1 Reactor: Flow diagram of the reaction system is shown in Figure 4.2. The system consists of a saturator, a microreactor, an electrical furnace, and a gas controlling system. The liquid phase reactant was filled in the saturator. Air is passed through the evaporator to carry the reactant to the microreactor.

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

4.3.2.2 Automation temperature controller: This unit consists of a magnetic switch connected to a variable voltage transfer and a temperature controller connected to a thermocouple attached to the catalyst bed in the reactor.

4.3.2.3 Gas supplying system: This unit consists of cylinders of ultra high purity 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.

4.3.2.4 Gas Chromatographs : 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 4.3 Operating conditions for gas chromatograph.

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

4.3.3 Oxidation procedure

The 2-prapanol oxidation was carried out by using a apparatus shown in Figure 4.2. A 0.1 gram portion of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

The procedure used to operate this reactor is as follows :

1. Adjust the outlet pressure of argon, and air to 1 kg/cm^2 , and allow the gas to flow through a rotarymeter. The outlet gas flow rate was measured by using a bubble flowmeter. 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% 2-propanol, 8 vol% oxygen and balance with argon .

2. Heat up the reactor by raising the temperature stepwise from 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, acetone, CO and CO_2 by calibration curves in Appendix D.

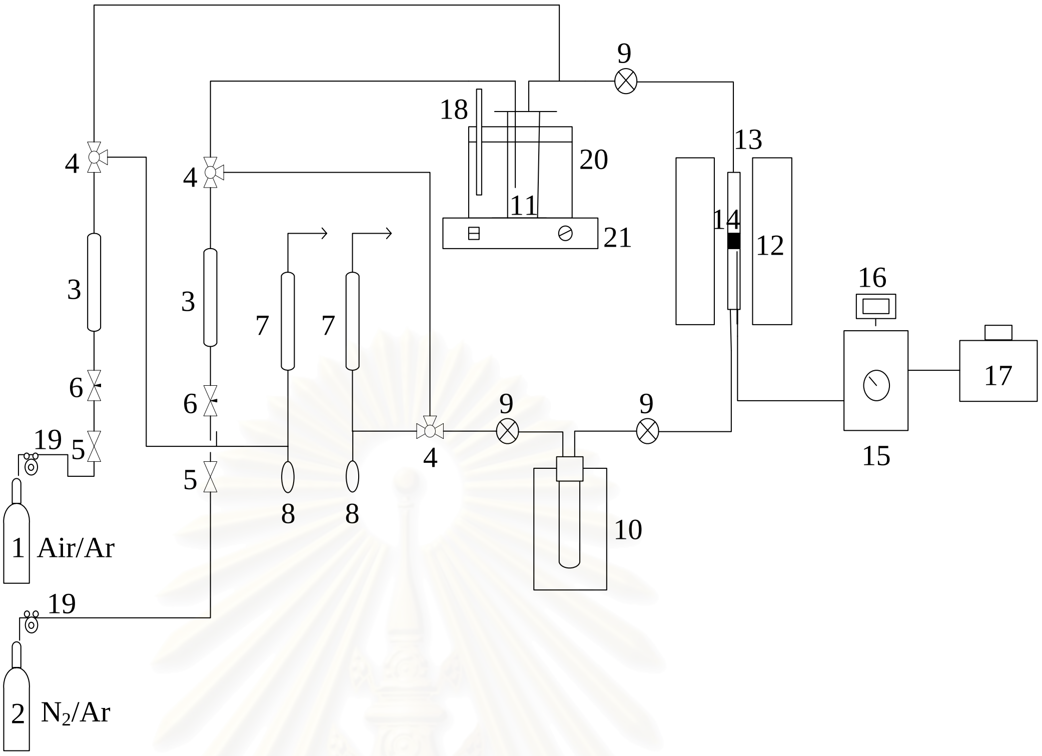
3. The result of catalytic test was calculated in the term of

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

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

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

Where, A is reactant
B is product



1. Air cylinder
2. Ar cylinder
3. Mass flow controller
4. Three-way-valve
5. Ball 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 4.2 Flow diagram of the oxidation reaction system.

CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two sections. In the first section, the catalyst characterization using XRD, BET, XRF, ESR, XPS, IR, SEM and NH_3-TPD is described. Next, the catalytic oxidation reaction of 2-propanol is discussed.

5.1 Characterization of synthesized samples.

5.1.1 X-Ray Diffraction Analysis

An important issue in the characterization of metal-substituted zeolites is establishing that the metal is, in fact, being incorporated into the lattice. Figure 5.1 shows the powder x-ray diffraction (XRD) of TS-1 and Cu silicalite-1 samples.

Figure 5.1 shows the XRD patterns of TS-1 zeolite. The XRD pattern shows six main peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 26.7. The pattern obtained is the pattern typical for a crystalline zeolite having a MFI structure. [The JCPDS (1996)] The result indicates that the catalyst contained well-defined single-phase and is consistent to those already reported for TS-1 [(Taramasso et al., (1983)]. Although the peaks are identified to that of TS-1, it shows less crystalline compared with the TS-1 synthesized employing the recipe in the original patent. This difference suggests that the methodology of catalyst preparation has some influences on the crystal structure of TS-1 catalyst.

Since the catalysts prepared in the laboratory by rapid crystallization method have the same XRD patterns. This indicated that the addition of copper into the framework of the catalysts does not change the main structure. Thus the XRD patterns are not changed.

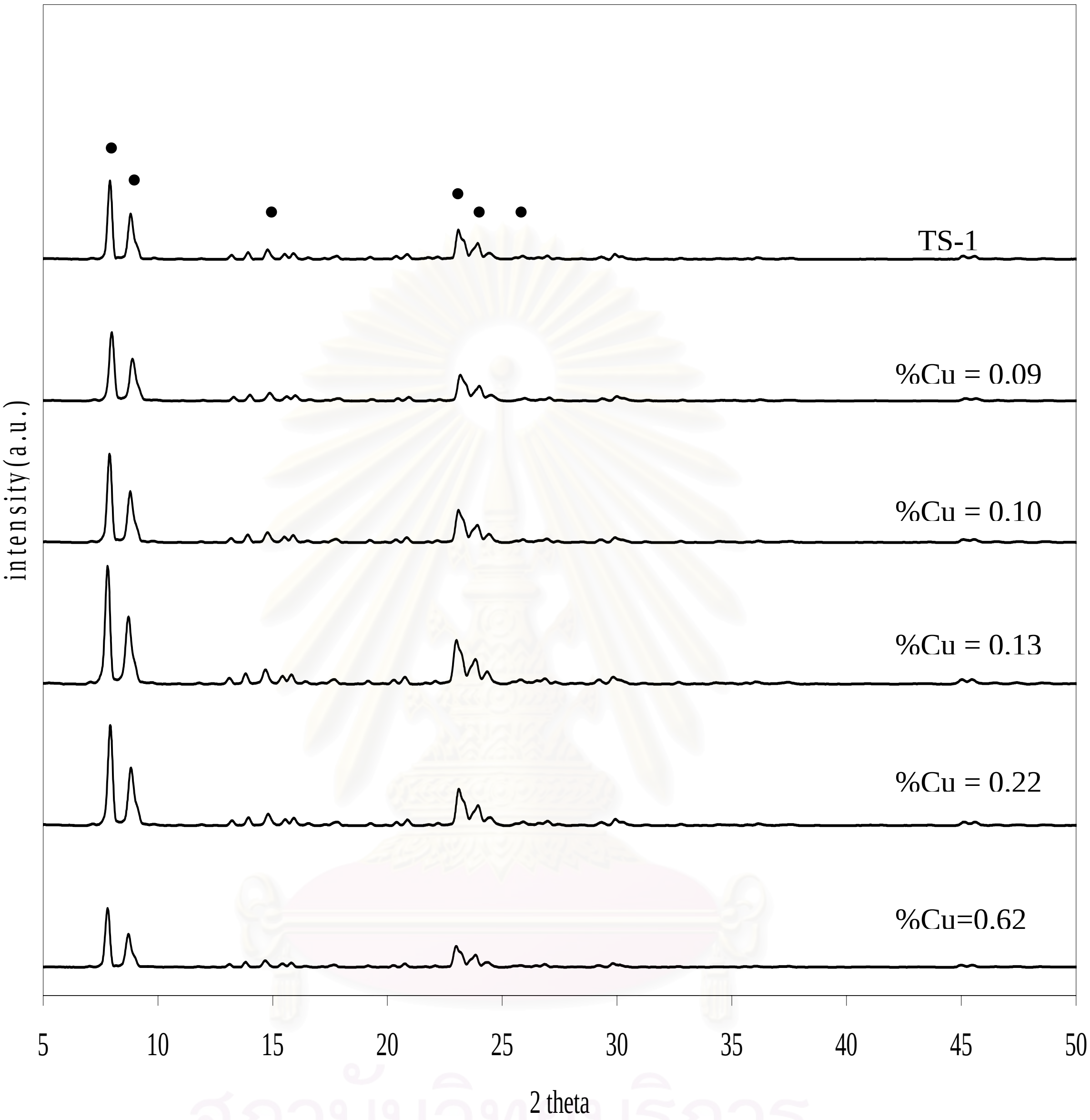


Figure 5.1 XRD spectra of the TS-1 zeolite

5.1.2. Surface area and porosity

The summary of the surface area and porosity of the samples are given in Tables 5.1. The data in the table encompass surface areas derived from the BET and Langmuir isotherms and porosity measurements by the BJH (Barrett, Joyner, Halenda) method which distinguishes the surface area and pore volume associated with pores of >17 Å diameter and the same parameters associated with micropores smaller than that. The micropores encompass the channels of the TS-1 zeolite. It is seen that almost Cu-TS-1 zeolite has only negligible changes in either the surface area or the porosity of the TS-1. Introducting of 0.62 mol% Cu into the zeolite leads to a small change in microporosity without a measurable loss of surface area.

Table 5.1 Surface area and Porosity of six samples TS-1, Si : Ti ratio 1:73

Catalyst	BET area (m^2/g)	Langmuir area(m^2/g)	Surface area(m^2/g)		Pore volume (cm^3/g)		
			BJH desorption	Micropore	17–3000 Å BJH desorption	Micropore	Single point total
TS-1	323.4	429.2	164.4	189.6	0.105	0.086	0.195
Cu-TS-1 (Cu:0.09 mol%)	300.6	398.8	180.2	201.5	0.150	0.093	0.209
Cu-TS-1 (Cu:0.10 mol%)	315.4	418.6	150.0	188.2	0.109	0.088	0.188
Cu-TS-1 (Cu:0.13 mol%)	311.2	412.6	148.8	191.7	0.129	0.089	0.205
Cu-TS-1 (Cu:0.22 mol%)	310.7	412.0	180.0	173.8	0.154	0.083	0.216
Cu-TS-1 (Cu:0.62 mol%)	302.0	401.5	132.1	163.7	0.096	0.075	0.177

5.1.3 Chemical Composition

X-Ray Fluorescence Spectrometer (XRF) was used, for the quantitative determination of the Cu, Ti, and Si contents in the modified TS-1 sample

The obtained results of the determination of the copper concentration in the synthesized samples of Cu-TS-1 are given in table 5.2

Table 5.2 XRF analysis of Cu-TS-1

Catalyst	%Si	%Ti	Si/Cu	Ti/Cu	Si/Ti
TS-1	32.15	0.441	none	none	72.78
Cu-TS-1 (Cu:0.09 mol%)	31.58	0.630	346.0	6.907	50.09
Cu-TS-1 (Cu:0.10 mol%)	31.96	0.487	307.2	4.648	65.53
Cu-TS-1 (Cu:0.13 mol%)	31.98	0.495	246.7	3.819	64.59
Cu-TS-1 (Cu:0.22 mol%)	31.94	0.478	146.3	2.191	66.78
Cu-TS-1 (Cu:0.62 mol%)	31.93	0.341	52.76	0.553	93.49

In Table 5.3, the measured concentrations of Cu in some samples of zeolite Cu-TS-1 are given. As can be seen, Si/Cu and Ti/Cu decreased from 346.0 to 52.46 and 6.907 to 0.553, respectively. Following the increase of the copper concentrations added in the synthesized procedure. Again, the copper offered to the gel is incorporated into the solid zeolite products.

5.1.4 ESR Measurements

Electron spin resonance (ESR) is a method to investigate the Cu(II) species in the catalysts. The room temperature ESR spectra of Cu-TS-1 catalysts are reported in Figure. 5.2

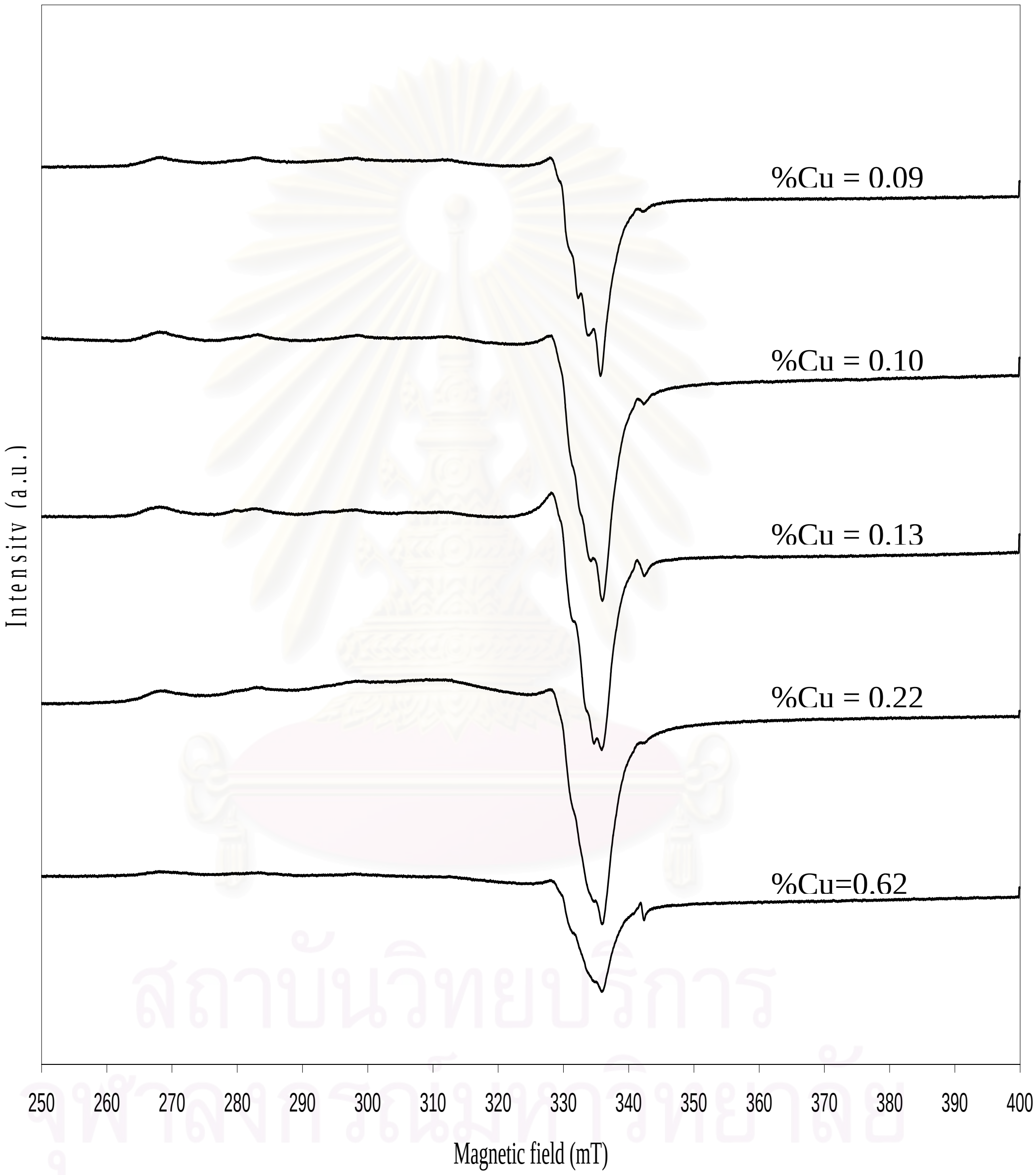


Figure 5.2 ESR profiles of Cu-TS-1 catalysts

A strong axially symmetric signal (*g* = 2.03) is obtained for Cu-TS-1 catalyst. The axially symmetrical signals, which are generally attributed to highly dispersed or isolated Cu(II) species interacting with the support, have been reported in the ESR studies. [Wang, et al. (2003)] The parameters $g_{xx} = g_{yy} = 2.03$ are close to the ones reported for highly dispersed Cu (II) coordinated with lattice oxygen of the support [Giamello, et al. (1992)] The phenomena suggest that highly dispersed Cu (II) species prevail in the Cu-TS-1 catalyst and that clusters are also present. $g_{xx} = g_{yy} = 1.96$ [Bonneviot, et al. (1988)] is the signal of only one type of cupper, incorporated into the network.

5.1.5 X-Ray photoelectron Spectra (XPS)

Chemical states of various elements on the surface were analyzed by the XPS technique. The preliminary results are shown in Table 5.3. The binding energy shift of each element is calculated using C 1s peak at 285 eV as reference. The binding energy of Cu 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(0.13) in which the binding energy shift of Cu is about zero. This indicates that Cu in Cu-TS-1(0.13) may exists as Cu^0 while Cu in Cu-TS-1(0.09) Cu-TS-1(0.10), Cu-TS-1(0.22) and Cu-TS-1(0.62) is likely to exist in the form Cu^{2+}.

Table 5.3 Binding energy (B.E.) of Copper 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)
Cu $2p_{3/2}$ (ref)	932.7	
Cu-TS-1(Cu:0.09mol%)	933.5	0.80
Cu-TS-1(Cu:0.10mol%)	933.9	1.20
Cu-TS-1(Cu:0.13mol%)	932.6	-0.10
Cu-TS-1(Cu:0.22mol%)	933.7	1.00
Cu-TS-1(Cu:0.62mol%)	933.5	0.80

Cu-TS-1 samples present the Cu $2p_{3/2}$ peak: near 933 eV associated with the CuO species. [Cordoba, et al. (1998)] These signals are accompanied by the typical satellite peaks characteristic of Cu (II). The peak intensity assigned to CuO decrease and its position is shifted to 933.5, 933.9, 933.7, and 933.5 in Cu-TS-1 (Cu:0.09mol%), Cu-TS-1(Cu:0.10mol%), Cu-TS-1(Cu:0.22mol%),and Cu-TS-1(Cu:0.62mol%) respectively, but Cu-TS-1(Cu:0.13mol%) assigned to CuO increase and its position is shifted to 932.6 eV. The existence of CuO is also observed by ESR.

5.1.6 Fourier transform Infrared (FT-IR)

A comparative IR spectrometric study was performed to obtain information concerning the existence of framework titanium. It is well known that the vibrational spectrum of TS-1 is characterized by an absorption band in the 900–975 cm^{-1} region [Taramasso, et al. (1983)]. It has been suggested that the presence of a 960–975 cm^{-1} band is a necessary, but not sufficient, condition for catalytic activity [Huybrechts, et al. (1991)]. Thus, defective orthorhombic silicalites, with fully hydroxylated nanocavities generated by extraction of a few adjacent (SiO_4) units, have been characterized by an extra-broad IR absorption at *ca*. 970 cm^{-1}. [Perego, et al. (1986)]

As shown in Figure 5.3., IR spectra of TS-1 and Cu-TS-1 catalyst exhibit the absorption band at the same position as TS-1. This can be indicated that the amount of copper on TS-1 are much less to observe the changes in IR bands.

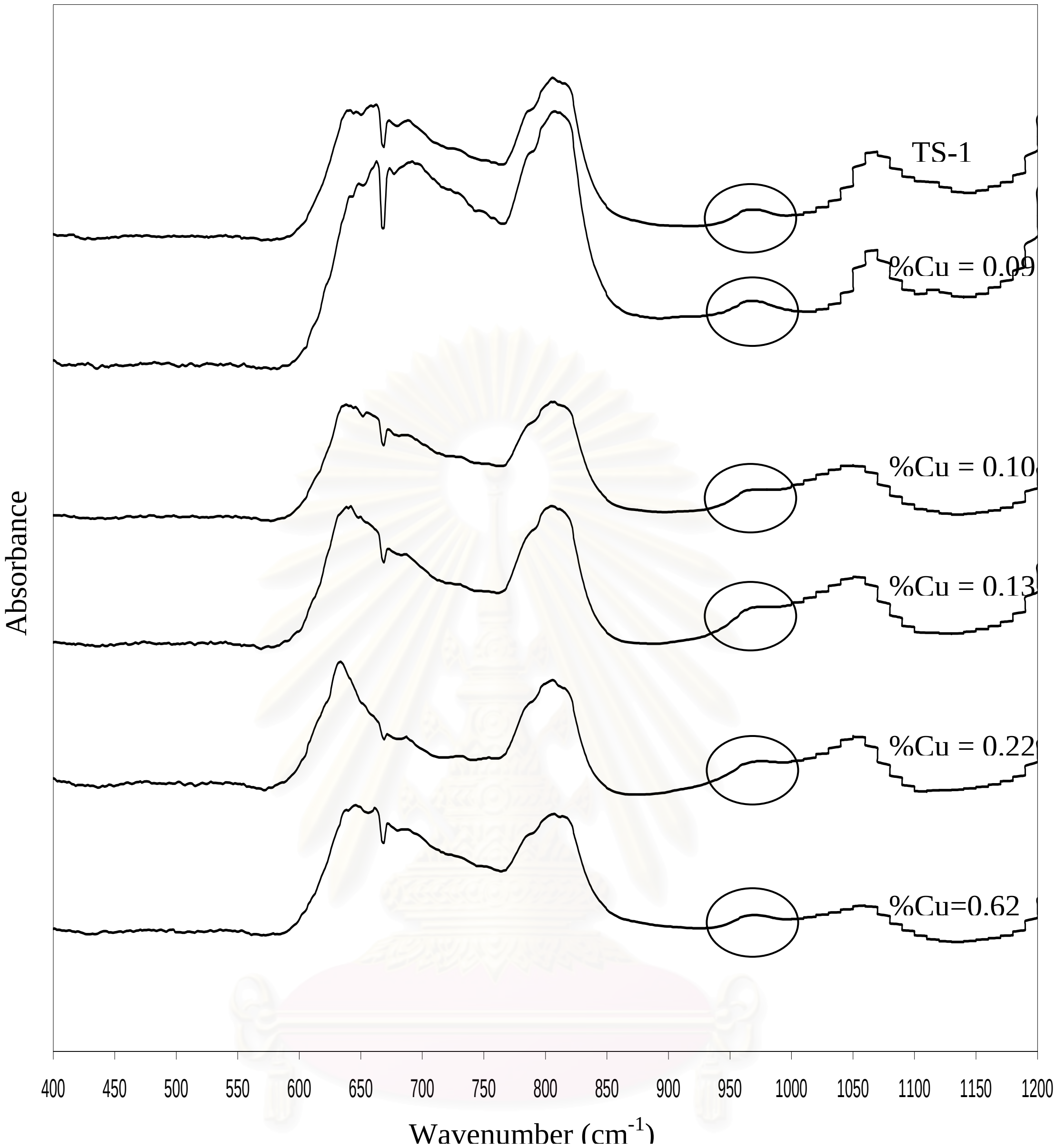
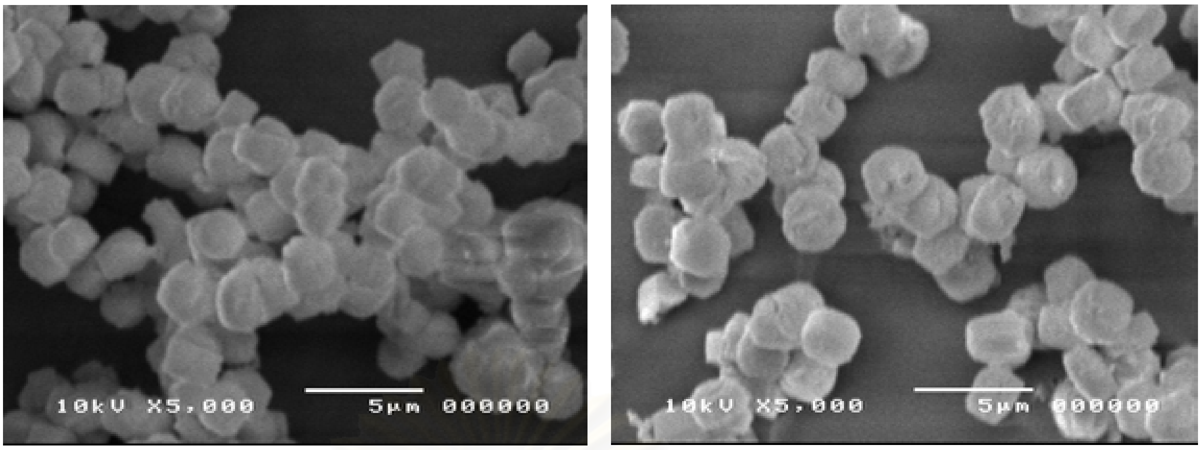


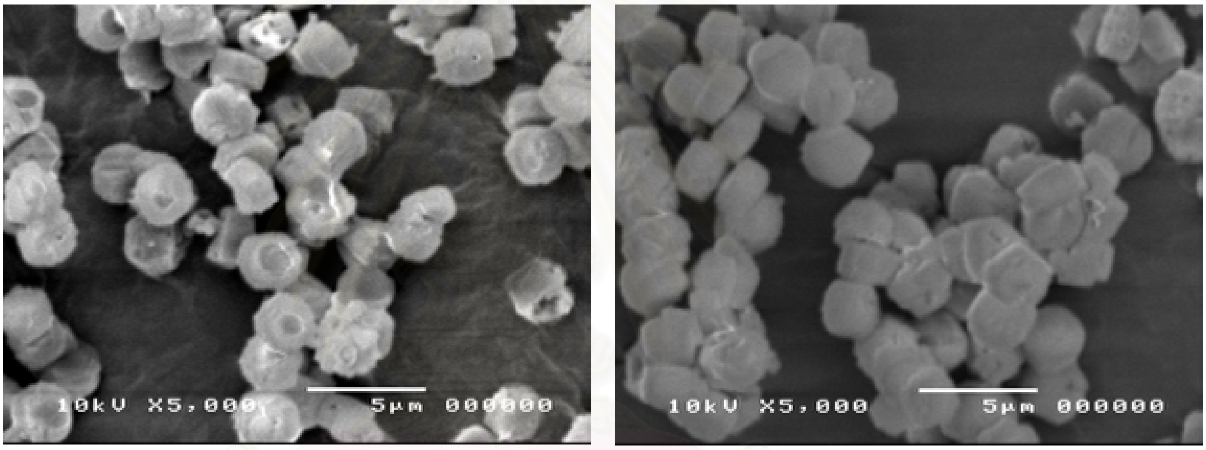
Figure 5.3 Ex-situ IR spectra of the synthesized TS-1 and Cu-TS-1

5.1.7 Morphology

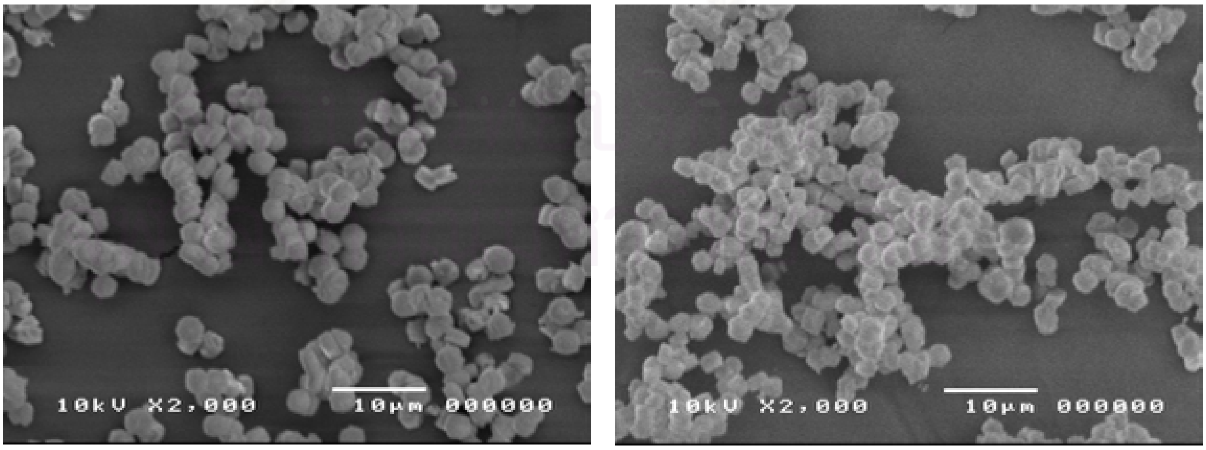
Scanning electron microscopy (SEM) is used to determine the catalyst granule morphology. Figure 5.4 displays scanning electron micrographs of TS-1 and Cu-TS-1. The crystalline morphology was nearly spherical sample. These particles were not neatly crystallized, the outer surface was covered with something looks like amorphous gel. It is suggested that this amorphous gel occurs during the catalyst preparation. It has an influence on the characteristic of TS-1 catalyst. The particle size is almost identical (2-3 μm).



TS-1 Cu-TS-1 (0.09%mol)



Cu-TS-1 (0.10%mol) Cu-TS-1 (0.13%mol)



Cu-TS-1 (0.22%mol) Cu-TS-1 (0.62%mol)

Figure 5.4 SEM photographs of catalyst granule

5.1.8 Acidity

The TPD profiles of desorbed ammonia from TS-1 and modified Cu-TS-1 are shown in Figure 5.5.

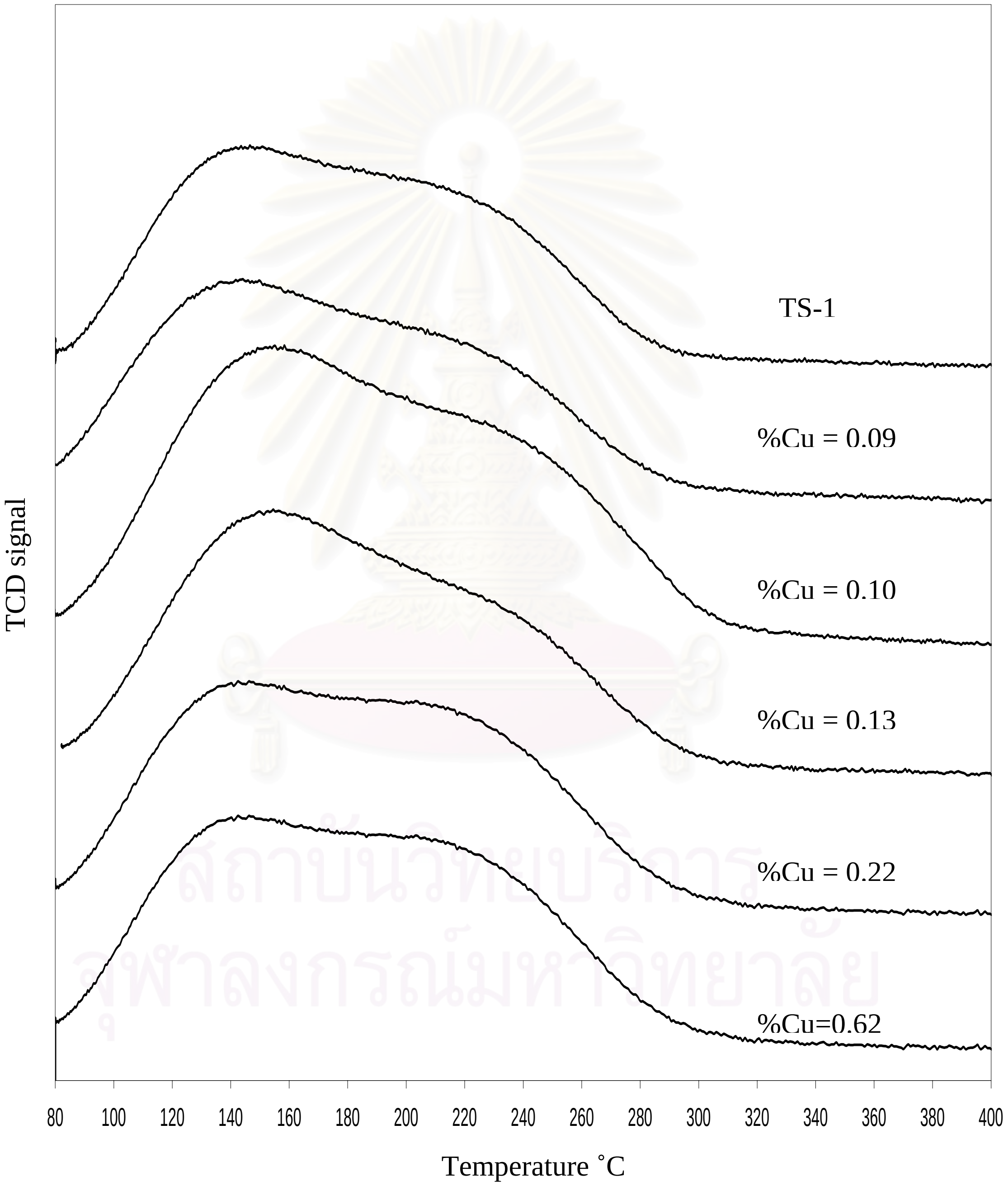


Figure 5.5 TPD profile of desorbed NH_3 from the catalysts

Table 5.3 Acid site of catalyst

Catalyst	Peak number	Max. temp ^{o}C	Acid site(umol/g)	Total Acid site(umol/g)
TS-1	1	127.6	131.4	
	2	217.4	103.2	234.6
Cu-TS-1 (Cu :0.09mol%)	1	132.2	118.2	
	2	223.35	91.54	209.7
Cu/TS-1 (Cu :0.10mol%)	1	146.6	189.7	
	2	242.6	98.52	288.2
Cu/TS-1 (Cu :0.13mol%)	1	145.3	142.91	
	2	232.3	93.06	235.9
Cu/TS-1 (Cu :0.22mol%)	1	134.5	109.6	
	2	223.3	91.88	201.4
Cu/TS-1 (Cu :0.62mol%)	1	134.6	133.7	
	2	224.6	106.58	240.2

The profile is composed of two main peaks. The low temperature peak ,will be named here “the weak acid site”, is found around 120-145 ˚C and the high temperature peak, will be named here the “strong acid site”,was found at around 220-240 ˚C. In Table 5.4, the total acid sites of the catalysts are found around 200-290 μmol/g.

The data on the table can separate from equation in fit ky program (see in appendix D)

5.2 Catalytic reaction

The catalytic activity and product selectivities of 2-propanol over TS-1 catalyst, is shown in figure 5.6a, the conversion of 2-propanol rapidly increased in the reaction temperature range 250-350 ˚C. The conversion rises up to about 98% conversion at about 400 ˚C. It is found that the main products of this system are acetone, carbon dioxide, and propylene. The amount of acetone was higher in the low reaction temperature range. At 500 ˚C, the product selectivities of acetone, carbon dioxide, and propylene are 58.35%, 29.44%, and 12.21%, respectively.

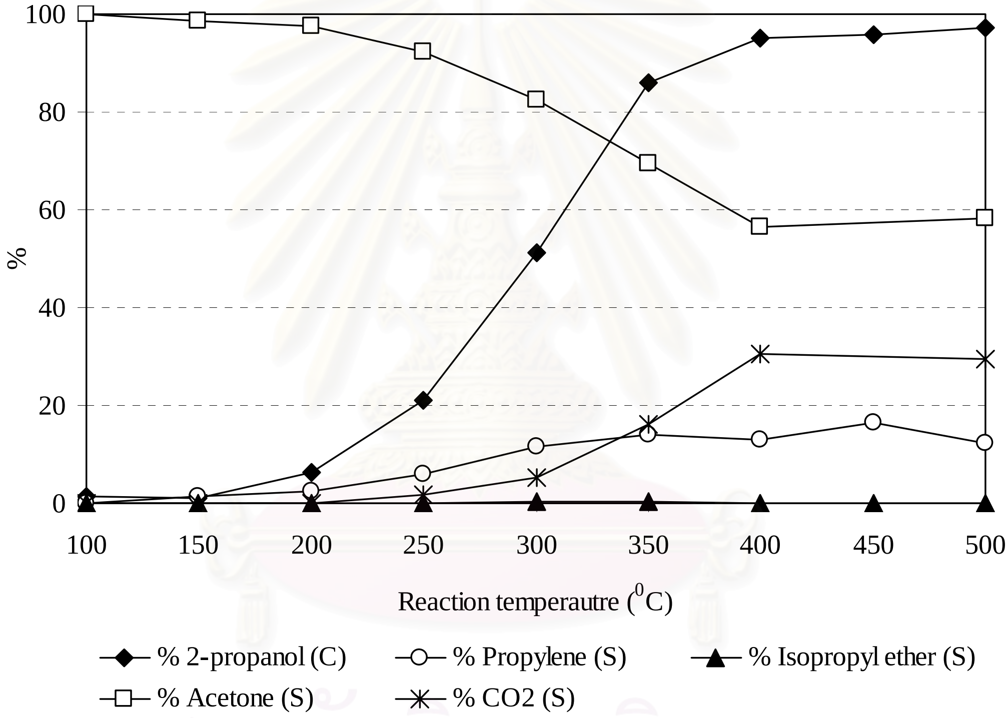


Figure 5.6a Product selectivity and conversion of 2-propanol over TS-1, Si/Ti=72.78 (C-Conversion, S-Selectivity)

The effects of reaction temperature on the catalytic activity and product selectivities of 2-propanol over Cu-TS-1 catalysts with Cu:0.09mol%, Cu:0.10mol%, Cu:0.13mol%, Cu:0.22mol%, and Cu:0.62mol% of copper concentration in Cu-TS-1, are shown in Figures 5.6b-5.6f respectively. It is found that the main products of this system are also acetone, carbon dioxide, and propylene. All of these catalysts, acetone is the only primary product with selectivity about 100% in the reaction temperature range 100-150˚C while carbon dioxide became significant in the reaction temperature above 300˚C. The maximum selectivities towards carbon dioxide are obtained at vary temperature.(30.49% in 450˚C, 33.26% in 400˚C, 41.28% in 350˚C, 25.89% in 300˚C and 30.99% in 300˚C for 0.09, 0.10, 0.13, 0.22, and 0.62 mol% Cu concentration in Cu-TS-1, respectively). This behavior indicates that carbon dioxide is the secondary product likely be produced via the further oxidation of acetone. It is believed that acetone is the primary oxidation product, which is produced directly from the 2-propanol oxidation reaction.

From these results, it can be concluded that acetone can be produced from the direct oxidation of 2-propanol reaction. But the formation of the dehydration was not totally excluded. The less of propylene formation shows that the oxidation well occurs than the dehydration. The reduction of propylene formation in the high reaction temperature region is possibly because of the fast oxidation of 2-propanol to acetone. Therefore, there was no enough 2-propanol to produced propylene.

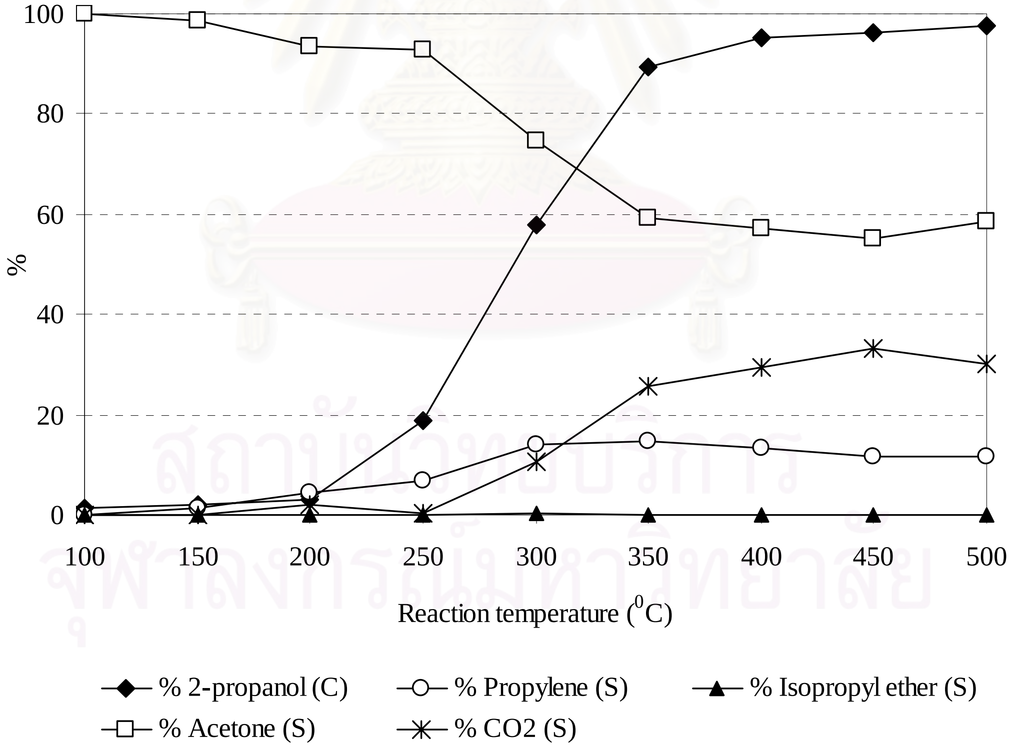


Figure 5.6b Product selectivity and conversion of 2-propanol over Cu-TS-1 (Cu:0.09mol %), (C-Conversion, S-Selectivity)

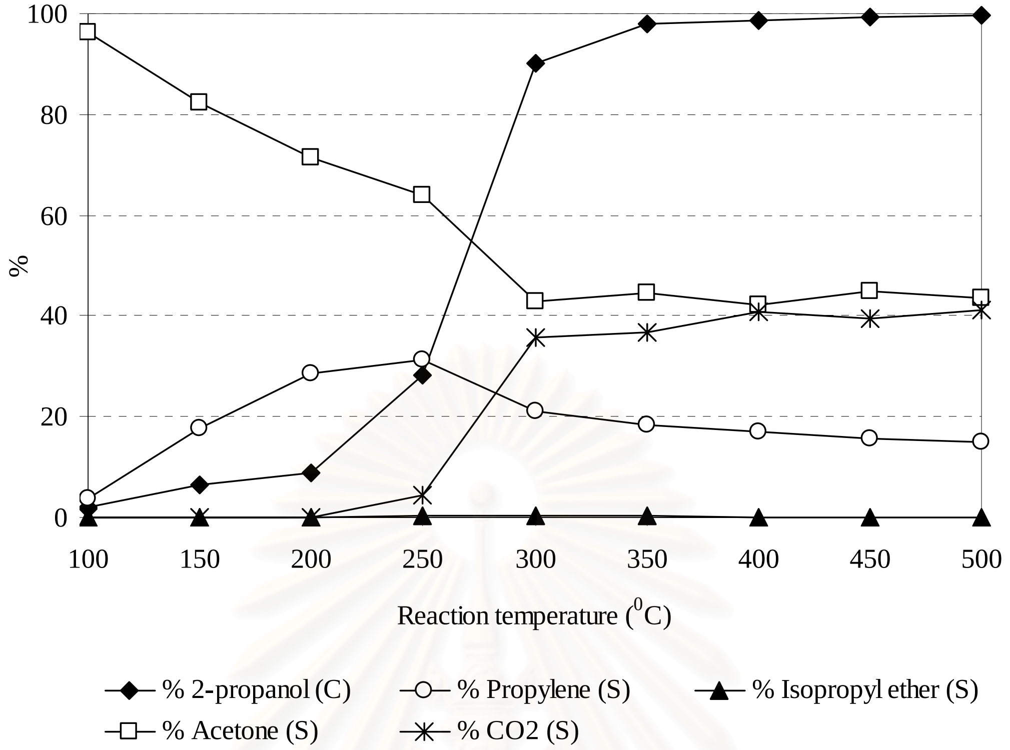


Figure 5.6c Product selectivity and conversion of 2-propanol over Cu-TS-1 (Cu:0.10mol%), (C-Conversion, S-Selectivity)

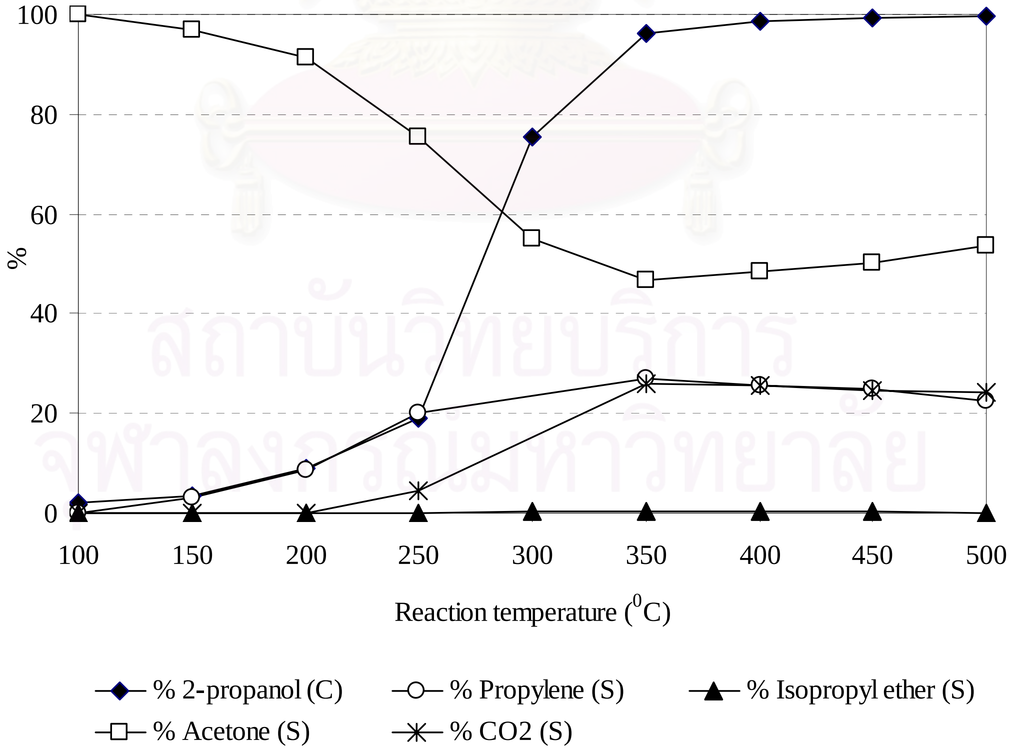


Figure 5.6d Product selectivity and conversion of 2-propanol over Cu-TS-1 (Cu:0.13mol%), (C-Conversion, S-Selectivity)

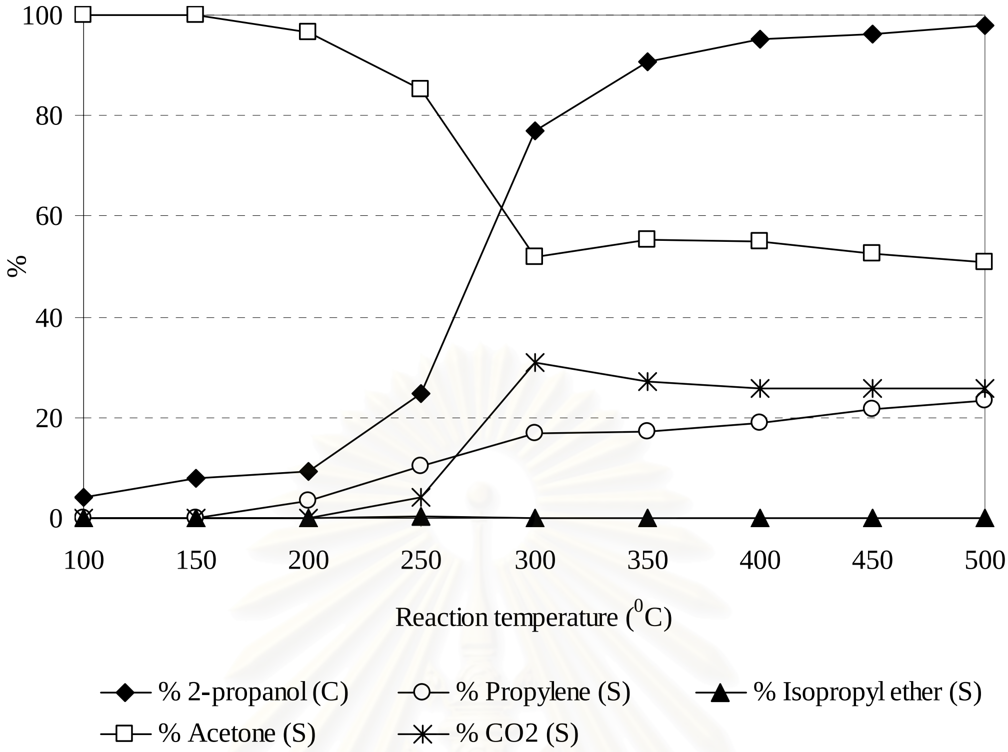


Figure 5.6e Product selectivity and conversion of 2-propanol over Cu-TS-1 (Cu:0.22mol %), (C-Conversion, S-Selectivity)

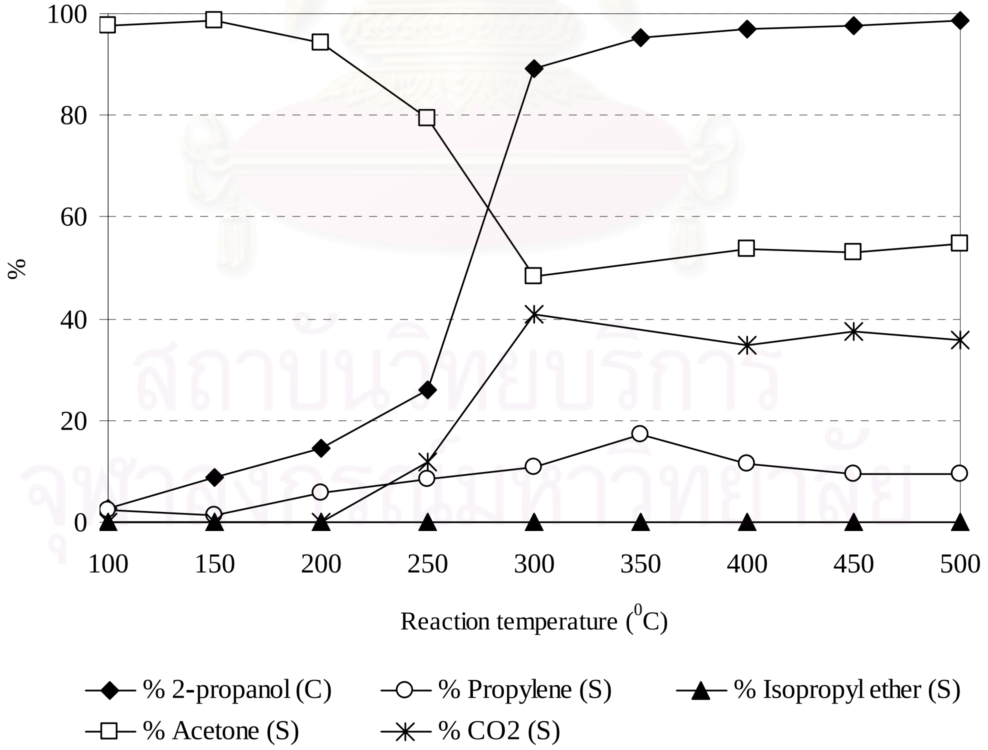


Figure 5.6f Product selectivity and conversion of 2-propanol over Cu-TS-1 (Cu:0.62mol%) ,(C-Conversion, S-Selectivity)

From all of the explained experimental results the pathway of product formation in 2-propanol oxidation reaction can be summarized in Figure 5.7. The pathway is as same as the pathway of TS-1 that ever present by Chairut (2004)

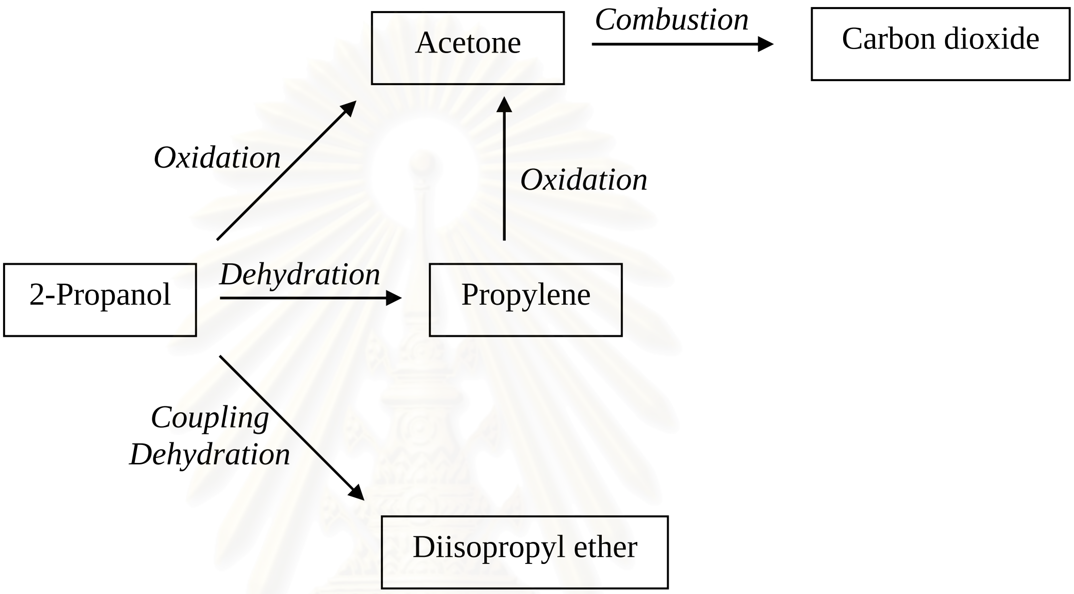


Figure 5.7 Schematic pathway of product formation in 2-propanol oxidation reaction.

5.3 Discussion

The catalytic activity of Cu-TS-1 in 2-propanol oxidation is higher than the activity of TS-1catalysts. The addition of Cu, by incorporation to TS-1 catalyst does not lead to unexpected effects. It strongly improved the catalytic activity for 2-propanol oxidation and to a small extent the high activity for 2-propanol dehydration. For this reason, the discussion will be mainly on the characteristics of the Cu-TS-1.

The TS-1 catalyst has a complex nature. During the preparation of the catalysts by incorporation, copper ions could be localized at different positions in the TS-1 structure: form a part of the TS-1 structure (from the ESR results), on the TS-1 outer surface (from the XPS results), and form crystalline and/or amorphous titania surfaces (no clear evidence in the present study, but in some reports this possibility can not be excluded [Petrov L. et al. (1996)]. As a result of this Cu distribution, the Cu-TS-1 catalyst will consist of several Cu-containing components of different nature and with different catalytic properties. This complicated composition does not allow one to obtain a clear idea on the reason for the strong enhancement of the Cu activity in Cu-TS-1 catalyst, but several suggestions can be put forward:

1. The specific influence of the TS-1 structure is due to the Cu ions located within the TS-1 structure.
2. The existence of synergism between Cu ions located within the TS-1 structure and Ti ions from the TS-1 framework.
3. The enhanced catalytic activity is due to exist Cu ions supported on titania located inside the TS-1 structure or on the outer surface of TS-1 crystals.
4. The formation of some active component from Cu supported on the outer surface of the TS-1.

The possible influence of these factors to the overall catalytic activity Cu-TS-1 catalyst is discussed in detailed below.

5.3.1 Catalyst composition

The amount of copper located in TS-1 is rather low, according to Table 5.2. During the hydrothermal synthesis of TS-1, copper is incorporated in an amount of

0.09-0.62 mol% from the total amount of TS-1 obtained. Copper exists on TiO_2 in two principal forms CuO phase (from the ESR results) and surface complexes of Cu ions with titania (from the XPS results, [Cordoba, et al. (1998)]). The latter is produced by interaction with the acidic OH groups of TiO_2. The conclusion obtained from this discussion is that the concentration of the Cu component in selective 2-propanol oxidation is very small and practically does not have influence on the catalytic properties of TS-1 catalyst.

The surface area Cu-TS-1 in vary concentration is about the same as of TS-1 since the amount of Cu incorporated in TS-1 is very small (see Table 5.2).

5.3.2 Cu-titanium silicalite

The titanium silicalite TS-1 contains small percentage of Ti “substituting site” in the MFI structure, 0.441%Ti in TS-1 and 0.341-0.630 %Ti in Cu-TS-1. The structure of the calcined TS-1 is orthorhombic [Thangaraj, et al. (1992)]. In this thesis, SEM photographs (Figure 5.4) show that all the prepared samples have a rather uniform orthorhombic shape with crystallite sizes in the range 2-3 μm.

The framework composition of TS-1 can be defined as a $\alpha TiO_2 \cdot (1-\alpha) SiO_2$ with α varying between 0 and 0.025. The inventors of TS-1 have reported that the value of $\alpha = 0.025$ is an upper limit for the incorporation of Ti in the silicalite structure and the excess Ti segregate as TiO_2 (anatase) and amorphous TiO_2 phase. [Thangaraj, et al. (1992)]

At least two different titanium species are present in TS-1 [Clerici, et al. (1991)]. The first consists of isolated titanium atoms located in channels. The second one consists of small TiO_2, (anatase) particles located in pore channels. According to Deo, et al. (1993), the type of titania phases present in the titanium silicalite depends on Ti content. When $\alpha < 0.016$ titania particles are not detected and titania presents as dispersed TiO_x, phase and when $\alpha > 0.016$, six coordinated TiO_2 (anatase) particles and dispersed TiO_x, phase are present.

The values of α, calculated from data in Table 5.3, vary from 0.010 to 0.019 in six samples. It indicated that Ti can incorporation in the silicalite structure too. One of these, Cu: 0.09mol% with $\alpha > 0.016$, shows the possibility of the existence of TiO_2 phase.

The Ti^{4+} ions present in TS-1 are different from those present in TiO_2-SiO_2. The first coordination shell of titanium in TS- 1 consists of four oxygen atoms at the distance of 1.80 Å in tetrahedral symmetry. According to Pei, et al. (1993), there is no evidence for the existence of 5- and 6-coordinated titanium species. TS- 1 is a weak acid and has organophilic character [Clerice et al. (1991)]. The presence of Ti in framework position does not substantially modify, compared to ZSM-5.

From the discussion presented above it follows that several possibilities exist for inserting Cu ions in the titanium silicalite framework due to incorporation or due to formation of surface complexes. At least part of the Cu ions located within the zeolite framework are incorporated and connected either with Ti-O-Si bridges as surface complexes or with some of the acidic -OH groups. A part of the incorporated Cu may locate in the defect places of the zeolite structure.

5.3.3 Catalytic activity

The strong enhancement of the selective oxidation activity of Cu-TS-1 compared with TS-1 can be explained by acid site and acid strength of Cu by migration processes within the zeolite structure. One could expect some similarity between the mechanism of this process and the above-mentioned data for Cu location within the TS-1 zeolite. In the case of TS- 1, other factors should also be taken into consideration. Part of the Cu ions can be kept within zeolite channels in the same way as in the case of TS-1, but a part can be bonded in some way to the existing Ti atoms or ions which leads to the enhancement of the 2-propanol oxidation and to the depress of the 2-propanol dehydration. It has been observed experimentally that Cu locates within the TS-1 framework, by recording the ESR spectra of Cu-TS-1 at different conditions. Freshly prepared Cu-TS-1 catalyst evacuated at room temperature (Figure 5.2) gives a signal with g = 2.03 which corresponds to the Cu^{2+} located in isolated position, probably within the TS-1 framework. The Cu located on the outer surface of the zeolite crystals can be better analyzed by XPS. Cu-TS-1 samples present the Cu $2p_{3/2}$ peak: near 933 eV associated with the CuO species in the outer surface.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

With careful experimental works, the effects of copper concentration on the physicochemical properties of TS-1 prepared by incorporation method, the characteristics of the corresponding Cu-TS-1 catalysts and there catalytic activity for 2-propanol oxidation were extensively investigated. The following conclusions can be drawn:

1. TS-1 can be successfully modified by copper incorporation. From the present study, it shown that copper(II) ions exist in three different environments in the samples. Isolated copper(II) ions incorporated into the titania network were detected by ESR spectroscopy, while two different copper(II) superficial species-one isolated on the titania surface and the other forming highly dispersed small CuO aggregates were observed by ESR, and XPS.

2. Cu-TS-1 prepared by the incorporation method with various Cu contents in the starting solution possess similar particle size (2-3μm) and surface area (300-315 m^2/g)

3. Similarities between structure, properties and catalytic activity of TS-1 and Cu-TS-1 catalysts exists.

4. The chemical composition of the zeolite framework plays a decisive role in determining the catalytic properties of the Cu containing catalysts.

5. Copper enhance the oxidation of 2-propanol, and/or acetone to carbondioxide due probably to higher acid strength.

6.2 Recommendations for future studies

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

1. Study the efficiency of Cu-TS-1 catalyst in other reaction such as reduction of nitrogen oxide, epoxidation of propylene with H_2 and O_2, and selective hydroxylation of benzene to phenol.

2. Study modified Cu-TS-1 by deposition precipitation, ion-exchange, and impregnation method.

3. Because the acid property influences the catalytic property, the role of Brönsted/Lewis acid site should be further studied.

REFERENCES

Bhaumik, A., Mukherjee, P., andKumar, R., Direct Hydroxylation of Benzene, *Catal.*, 1998, **178**, 101-107

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

Bonneviot, L., and Hakker, L., EPR characterization of Ti $^{3+}$ ions at the metal-support interface in Pt/TiO$_2$ catalysts, *Catal.*, 1988, **113**, 96 .

Centi, G., Cerrato, G., D'Angelo, S., Finardi, U., Giamello, E. Morterra, C., and Perathoner, S, Catalytic behaviour and nature of the active sites in Copper-on-Zirconia catalysts for the decomposition of N$_2$O, *Catal.*, *Today*, 1995, **27**, 265.

Clerici, G., a, Bellussi, and Romano, U., Highly Selective Epoxidation of 1-Pentene with HO over TS-1, *J. Catal.*, 1991, **129**, 159.

Clerici, M.G., b, and Ingallina, P., Highly Selective Epoxidation of 1-Pentene with HO over TS-1, *Catal.*, 1993, **140**, 71.

Cordoba, G., Viniegra, M., Fierro, J. L. G., Padilla, J., and. Arroyo, R., TPR, ESR, and XPS Study of Cu^{2+} Ions in Sol–Gel-Derived TiO$_2$, *Solid, State, Chem.*, 1998, **138**, 1-6.

Deo, G., Turel, A.M., Wachs, I.E., Huybrechts, D.R.C., and P.A. Jacobs, Characterization of Titania Silicalite, *Zeolites*, 1993, **13,** 365.

Giamello, E., Murphy, G., Magnacca, C., Morterra, M., Anpo, T., Nomura, Y., and Shyoya, The interaction of NO with copper ions in ZSM5. An EPR and IR investigation, *Catal.*, 1992, **136**, 510.

Gregor Jenzer, Tamas Mallat, Marek Maciejewski, Florian Eigenmann, and Alfons Baiker, Continuous epoxidation of propylene with oxygen and hydrogen on a Pd–Pt/TS-1 catalyst, *Appl. Catal., A*, 2001, **208**, 125-133.

Gao, H., Lu, G., Suo, J., and Shuben L., Epoxidation of allyl chloride with hydrogen peroxide catalyzed by titanium silicalite 1, *Appl. Catal., A*, 1996, **138**, 27-38.

Guo, X., Ruipu Wang, R., Wang, X., and Hao, J., Effects of preparation method and precipitator on the propylene epoxidation over Ag/TS-1 in the gas phase, *Catal., Today*, 2004, **93-95**, 211-216.

Hayashibara, H., Nishiyama, S., Tsuruya, S., and Masai, M., The effect of alkali promoters on Cu-Na-ZSM-5 catalyst in the oxidation of benzyl alcohol, *Catal.*, 1994, **153**, 254-264.

Huybrechts, D.R.C. a, De Bruycker, L., and Jacobs, P.A. a, Factors influencing the catalytic activity of titanium silicalites in selective oxidations, *Nature*, 1990, **345**, 240.

Huybrechts, D. R. C. b, Vaesen, I., Li, H. X. and Jacobs, P. A. b, Factors influencing the catalytic activity of titanium silicalites in selective oxidations, *Catal. Lett.*, 1991, **8**, 237-244.

Honglin, W., Xinwen, G. & Xiangshen, W., Fenzi Cuihua, Solvent-free, triphase catalytic oxidation reactions over TS-1 /H_2O_2 system, *Stud. Surf. Sci. Catal.*, 1998, **12**, 321.

Kraushaar-Czarnetzki, B., and Van Hooff, J.H.C., A Test Reaction for Titanium Silicalite Catalysts, *Catal. Lett.*, 1988, **2**, 43-48.

Landong Li a , Jixin Chena, Shujuan Zhang a, Naijia Guana, Tianyou Wang b, Shuliang Liu b, Selective catalytic reduction of nitrogen oxides from exhaust of lean burn engine over in situ synthesized monolithic Cu–TS-1/cordierite, *Catal. Today*, 2004, **90**, 207–213.

Li, G., Wang, X., Guo, X., Liu, S., Zhao, Q., Bao, X., and Lin, L., Titanium species in titanium silicalite TS-1 prepared by hydrothermal method, *Mater. Chem. Phys*, 2001, **71**, 195-201.

Notari, B., Highly Selective Epoxidation of 1-Pentene with HO over TS-1, *Catal. Today.*, 1993, **18**,163.

Pei, S., Zajac, G.W., Kaduk, J.A., Faber, J., Boyanov, B.I., Duck, D., Fazzini, D., Morrison T.I., and Yang, D.S., In Situ Characterization of Catalysts Active in Partial Oxidations: TS-1 and Fe-MFI Case Studies, *Catal. Lett.*, 1993, **21**, 333.

Perego, G., Bellussi, G., Corno, C., Taramasso, M., Buonomo, F. and Esposito, A., Titanium-silicalite: a noval derivative in the pentasil family, *Stud. Surf. Sci. Catal.*, 1986, **28**, 129-136.

Petrov, L., Soria, J., Dimitrov, L., Cataluna, R., Spasov L., and Dimitrov, P., Cu exchanged microporous titanium silicalite (TS-1) coated on polycrystalline mullite fibres as catalyst for the CO and NO conversion, *Appl., Catal., B*, 1996, **8**, 9-31.

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

Rafael van Grieken, David P. Serrano, Juan Antonio Melero, and Alicia García, Effect of the solvent in the liquid phase rearrangement of 1,2-epoxyoctane over Al-MCM-41 and Al-TS-1, *Mole. Catal., A*, 2004, **222**, 167-174.

Schuster, W., Niederer, John P.M., and Hoelderich, W F., The gas phase oxidative dehydrogenation of propane over TS-1, *Appl. Catal., A*, 2001, **209**, 131-143.

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

Taylor, B., Lauterbach, J., and Delgass, W.N., Gas-phase epoxidation of propylene over small gold ensembles on TS-1, *Appl. Catal., A*, 2005, **291**, 188-198.

Thangaraj, Eapen, M.J., Sivasanker, S., and Ratnasamy, P., “Titanium Containing Molecular Sieves as Catalysts for Selective Oxidation Reactions with Hydrogen Peroxide” *Zeolite*s, 1992, **12**, 943.

Tuel, A., Moussa-Khouzami, S., Ben-Ta~xit, Y., and Naccache, C., Selective oxidation reactions over titanium and vanadium metallosilicate molecular sieves, *J. Mol. Catal*., 1991, **68**, 45.

Uguina, M.A., Ovejero, G., Grieken, R. van., Serrano, D.P, and Camacho, M., The Molecular Sieves Materials for Shape-Selective Catalysis and High Selectivity Catalysis, *Chem. Commun*., 1994, **27**, 29.

Van der Pol, A.J.H.P., and van Hooff, J.H.C., Oxidation of linear alcohols with hydrogen peroxide over titanium silicate 1, *Appl. Catal., A*, 1993, 106, 97.

Wang, Z., Liu, Q., Yu, J., Wu, T., Wang, G., Surface structure and catalytic behavior of silica-supported copper catalysts prepared by impregnation and sol–gel methods, *Appl. Catal., A*, 2002, **241,** 7-10.

Wang, R., Guo, X., Wang, X., Hao, J., Li, G. and Xiu, J., Effect of preparation conditions and reaction conditions on the epoxidation of propylene with molecular oxygen over Ag/TS-1 in the presence of hydrogen, *Appl. Catal., A*, 2003, **261**, 7-13.

Weitkamp, J., Ermst. S., Roland, E. and Thiele, G. F., The modified hydrophobicity index as a novel method for characterizing the surface properties of titanium silicalites, *Stud. Surf. Sci. Catal*., 1997, **105**, 763-770.

Xinbin Ma, Jinlong Gong, Shengping Wang, Fei He, Hongli Guo, Xia Yang, and Genhui Xu, Characterization and reactivity of stannum modified titanium silicalite TS-1 catalysts for transesterification of dimethyl oxalate with phenol, *Appl. Catal., A*, 2005, **237**, 1-8.

Yamashita, H., Matsuoka, M., Tsuji, K., Shioya, Y., Giamello, E., Che, M., and Anpo, M., In situ investigation on the interaction of NO and CO with Cu+/ZSM-5 catalyst, *Stud. in Surf. Sci. and Catal.*, 1995, **92**, 227.

Yap, N., Andres, R.P., and Delgass, W.N., Reactivity and stability of Au in and on TS-1 for epoxidation of propylenewith H_2 and O_2, *Catal., 2004,* ***226***, 156–170.

Zecchina, A., Spoto, G., Bordiga, S., Padovan, M., Leofanti, G., and Pertini, G., Hydroxylation of phenol over Ti-MCM-41 and TS-1, *Stud. Surf. Sci. Catal*., 1992, **65**, 120.

Zhang, G., Sterte, J & Schoeman, B., Discrete Colloidal Crystals of. Titanium Silicalite-1, *Chem.Soc.Chem.Commun*, 1995, **22**, 2259.

APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of Si/Ti Atomic Ration for TS-1

The calculation is based on weight of Sodium Silicalite ($Na_2O^{\cdot}SiO_2{}^{\cdot}H_2O$) in B1 and B2 solutions (Topic 4.1.2).

Molecular weight of Si = 28.0855

Molecular weight of SiO_2 = 60.0843

Weight percent of SiO_2 in sodium Silicate = 28.5

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

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

$$= 69 \times (28.5/100) \times (1/60.0843)$$

$$= 0.3273$$

For example, to prepare TS-1 at Si/Ti atomic ratio of 52 by using $Ti[O(CH_2)_3CH_3]_4$ for Ti source.

Molecular weight of Ti = 47.88

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

Weight percent purity of $Ti[O(CH_2)_3CH_3]_4$ = 97

Si/Ti atomic ratio = 52

mole of $Ti[O(CH_2)_3CH_3]_4$ required = 0.3273/52

= 6.29×10^{-3} mole

amount of $Ti[O(CH_2)_3CH_3]_4$ = $6.29 \times 10^{-3} \times 340.36\ (100/97)$

= 2.2085 g

which used in A1 and A2 solutions.

For example, to prepare Cu-TS-1 at Si/Cu atomic ratio of 10 by using $Cu(NO_3)_2$ for Cu source.

Molecular weight of Cu = 63.54
Molecular weight of $Cu(NO_3)_2$ = 187.6

Si/Cu atomic ratio = 10

mole of $Cu(NO_3)_2$ required = 0.3273/10
= 3.273×10^{-2} mole
amount of $Cu(NO_3)_2$ = $3.273 \times 10^{-2} \times 187.6$
= 6.14 g

which used in A1 and A2 solutions.

APPENDIX B

CALIBRATION CURVE

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

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

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

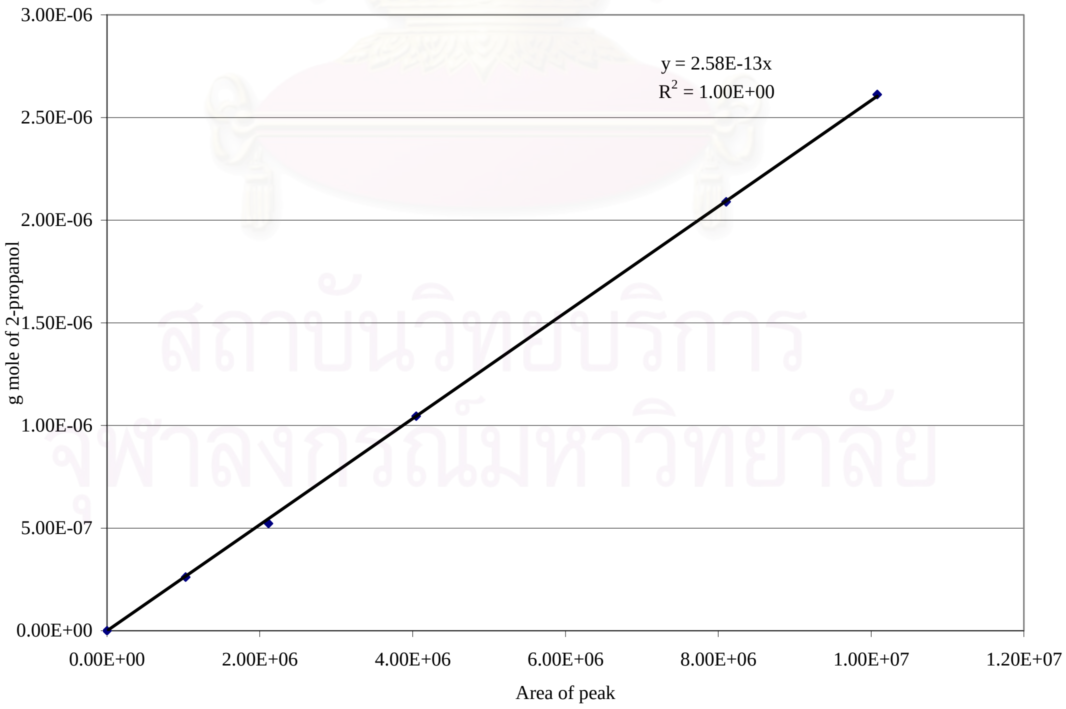


Figure B1 The calibration curve of 2-propanol

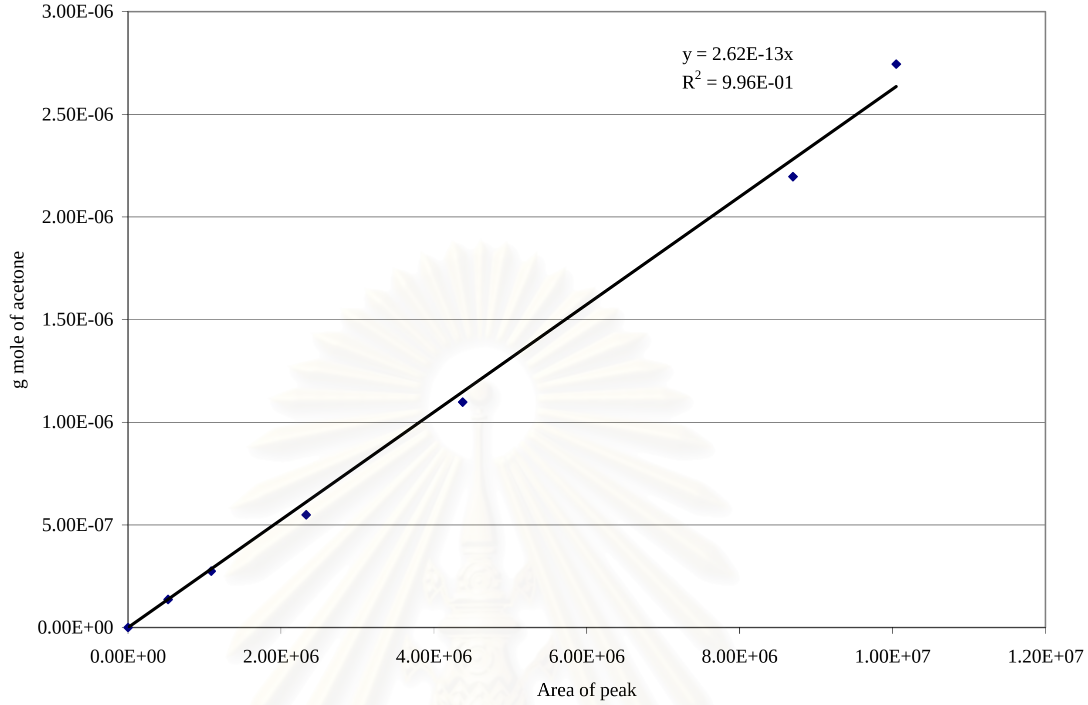


Figure B2 The calibration curve of acetone

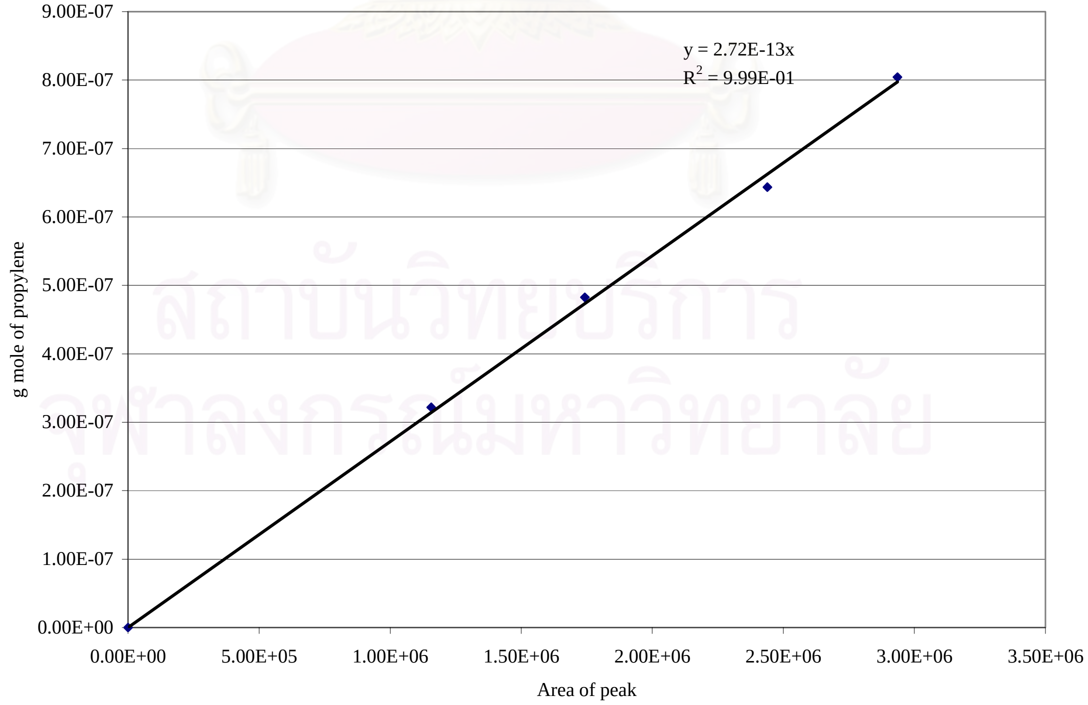


Figure B3 The calibration curve of propylene

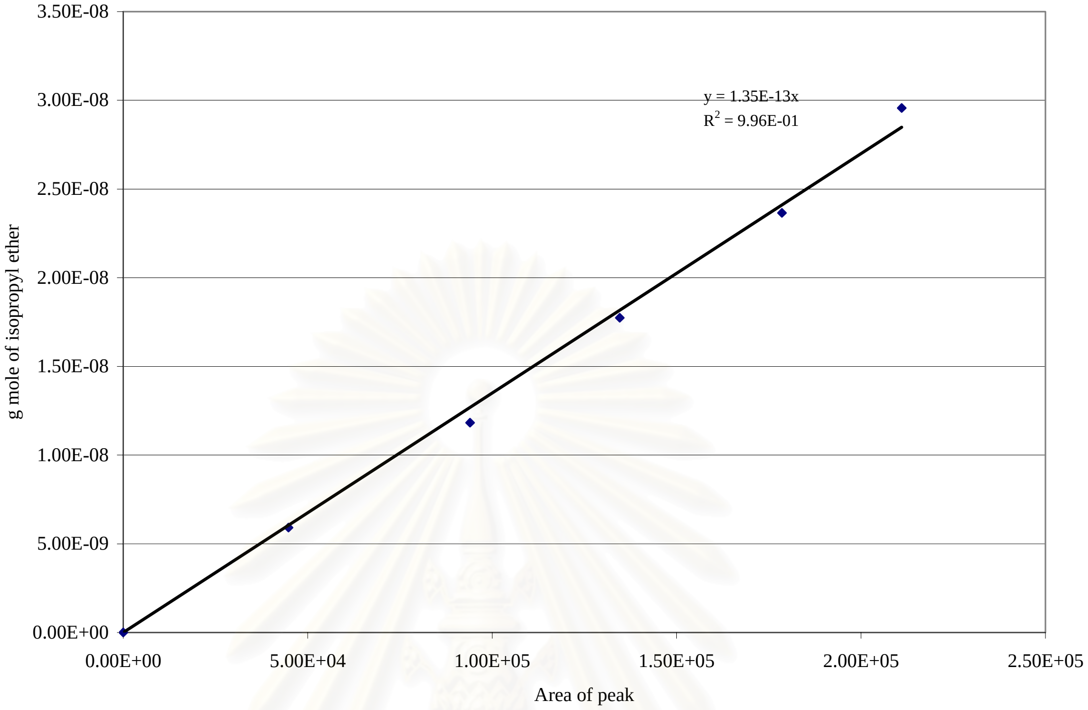


Figure B4 The calibration curve of isopropyl ether

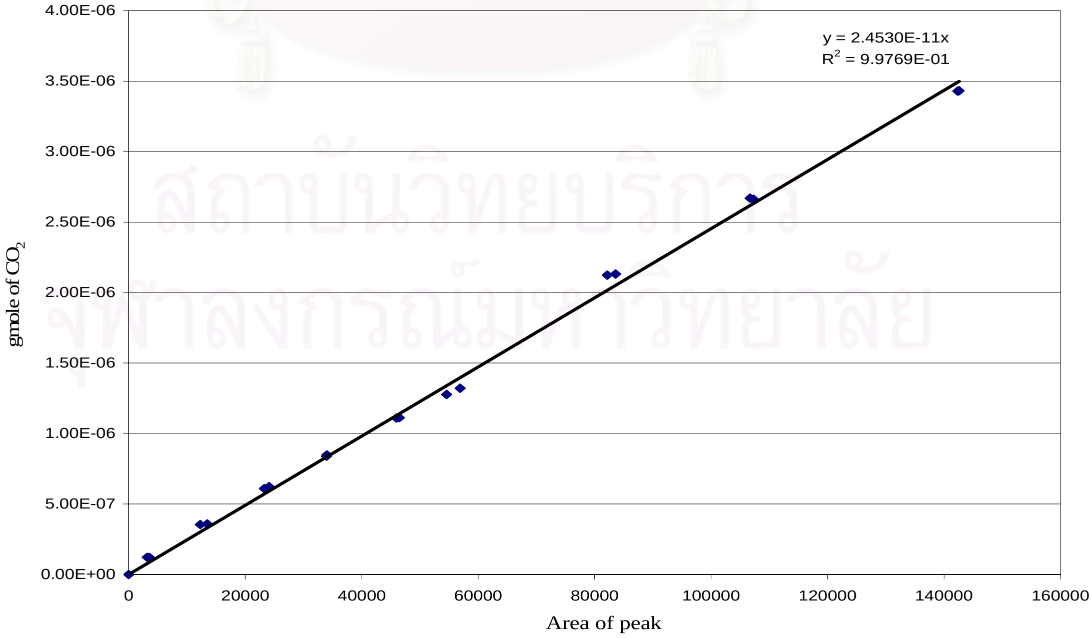


Figure B5 The calibration curve of carbon dioxide

APPENDIX C

DATA OF EXPERIMENTS

Table C1 Data of Figure 5.6a

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	1.50	0.00	0.00	100.00	0.00	0.00	0.00	1.50	0.00
150	0.99	1.25	0.00	98.75	0.00	0.01	0.00	0.98	0.00
200	6.21	2.47	0.00	97.53	0.00	0.15	0.00	6.05	0.00
250	20.94	5.96	0.00	92.36	1.68	1.25	0.00	19.34	0.35
300	51.33	11.75	0.31	82.58	5.36	6.03	0.16	42.39	2.75
350	85.82	14.06	0.20	69.50	16.23	12.07	0.17	59.65	13.93
400	95.09	13.05	0.07	56.40	30.49	12.41	0.06	53.63	28.99
450	95.63	16.57	0.05	76.47	6.92	15.84	0.05	73.13	6.61
500	97.29	12.21	0.00	58.35	29.44	11.88	0.00	56.77	28.64

Table C2 Data of Figure 5.6b

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	1.42	0.00	0.00	100.00	0.00	0.00	0.00	1.42	0.00
150	1.97	1.54	0.00	98.46	0.00	0.03	0.00	1.94	0.00
200	2.94	4.58	0.00	93.41	2.01	0.13	0.00	2.75	0.06
250	18.72	6.89	0.00	92.67	0.44	1.29	0.00	17.35	0.08
300	57.90	14.18	0.41	74.66	10.76	8.21	0.24	43.23	6.23
350	89.49	14.88	0.10	59.30	25.72	13.31	0.09	53.07	23.02
400	95.09	13.36	0.06	57.22	29.35	12.71	0.06	54.41	27.91
450	96.08	11.53	0.03	55.18	33.26	11.08	0.03	53.01	31.95
500	97.46	11.49	0.00	58.39	30.11	11.20	0.00	56.91	29.35

Table C3 Data of Figure 5.6c

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	2.00	3.63	0.00	96.37	0.00	0.07	0.00	1.93	0.00
150	6.30	17.62	0.00	82.38	0.00	1.11	0.00	5.19	0.00
200	8.70	28.50	0.00	71.50	0.00	2.48	0.00	6.22	0.00
250	28.17	31.32	0.18	63.93	4.57	8.82	0.05	18.01	1.29
300	90.15	21.21	0.24	42.90	35.65	19.12	0.22	38.68	32.14
350	97.92	18.24	0.27	44.67	36.82	17.86	0.26	43.74	36.05
400	98.57	16.87	0.07	42.09	40.97	16.62	0.07	41.49	40.39
450	99.18	15.65	0.00	44.76	39.59	15.53	0.00	44.39	39.26
500	99.56	15.10	0.00	43.62	41.28	15.04	0.00	43.43	41.09

Table C4 Data of Figure 5.6d

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	2.05	0.00	0.00	100.00	0.00	0.00	0.00	2.05	0.00
150	3.38	3.22	0.00	96.78	0.00	0.11	0.00	3.27	0.00
200	9.01	8.69	0.00	91.31	0.00	0.78	0.00	8.23	0.00
250	19.12	19.99	0.00	75.35	4.66	3.82	0.00	14.41	0.89
300	75.29	39.86	0.39	55.07	4.68	30.01	0.30	41.46	3.52
350	96.25	26.85	0.44	46.81	25.89	25.85	0.43	45.06	24.92
400	98.60	25.61	0.34	48.38	25.67	25.25	0.33	47.70	25.31
450	99.14	24.99	0.17	50.31	24.53	24.77	0.17	49.88	24.32
500	99.54	22.32	0.09	53.53	24.06	22.22	0.09	53.28	23.95

Table C5 Data of Figure 5.6e

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	4.12	0.00	0.00	100.00	0.00	0.00	0.00	4.12	0.00
150	7.90	0.00	0.00	100.00	0.00	0.00	0.00	7.90	0.00
200	9.15	3.28	0.00	96.72	0.00	0.30	0.00	8.85	0.00
250	24.88	10.18	0.44	85.38	3.99	2.53	0.11	21.24	0.99
300	76.89	16.96	0.03	52.02	30.99	13.04	0.03	40.00	23.83
350	90.64	17.35	0.13	55.46	27.06	15.73	0.12	50.27	24.53
400	95.20	19.05	0.12	54.92	25.91	18.13	0.11	52.29	24.67
450	96.10	21.48	0.05	52.70	25.77	20.65	0.04	50.65	24.76
500	97.98	23.42	0.04	50.80	25.73	22.95	0.04	49.77	25.21

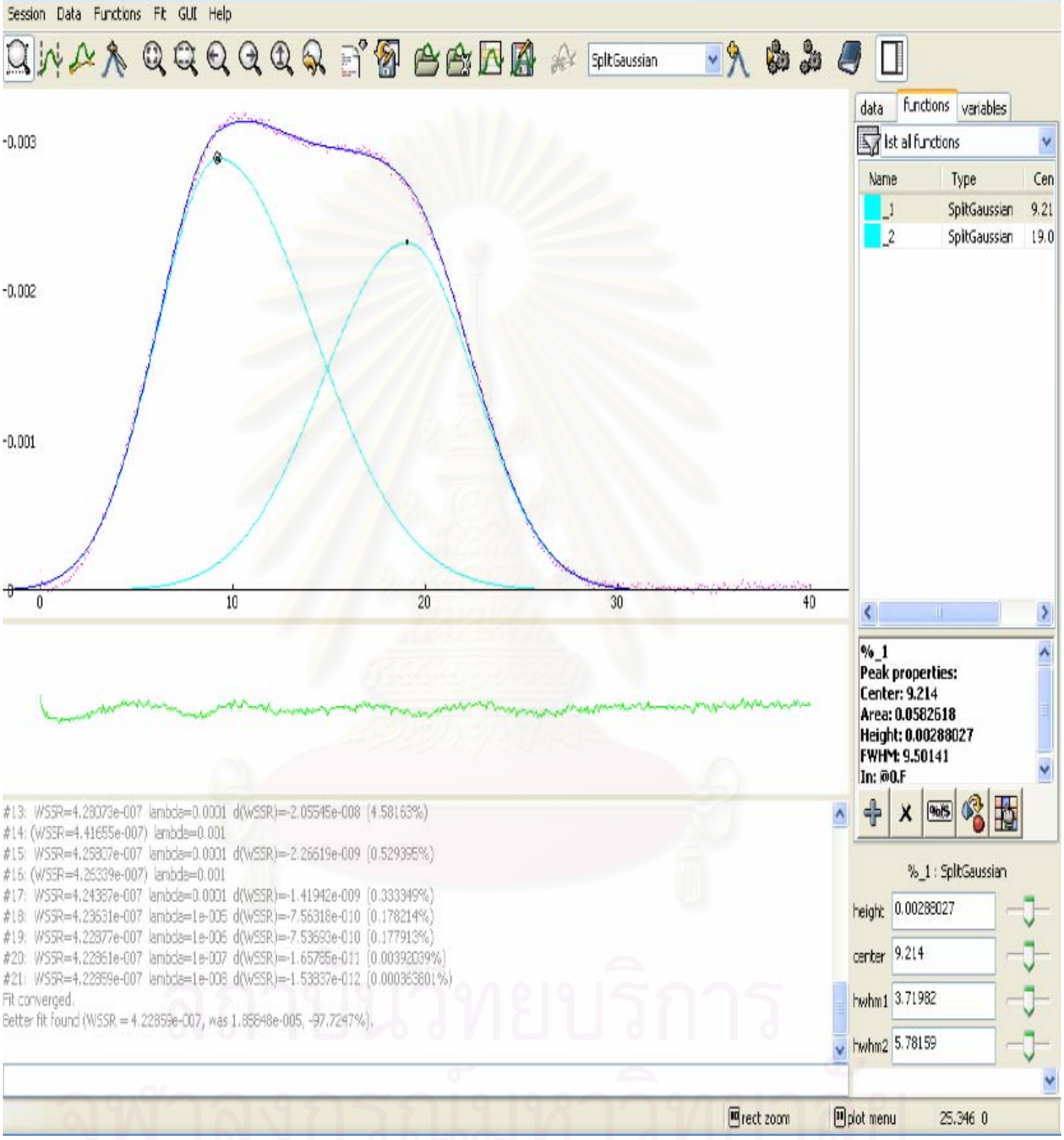
Table C6 Data of Figure 5.6f

temp. (^{0}C)	% conv.	% selec. to propylene	% selec. to isopropyl ether	% selec. to acetone	% selec. to CO2	% yield to propylene	% yield to isopropyl ether	% yield to acetone	% yield to CO2
100	2.86	2.44	0.00	97.56	0.00	0.07	0.00	2.79	0.00
150	8.87	1.22	0.00	98.78	0.00	0.11	0.00	8.76	0.00
200	14.62	5.63	0.00	94.37	0.00	0.82	0.00	13.80	0.00
250	25.98	8.43	0.13	79.46	11.98	2.19	0.03	20.65	3.11
300	89.24	10.86	0.20	48.16	40.78	9.69	0.18	42.98	36.39
350	95.20	17.19	0.13	68.70	13.98	16.36	0.12	65.40	13.31
400	96.92	11.54	0.03	53.64	34.79	11.18	0.03	51.99	33.72
450	97.65	9.51	0.00	53.00	37.49	9.29	0.00	51.76	36.61
500	98.59	9.31	0.00	54.85	35.84	9.18	0.00	54.07	35.33

APPENDIX D

DECONVOLUTION OF NH_3-TPD PROFILES

Figure D1 Fit peak of TS-1



```
#13:  WSSR=4.28073e-007  lambda=0.0001  d(WSSR)=-2.05545e-008  (4.58163%)
#14: (WSSR=4.41655e-007)  lambda=0.001
#15:  WSSR=4.25807e-007  lambda=0.0001  d(WSSR)=-2.26619e-009  (0.529395%)
#16: (WSSR=4.26339e-007)  lambda=0.001
#17:  WSSR=4.24387e-007  lambda=0.0001  d(WSSR)=-1.41942e-009  (0.333349%)
#18:  WSSR=4.23631e-007  lambda=1e-005  d(WSSR)=-7.56318e-010  (0.178214%)
#19:  WSSR=4.22877e-007  lambda=1e-006  d(WSSR)=-7.53693e-010  (0.177913%)
#20:  WSSR=4.22861e-007  lambda=1e-007  d(WSSR)=-1.65785e-011  (0.00392039%)
#21:  WSSR=4.22859e-007  lambda=1e-008  d(WSSR)=-1.53837e-012  (0.000363801%)
Fit converged.
Better fit found (WSSR = 4.22859e-007, was 1.85848e-005, -97.7247%).
```

%_1
Peak properties:
Center: 9.214
Area: 0.0582618
Height: 0.00288027
FWHM: 9.50141
In: @0.F

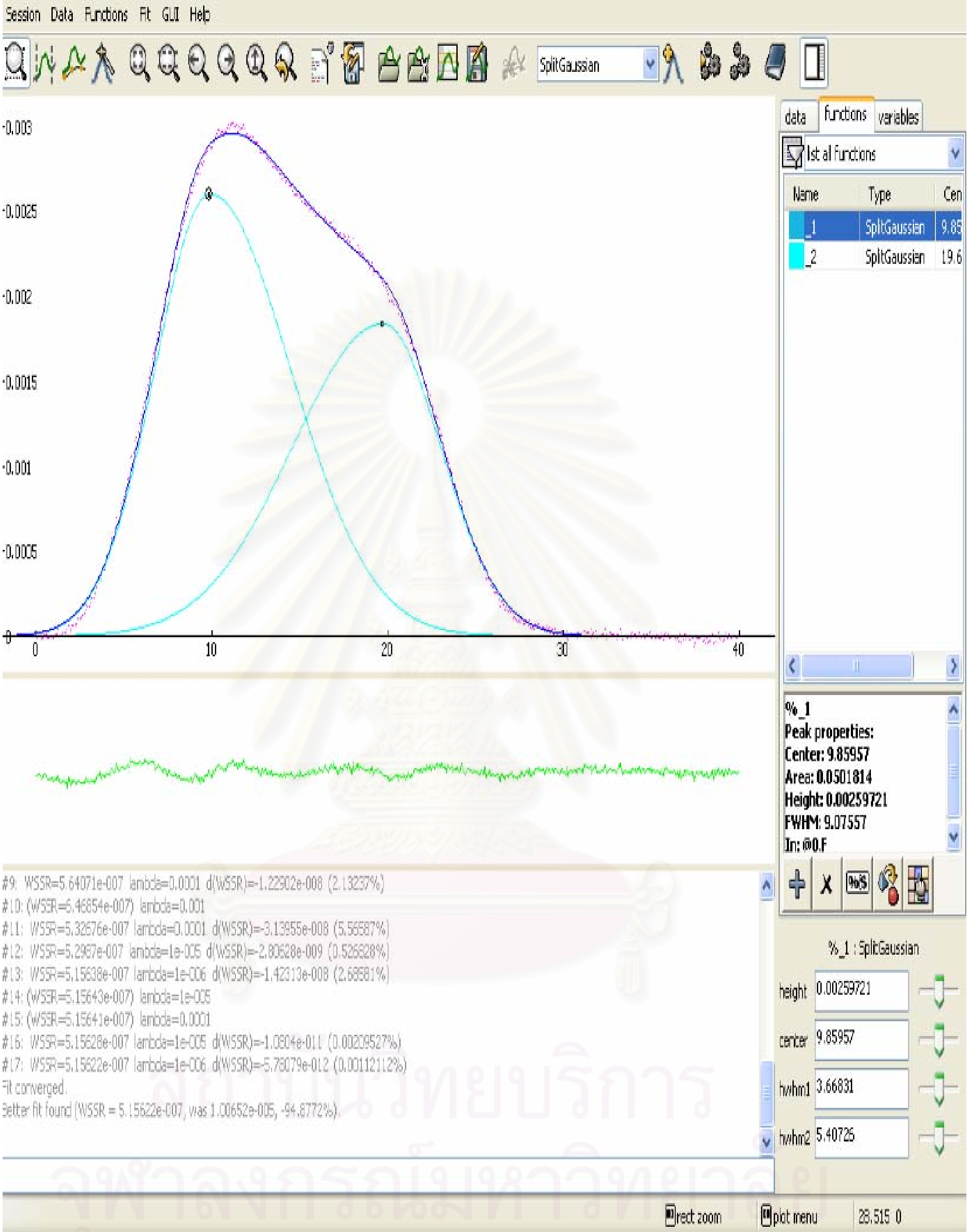
%_1 : SplitGaussian

height 0.00288027
center 9.214
hwhm1 3.71982
hwhm2 5.78159

Peak properties:
Center: 9.214
Area: 0.0582618
Height: 0.00288027

Peak properties:
Center: 19.0248
Area: 0.0457282
Height: 0.00231941

Figure D2 Fit peak of Cu-TS-1(Cu:0.09mol%)



```
%_1
Peak properties:
Center: 9.85957
Area: 0.0501814
Height: 0.00259721
FWHM: 9.07557
In: @0.F
```

%_1 : SplitGaussian

height 0.00259721

center 9.85957

hwhm1 3.66831

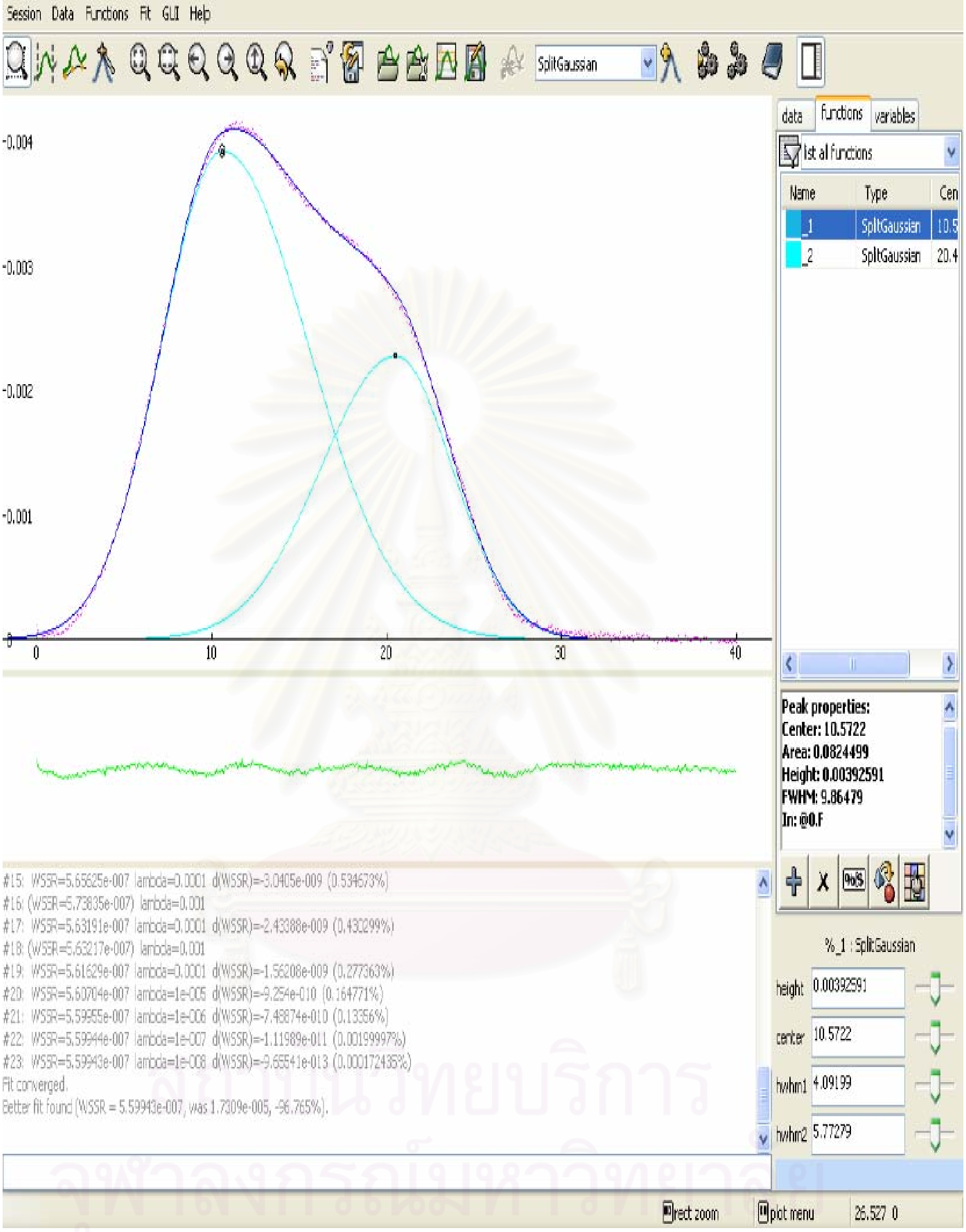
hwhm2 5.40726

```
#9:  WSSR=5.64071e-007 lambda=0.0001 d(WSSR)=-1.22902e-008 (2.13237%)
#10: (WSSR=6.46854e-007) lambda=0.001
#11:  WSSR=5.32676e-007 lambda=0.0001 d(WSSR)=-3.13955e-008 (5.56587%)
#12:  WSSR=5.2987e-007 lambda=1e-005 d(WSSR)=-2.80628e-009 (0.526828%)
#13:  WSSR=5.15638e-007 lambda=1e-006 d(WSSR)=-1.42313e-008 (2.68581%)
#14: (WSSR=5.15643e-007) lambda=1e-005
#15: (WSSR=5.15641e-007) lambda=0.0001
#16:  WSSR=5.15628e-007 lambda=1e-005 d(WSSR)=-1.0804e-011 (0.00209527%)
#17:  WSSR=5.15622e-007 lambda=1e-006 d(WSSR)=-5.78079e-012 (0.00112112%)
Fit converged.
Better fit found (WSSR = 5.15622e-007, was 1.00652e-005, -94.8772%).
```

Peak properties:
Center: 9.85957
Area: 0.0501814
Height: 0.00259721

Peak properties:
Center: 19.6953
Area: 0.038848
Height: 0.0018372

Figure D3 Fit peak of Cu-TS-1(Cu:0.10mol%)



Name	Type	Cen
_1	SplitGaussian	10.5
_2	SplitGaussian	20.4

Peak properties:
Center: 10.5722
Area: 0.0824499
Height: 0.00392591
FWHM: 9.86479
In: @0.F

%_1 : SplitGaussian

height 0.00392591
center 10.5722
hwhm1 4.09199
hwhm2 5.77279

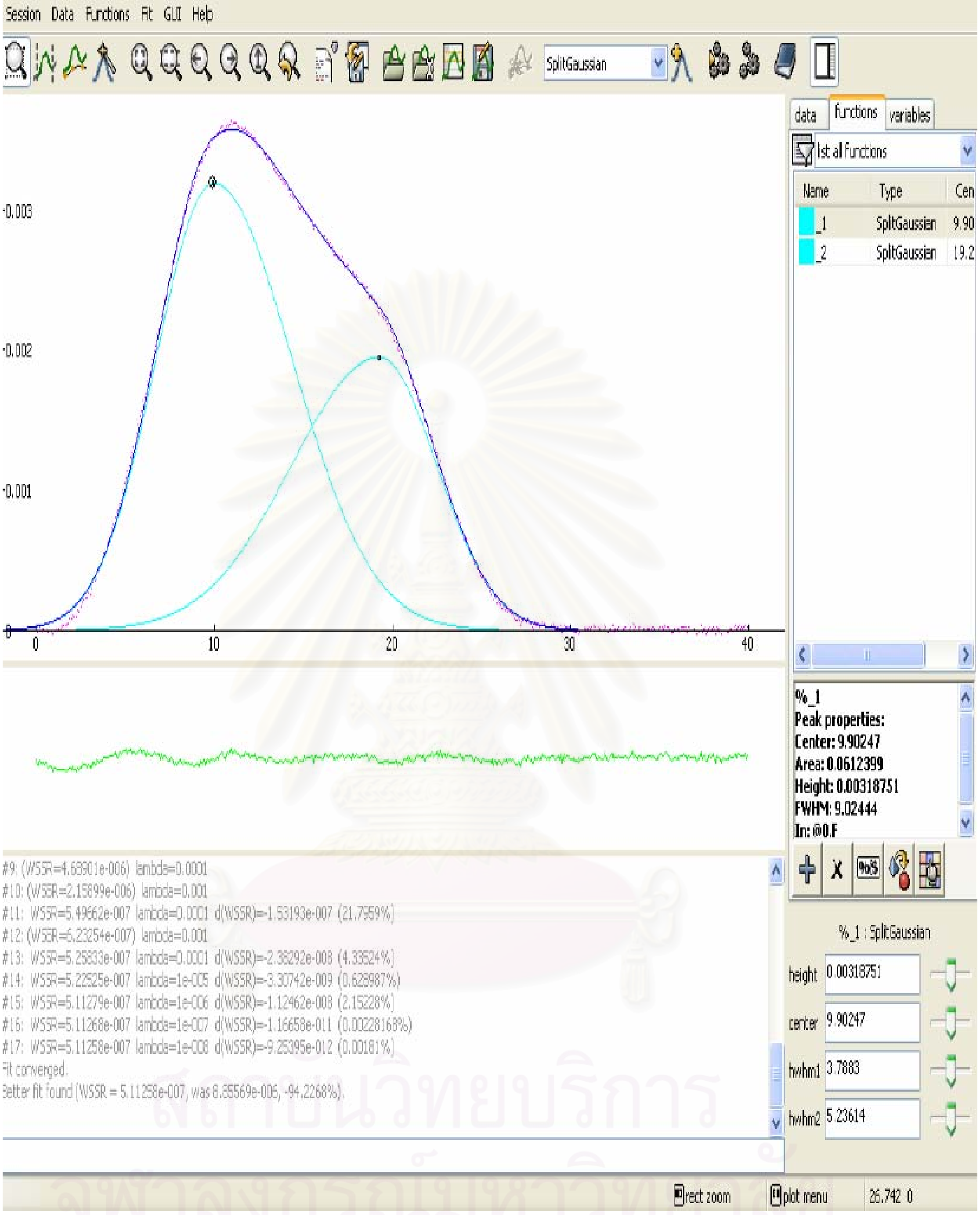
```
#15:  WSSR=5.65625e-007  lambda=0.0001  d(WSSR)=-3.0405e-009  (0.534673%)
#16: (WSSR=5.73835e-007)  lambda=0.001
#17:  WSSR=5.63191e-007  lambda=0.0001  d(WSSR)=-2.43388e-009  (0.430299%)
#18: (WSSR=5.63217e-007)  lambda=0.001
#19:  WSSR=5.61629e-007  lambda=0.0001  d(WSSR)=-1.56208e-009  (0.277363%)
#20:  WSSR=5.60704e-007  lambda=1e-005  d(WSSR)=-9.254e-010  (0.164771%)
#21:  WSSR=5.59955e-007  lambda=1e-006  d(WSSR)=-7.48874e-010  (0.13356%)
#22:  WSSR=5.59944e-007  lambda=1e-007  d(WSSR)=-1.11989e-011  (0.00199997%)
#23:  WSSR=5.59943e-007  lambda=1e-008  d(WSSR)=-9.65541e-013  (0.000172435%)
Fit converged.
Better fit found (WSSR = 5.59943e-007, was 1.7309e-005, -96.765%).
```

26.527 0

Peak properties:
Center: 10.5722
Area: 0.0824499
Height: 0.00392591

Peak properties:
Center: 20.4741
Area: 0.0428232
Height: 0.0022780

Figure D4 Fit peak of Cu-TS-1(Cu:0.13mol%)



Name	Type	Cen
_1	SplitGaussian	9.90
_2	SplitGaussian	19.2

```
#9: (WSSR=4.68901e-006) lambda=0.0001
#10: (WSSR=2.15899e-006) lambda=0.001
#11:  WSSR=5.49662e-007 lambda=0.0001 d(WSSR)=-1.53193e-007 (21.7959%)
#12: (WSSR=6.23254e-007) lambda=0.001
#13:  WSSR=5.25833e-007 lambda=0.0001 d(WSSR)=-2.38292e-008 (4.33524%)
#14:  WSSR=5.22525e-007 lambda=1e-005 d(WSSR)=-3.30742e-009 (0.628987%)
#15:  WSSR=5.11279e-007 lambda=1e-006 d(WSSR)=-1.12462e-008 (2.15228%)
#16:  WSSR=5.11268e-007 lambda=1e-007 d(WSSR)=-1.16658e-011 (0.00228168%)
#17:  WSSR=5.11258e-007 lambda=1e-008 d(WSSR)=-9.25395e-012 (0.00181%)
Fit converged.
Better fit found (WSSR = 5.11258e-007, was 8.85569e-006, -94.2268%).
```

%_1
Peak properties:
Center: 9.90247
Area: 0.0612399
Height: 0.00318751
FWHM: 9.02444
In: @0.F

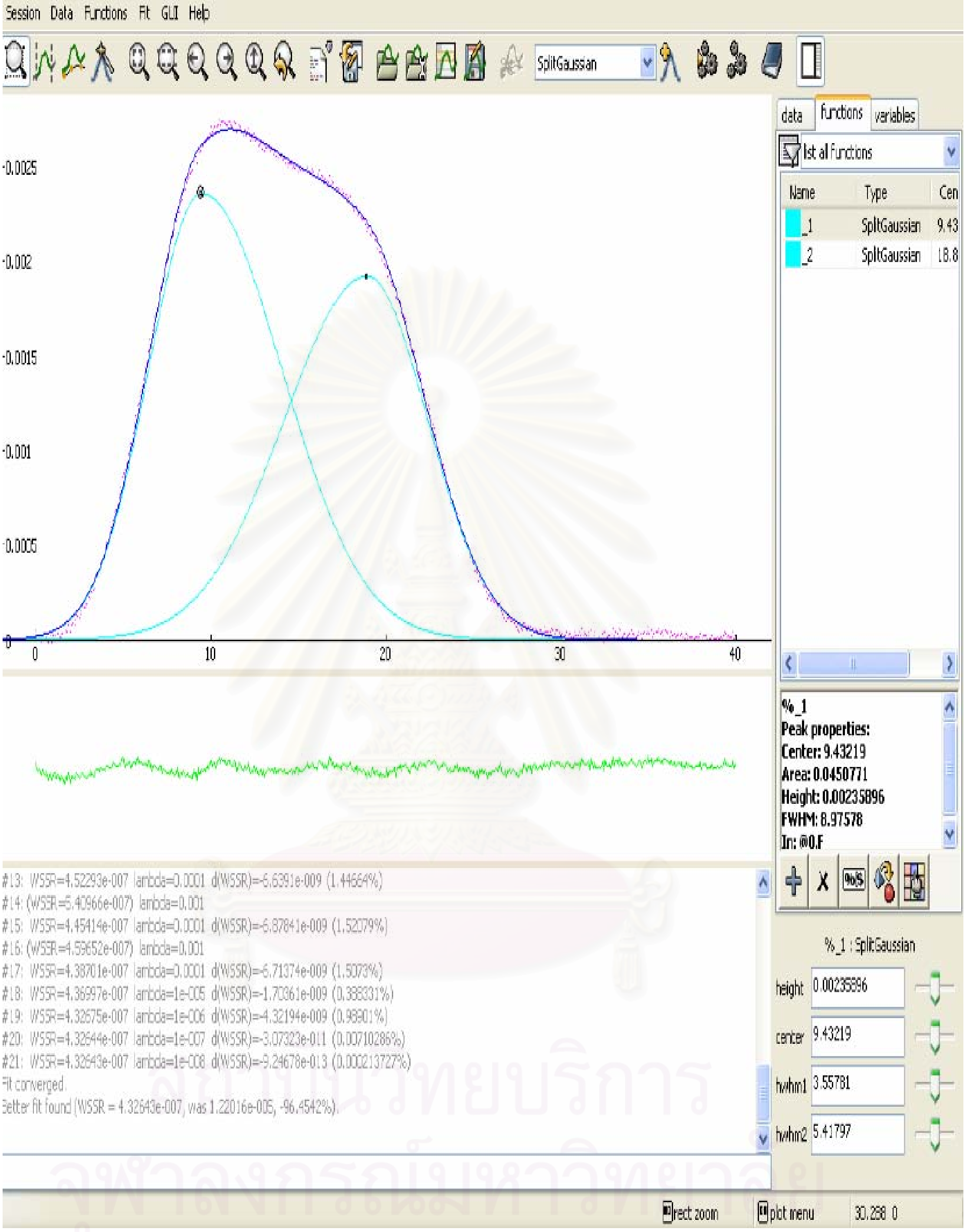
%_1 : SplitGaussian

height 0.00318751
center 9.90247
hwhm1 3.7883
hwhm2 5.23614

Peak properties:
Center: 9.90247
Area: 0.0612399
Height: 0.00318751

Peak properties:
Center: 19.2414
Area: 0.039778
Height: 0.00194869

Figure D5 Fit peak of Cu-TS-1(Cu:0.22mol%)



```
#13:  WSSR=4.52293e-007  lambda=0.0001  d(WSSR)=-6.6391e-009 (1.44664%)
#14: (WSSR=5.40966e-007)  lambda=0.001
#15:  WSSR=4.45414e-007  lambda=0.0001  d(WSSR)=-6.87841e-009 (1.52079%)
#16: (WSSR=4.59652e-007)  lambda=0.001
#17:  WSSR=4.38701e-007  lambda=0.0001  d(WSSR)=-6.71374e-009 (1.5073%)
#18:  WSSR=4.36997e-007  lambda=1e-005  d(WSSR)=-1.70361e-009 (0.388331%)
#19:  WSSR=4.32675e-007  lambda=1e-006  d(WSSR)=-4.32194e-009 (0.98901%)
#20:  WSSR=4.32644e-007  lambda=1e-007  d(WSSR)=-3.07323e-011 (0.00710286%)
#21:  WSSR=4.32643e-007  lambda=1e-008  d(WSSR)=-9.24678e-013 (0.000213727%)
Fit converged.
Better fit found (WSSR = 4.32643e-007, was 1.22016e-005, -96.4542%).
```

```
%_1
Peak properties:
Center: 9.43219
Area: 0.0450771
Height: 0.00235896
FWHM: 8.97578
In: @0.F
```

%_1 : SplitGaussian

height 0.00235896

center 9.43219

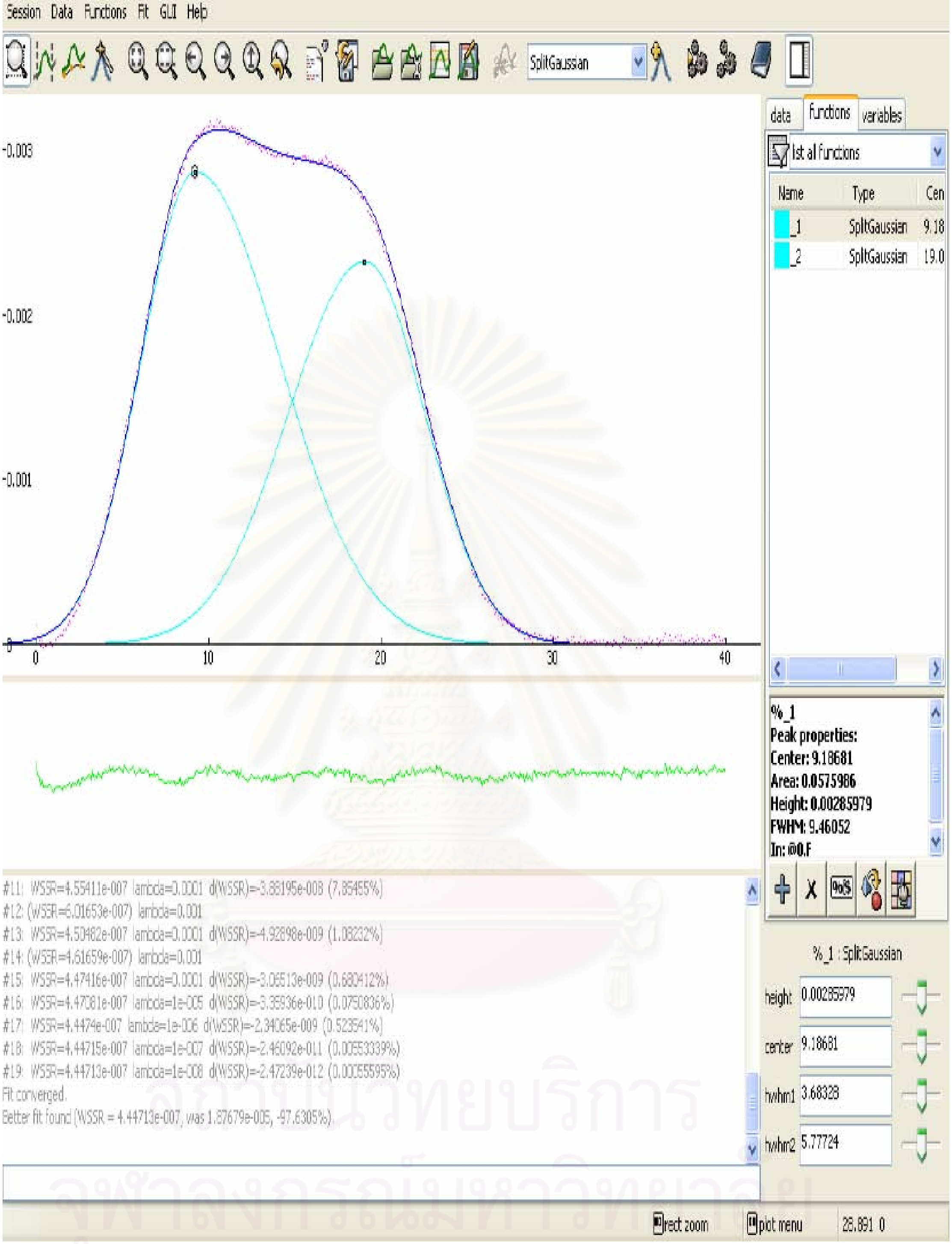
hwhm1 3.55781

hwhm2 5.41797

Peak properties:
Center: 9.43219
Area: 0.0450771
Height: 0.00235896

Peak properties:
Center: 18.8882
Area: 0.039443
Height: 0.00192252

Figure D6 Fit peak of Cu-TS-1(Cu:0.09mol%)



```
#11:  WSSR=4.55411e-007  lambda=0.0001  d(WSSR)=-3.88195e-008 (7.85455%)
#12: (WSSR=6.01653e-007)  lambda=0.001
#13:  WSSR=4.50482e-007  lambda=0.0001  d(WSSR)=-4.92898e-009 (1.08232%)
#14: (WSSR=4.61659e-007)  lambda=0.001
#15:  WSSR=4.47416e-007  lambda=0.0001  d(WSSR)=-3.06513e-009 (0.680412%)
#16:  WSSR=4.47081e-007  lambda=1e-005  d(WSSR)=-3.35936e-010 (0.0750836%)
#17:  WSSR=4.4474e-007  lambda=1e-006  d(WSSR)=-2.34065e-009 (0.523541%)
#18:  WSSR=4.44715e-007  lambda=1e-007  d(WSSR)=-2.46092e-011 (0.00553339%)
#19:  WSSR=4.44713e-007  lambda=1e-008  d(WSSR)=-2.47239e-012 (0.000555595%)
Fit converged.
Better fit found (WSSR = 4.44713e-007, was 1.87679e-005, -97.6305%).
```

%_1
Peak properties:
Center: 9.18681
Area: 0.0575986
Height: 0.00285979
FWHM: 9.46052
In: @0.F

%_1 : SplitGaussian

height 0.00285979
center 9.18681
hwhm1 3.68328
hwhm2 5.77724

Peak properties:
Center: 9.18681
Area: 0.0575986
Height: 0.00285979

Peak properties:
Center: 19.0243
Area: 0.0459059
Height: 0.00232039

APPENDIX E

MATERIAL SAFETY DATA SHEET

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

APPENDIX F

LIST OF PUBLICATION

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

Synthesis and Characterisation of Metal Modified TS-1

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Email:tharathon.m@chula.ac.th)

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. 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

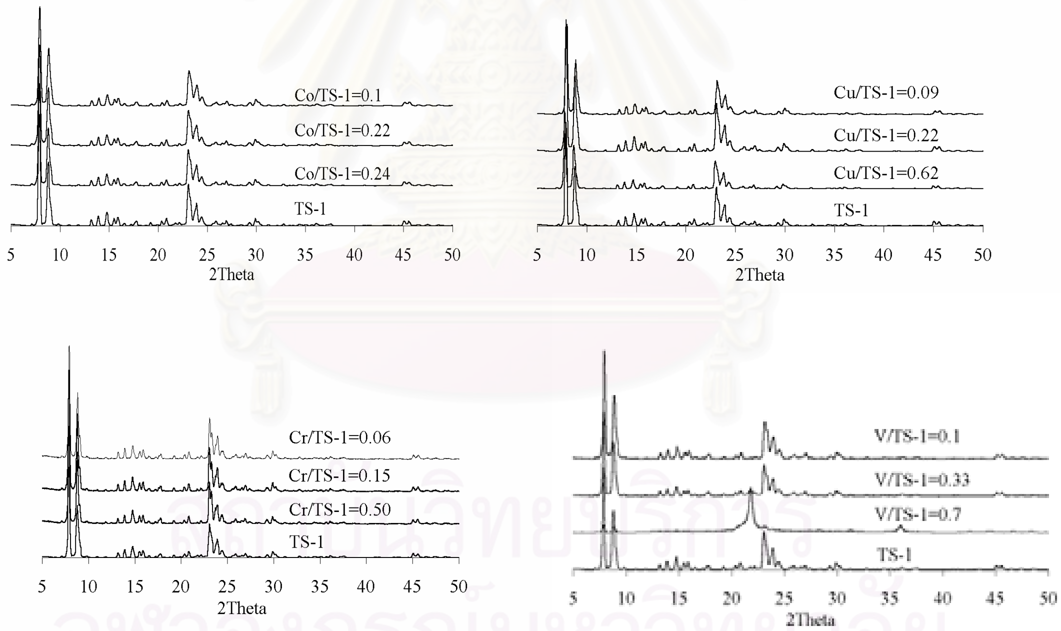

Figure 1 XRD Patterns of Top left : Co/TS-1, Top right : Cu/TS-1, Bottom left : Cr/TS-1 and Bottom right : V/TS-1

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.

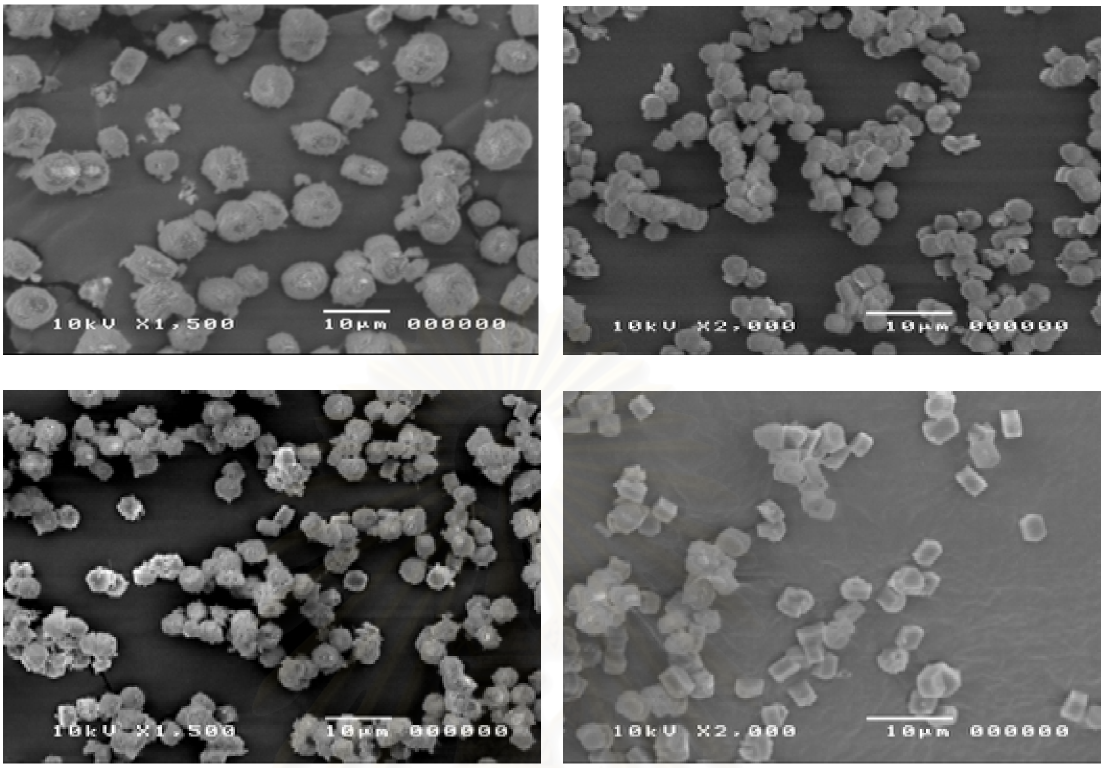

Figure 2 SEM photo of Top left : Co/TS-1, Top right : Cu/TS-1, Bottom left : Cr/TS-1 and Bottom right : V/TS-1

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

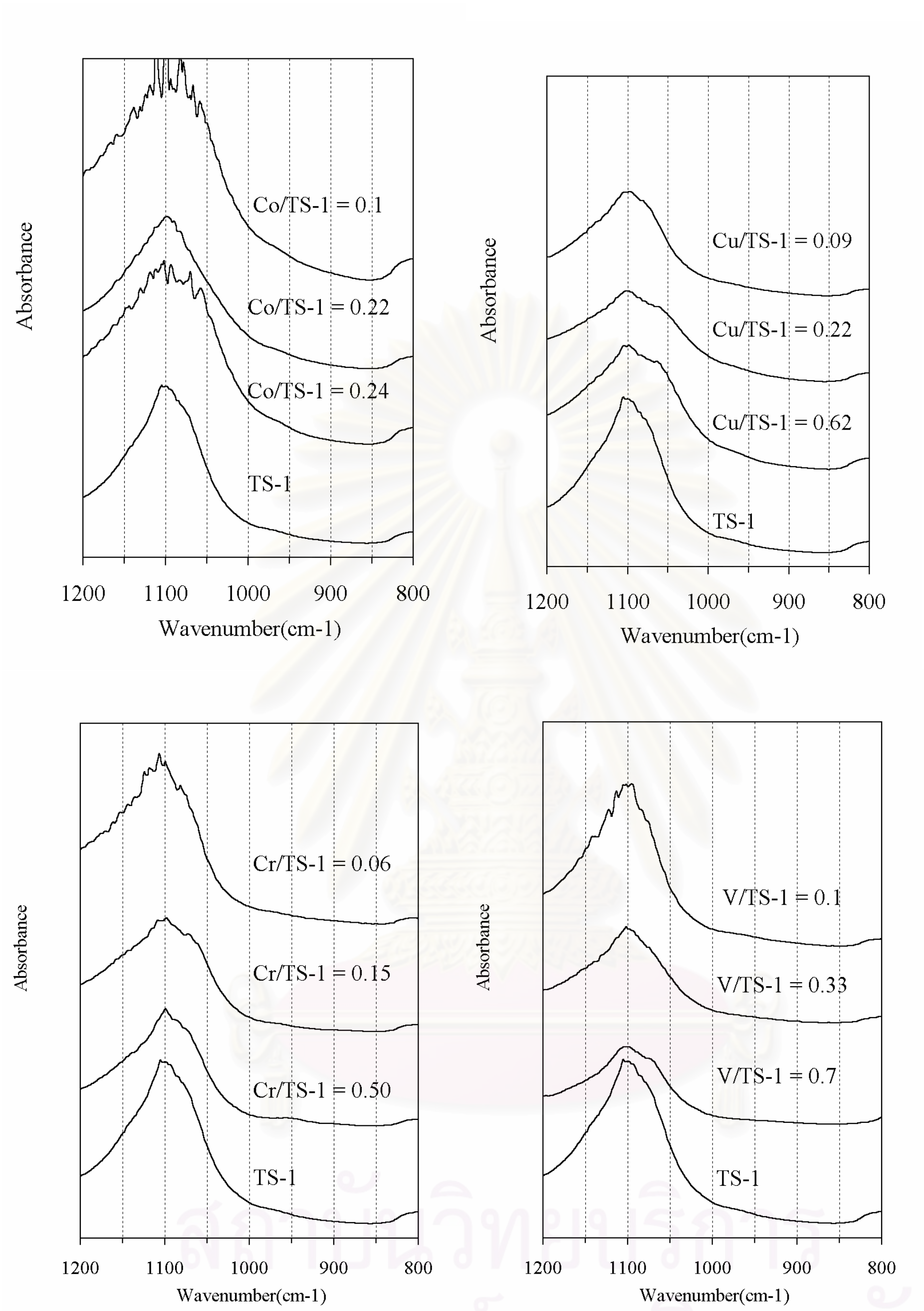

Figure 3 IR absorption spectra of modified and unmodified TS-1 samples.

Chemical states of various elements on the surface were analyzed by the XPS technique. The preliminary results are shown in table 2. The binding energy shift of each element is calculated using C 1s peak at 286.7 eV as reference. The binding energy of Co, Cu, Cr and V in metal form (M^0) is also shown in the table for comparison (ref). It is found that in all samples the second metals exist as cation. The exception is Cu/TS-1(0.09) in which the binding energy shift of Cu is about zero. This indicates that Cu in Cu/TS-1(0.09) may exists as Cu^0 while Cu in Cu/TS-1(0.22) and Cu/TS-1(0.62) is likely to exist in the form Cu^{2+}. The state of Co cation in Co/TS-1(0.1) and Co/TS-1(0.22) is likely to be Co^{3+} while both Co^{2+} and Co^{3+}. may exists in Co/TS-1(0.24). The oxidation state of vanadium in V/TS-1 may vary V^{5+} in V/TS-1(0.7) down to V^{3+} in V/TS-1(0.1). The largest binding energy shift of Cr/TS-1(0.5) possibly dues to Cr^{6+} while the lower binding shifts of Cr/TS-1(0.15) and Cr/TS-1(0.06) suggest the present of both Cr^{3+} and Cr^{6+} or only Cr^{3+}. The exact oxidation state of each element in each sample, however, has yet to be confirmed.

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

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

Conclusion

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

Acknowledgements

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

References

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

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

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

VITA

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