SYNTHESIS OF BIMETALLIC Pt-Cu/TiO_2 CATALYSTS FOR LIQUID-PHASE SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL

NUTCHAPA KONGSAKPAIBOON

PICHAYA CHUANGPUSRI

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โครงการพิเศษ	การสังเคราะห์ตัวเร่งปฏิกิริยาแบบโลหะผสมของแพททินัมคอปเปอร์บนตัวรองรับไทเทเนียสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟูรอลเป็นเฟอร์ฟูริลแอลกอฮอล์
ชื่อนักศึกษา	นางสาวณัชภา คงศักดิ์ไพบูลย์ รหัสนักศึกษา 58050461
	นางสาวพิชญา ช่วงภูศรี รหัสนักศึกษา 58050513
ปริญญา	วิทยาศาสตร์บัณฑิต (เคมีอุตสาหกรรม)
ภาควิชา	เคมี
คณะ	วิทยาศาสตร์
มหาวิทยาลัย	สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง (สจล.)
ปีการศึกษา	2560
อาจารย์ที่ปรึกษา	ดร.พัชราภรณ์ วีระชวนะศักดิ์
อาจารที่ปรึกษาร่วม	ศ.ดร.ตะวัน สุขน้อย

บทคัดย่อ

โครงงานพิเศษนี้ได้สังเคราะห์และศึกษาตัวเร่งปฏิกิริยาแบบโลหะผสมแพททินัมคอปเปอร์บนตัวรองรับไทเทเนียมไดออกไซด์สำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟูรอลเปลี่ยนเป็นเฟอฟูริวแอลกอฮอล์ โดยตัวเร่งปฏิกิริยาแบบโลหะชนิดเดียวทั้งหมดคือ 5%Cu/TiO_2 และ 0.5%Pt/TiO_2 ตังเร่งปฏิกิริยาแบบโลหะผสมสองชนิดคือ 0.5%Pt-5%Cu/TiO_2 และ 0.5%Pt-0.5%Cu/TiO_2 ถูกเตรียมด้วยวิธีการจุ่มชุบแบบพอดีเปียก (Incipient wetness impregnation) จากผลการวิเคราะห์ด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ (X-ray Diffractometer, XRD), การรีดักชันโดยการใช้โปรแกรมอุณหภูมิ (Temperature Programed Reduction, TPR) และ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (Scanning Electron Microscope, SEM) พบว่าตัวเร่งปฏิกิริยา 0.5%Pt-0.5%Cu/TiO_2 แสดงให้เห็นถึงการเกิดเป็นโลหะผสมอย่างสมบูรณ์ระหว่างแพททินัมและคอปเปอร์ในขณะที่ตัวเร่งปฏิกิริยา 0.5%Pt-5%Cu/TiO_2 เกิดเป็นโลหะผสมระหว่างแพททินัมและคอปเปอร์และเกิดการรวมตัวกันของอนุภาคคอปเปอร์ออกซ์ไซด์บางส่วนขึ้น ตัวเร่งปฏิกิริยาแบบโลหะผสมได้แก่ 0.5%Pt-5%Cu/TiO_2 และ 0.5%Pt-0.5%Cu/TiO_2 ทั้งสองตัวนั้นแสดงประสิทธิภาพในการเร่งปฏิกิริยาที่สูงกว่าตัวเร่งปฏิกิริยา 5%Cu/TiO_2 แต่ต่ำกว่าตัวเร่งปฏิกิริยา 0.5%Pt/TiO_2 การเกิดอนุภาคโลหะผสมแพททินัมคอปเปอร์ที่มีการกระจายตัวสูงส่งผลต่อค่าการแปรผันของเฟอร์ฟูรอลที่สูงขึ้น แต่อย่างไรก็ตามค่าการเลือกเกิดของเฟอร์ฟูริลแอลกอฮอล์ดูเหมือนว่าขึ้นอยู่กับสัดส่วนที่เหมาะสมระหว่างปริมาณของไทเทเนียมไดออกไซด์ที่ถูกรีดิวส์ (TiO_x) และปริมาณโลหะที่ว่องไวทั้งหมด นอกจากนี้ไทเทเนียมไดออกไซด์ที่ถูกรีดิวส์แล้วทำหน้าที่เป็นตำแหน่งกรดลิวอีส (lewis acid site) ที่ส่งเสริมให้เกิดปฏิกิริยาอะเซทอลไรเซชัน(Acetalization) ระหว่างเฟอร์ฟูรอล

และบิวทานอล แต่อย่างไรก็ตามตัวเร่งปฏิกิริยาแบบโลหะชนิดเดียว 0.5%Pt/TiO_2 แสดงประสิทธิภาพในการเร่งปฏิกิริยาที่ดีที่สุดซึ่งให้ค่าการแปรผันของเฟอร์ฟูรอลสูงที่สุดที่ 65.57% และค่าการเลือกเกิดเป็นเฟอร์ฟูริลแอลกอฮอล์สูงถึง 76.4% ปฏิกิริยาออกซิเดทีฟคัปปลิง (Oxidetive Copling) ที่ทำให้เกิด เอสเตอร์สามารถถูกยับยั้งได้เมื่อทำการลดอุณหภูมิในการทำปฏิกิริยาลงจาก 100 องศาเซลเซียส เป็น 50 องศาเซสเซียส

คำสำคัญ : ตัวเร่งปฏิกิริยาแพททินัมคอปเปอร์บนตัวรองรับไทเทเนียมไดออกไซส์, เฟอร์ฟูรอล, เฟอร์ฟูริลแอลกอฮอล์, วิธีการจุ่มชุบแบบพอดีเปียก

Title	Synthesis of bimetallic Pt-Cu/TiO_2 catalysts for liquid-phase selective hydrogenation of furfural to furfuryl alcohol
Student	Miss Nutchapa Kongsakpaiboon Student ID 58050461
	Miss Pichaya Chuangpusri Student ID 58050513
Degree	Bachelor of Science (Industrial Chemistry)
Department	Chemistry
Faculty	Science
University	King Mongkut's Institute of Technology Ladkrabang (KMITL)
Academic Year	2018
Advisor	Dr. Patcharaporn Weerachawanasak
Co-advisor	Prof. Dr. Tawan Sooknoi

ABSTRACT

This special project has been synthesized and studied the bimetallic Pt-Cu supported on TiO_2 catalysts for the liquid-phase selective hydrogenation of furfural to furfuryl alcohol. All monometallic 5%Cu/TiO_2, 0.5%Pt/TiO_2 and bimetallic 0.5%Pt-5%Cu/TiO_2, 0.5%Pt-0.5%Cu/TiO_2 catalysts were prepared by incipient wetness impregnation method. According to XRD, TPR, and SEM results, 0.5%Pt-0.5%Cu/TiO_2 catalyst showed completely PtCu alloys forming whereas 0.5%Pt-5%Cu/TiO_2 gave PtCu alloy and some agglomeration of CuO particles. Both of bimetallic 0.5Pt-0.5Cu/TiO_2 and 0.5Pt-5Cu/TiO_2 catalysts exhibited higher catalytic performance than monometallic 5%Cu/TiO_2 but lower than 0.5%Pt/TiO_2. Forming of PtCu alloy particles with high dispersion effect to higher conversion of furfural. However, the selectivity of furfuryl alcohol seem to be depended on suitable proportion between the amount of reduced TiO_x and the total active metals (Pt, Cu). Moreover, reduced TiO_x acted as the lewis acid site promoted acetalization between furfural and butanol. However, the monometallic 0.5%Pt/TiO_2 catalyst shows the best catalytic performance that gave the highest furfural conversion 65.75% and furfuryl alcohol selective 76.4%. The oxidative coupling reaction to produced ester could be suppressed when decreased the reaction temperature from 100 to 50 °C.

Keywords: Pt-Cu/TiO_2 catalyst, Furfural, Furfuryl alcohol, Incipient wetness impregnation, Selective hydrogenation

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Nutchapa Kongsakpaiboon
Pichaya Chuangpusri

LIST OF CONTENTS

LIST OF CONTENTS (CONTINUED)

LIST OF TABLES

LIST OF TABLES (CONTINUED)

TABLE **PAGE**

LIST OF FIGURES

FIGURES PAGE

LIST OF SCHEMES

CHAPTER 1

Introduction

1.1 Rationale

Furfural is a promising biomass-derived platform molecule that is a key intermediate for variety of chemicals. The presence of an aldehyde group and conjugated double C-C bonds in furfural provides high versatility for synthesis of other high valuable compounds, by means of a large variety of reactions such as oxidation, decarbonylating, aldol reaction, alkylation, ring opening, and hydrogenation. Among of these reactions, the selective hydrogenation of furfural to furfuryl alcohol is the most popular application with approximately 80% of the worldwide furfural produced [1]. Furfuryl alcohol is mainly used in the polymer industry together with the production of plasticizers, synthesis of fibers, rubbers, resin, lubricants and farm chemicals. Moreover, it also used in the manufacture of vitamin C, lysine, drug synthesis and commercially important fine chemicals [2]. However, hydrogenation of furfural in the presence of H_2 and metallic catalysts can lead to complex reactions and produce many undesired products via the side reactions when the suitable catalysts are not used.

Various catalysts including transition metals and noble metals such as Cu, Ni, Fe, Ru, Co, Pd, and Pt catalysts have been investigated for gas phase and liquid phase hydrogenation of furfural to furfuryl alcohol. [3-7] Among of these catalysts, supported Pt catalyst is an interesting choice for the selective hydrogenation of furfural to furfuryl alcohol because it gives a high conversion of furfural with moderate to high selectivity of furfuryl alcohol. [3,5] However, Pt is an expensive metal and trends to increase the price in every year. It resulted in higher production cost. Many literatures reported the development of Pt catalysts by adding some second metal as a promotor, that its price is cheaper than Pt such as Fe, Mn, Cr, Co, Cu [7-8], etc. Adding second metal or promotor to form the bimetal/alloy effects to difference adsorption mechanism resulted in the catalytic performance. Moreover, the catalyst performances are usually depended on several factors such as morphology (size and shape) of catalysts, the oxidation states of active metal, and type of catalyst supports. In the catalytic hydrogenation, TiO_2 is one of the most versatile material and frequency employed as the catalyst support because it occupies a moderated-acid base support and difference TiO_2 polymorphs; anatase, rutile, or brookite, related to difference catalytic performances. Moreover, TiO_2 can be occurred the strong-metal support interaction which effect to high selectivity and conversion for hydrogenation. Therefore, TiO_2 is a good candidate support for selective hydrogenation of furfural.

Therefore, this work aims to develop the highly effective Cu/TiO_2 catalyst by adding Pt as a second metal for liquid-phase selective hydrogenation of furfural to furfuryl alcohol. The monometallic Pt/TiO_2, Cu/TiO_2 and a series of bimetallic Pt-Cu/TiO_2 catalysts were prepared by incipient wetness impregnation method. The suitable Pt/Cu ratio will be optimized. In addition, the characteristics and catalytic properties of Pt/TiO_2 and Pt-Cu/TiO_2 catalysts will be investigated in several techniques.

1.2 Objectives of research

1.2.1 To synthesize a series of bimetallic Pt-Cu/TiO_2 catalysts and determine the suitable Pt/Cu ratio for liquid-phase selective hydrogenation of furfural to furfuryl alcohol.

1.2.2 To study the characteristics and catalytic properties of bimetallic Pt-Cu/TiO_2 catalysts compare with monometallic Cu/TiO_2 and Pt/TiO_2 catalysts in liquid-phases selective hydrogenation of furfural to furfuryl alcohol

1.3 Scopes of research

1.3.1 The monometallic Pt/TiO_2, Cu/TiO_2 and a series bimetallic Pt-Cu/TiO_2 catalysts (Pt/Cu %wt./wt. at 0.5:0.5 and 0.5:5) were prepared by incipient wetness impregnation method.

1.3.2 The characteristics and catalytic properties of monometallic Pt/TiO_2, Cu/TiO_2 and bimetallic Pt-Cu/TiO_2 catalysts were determined by following techniques

- X-ray diffraction (XRD)
- X-ray fluorescence spectrometer (XRF)
- Temperature programmed reduction (TPR)
- Brunauer Emmett Teller (BET)
- Scanning electron microscopy (SEM)

1.3.3 The catalytic performance of monometallic Pt/TiO_2, Cu/TiO_2 and bimetallic $Cu\text{-}Pt/TiO_2$ catalysts were investigated in liquid-phase selective hydrogenation of furfural to furfuryl alcohol.

1.4 Benefit of study

1.4.1 To obtain highly efficient bimetallic Pt-Cu $/TiO_2$ catalyst which is an economical catalyst for liquid-phase selective hydrogenation of furfural to furfuryl alcohol.

1.4.2 To understand the catalytic mechanism of $Pt\text{-}Cu/TiO_2$ catalyst in liquid phase selective hydrogenation of furfural to furfuryl alcohol.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Furfural [9]

Furfural is one of the main products derived from biomass such as corn cobs, sugarcane bagasse, rice and oat hulls [2]. The molecular formula of furfural is C_4H_3O-CHO that its structure is illustrated in **Figure 2.1**. The structure of furfural consists of two part, an aldehyde functional group connected to furan ring. These make furfural an interesting platform molecule to manufacture a variety of products. The Pure form of furfural is colorless however the color can change from yellow to dark-brown when it exposes in air and moisture. Furfural dissolves readily in most polar organic solvents, but it is only slightly soluble in either water or alkanes. The physical properties of furfural are summarized in **Table 2.1**

Furfural may be obtained by the acid catalyzed dehydration of 5-carbon sugars (pentose), particularly xylose

$$C_5H_{10}O_5 \longrightarrow C_5H_4O_2 + 3H_2O$$

These sugars may be obtained from hemicellulose present in lignocellulosic biomass, which can be extracted from most terrestrial paints. In the laboratory, furfural can be synthesized from plant material by reflux with dilute sulfuric acid or other acids.

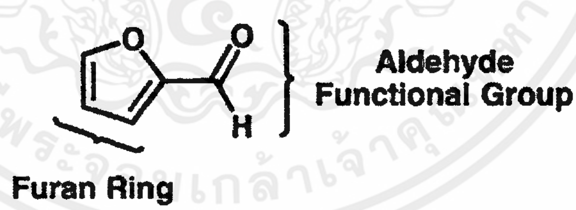


Figure 2.1 Chemical structure of furfural [10]

2.2 Furfuryl alcohol [11]

Furfuryl alcohol (FA) is an organic compound which has molecular formula of $C_5H_6O_2$. and the chemical structure of furfuryl alcohol is illustrated in **Figure 2.2.** The physical properties of FA are showed in **Table 2.1** The furfuryl alcohol is considered as an important chemical intermediate to produce many high valuable compounds such as polymers, resin, adhesive, farm chemicals, lysine, vitamin C and other pharmaceutical compounds, etc. Commercially furfuryl alcohol has been produced from the hydrogenation of furfural using a copper-chromite catalyst. However, hydrogenation of furfuryl alcohol can proceed to give hydroxymethyl derivative of tetrahydrofuran and 1,5-pentanediol, etc.

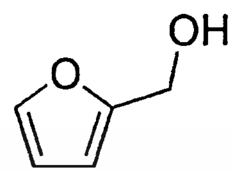


Figure 2.2 Chemical structure of furfuryl alcohol [11]

Moreover, furfural undergoes many reactions including Diels-Alder additions to electrophilic alkenes and alkynes. For example Hydroxymethylation gives 1,5-bis(hydroxymethyl)furan. Hydrolysis gives levulinic acid. Upon treatment with acids, heat and catalysts, furfuryl alcohol can be made to polymerize into a resin, poly(furfuryl alcohol). Hydrogenation of furfuryl alcohol can proceed to give hydroxymethyl derivative of tetrahydrofuran and 1,5-pentanediol.

Table 2.1 The physical properties of Furfural and Cu Furfuryl alcohol [9,11]

Properties	Furfural	Furfuryl alcohol
Molar mass ($g.mol^{-1}$)	96.08	98.10
Density (g/ml)	1.16	1.12
Melting point (°C)	-37	-29
Boiling point (°C)	162	170

2.3 Hydrogenation pathways of furfural [3,13]

The hydrogenation pathways of furfural are illustrated in **Figure 2.3**. Furfural can be hydrogenated at two position, that are carbonyl group (C=O) in the exocyclic of furan ring and unsaturated bond in furan ring. If the carbonyl group is hydrogenated, furfuryl alcohol will obtained the main product whereas if unsaturated bond in furan ring is hydrogenated tetrahydrofurfural will be obtain as the major product. In addition, other products are formed via furfural hydrogenation and oxidation.

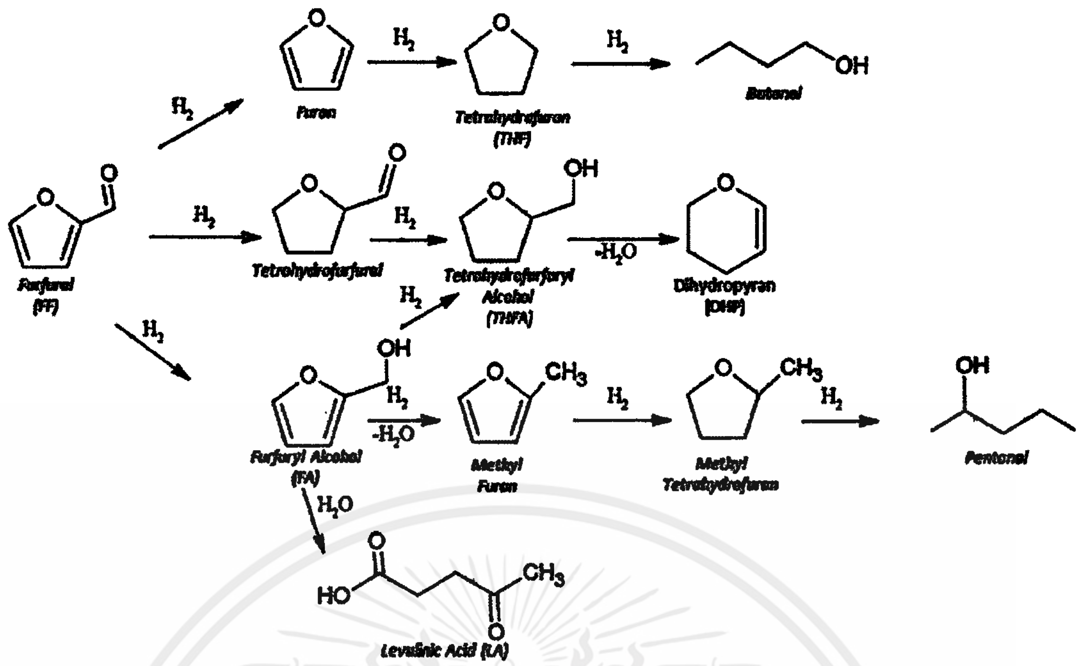


Figure 2.3 Hydrogenation pathways of furfural [3]

2.4 Catalysis

2.4.1 Platinum and Copper metals [14,15]

Copper is a chemical element that is a soft malleable, and ductile metal. The physical properties of Cu show in **Table 2.2.** It is very high thermal and electrical conductivity. In the most compounds it can have the valency (oxidation state) of +I or the valency state +II. The aqueous solution of copper ions in the oxidation +II has a blue color. The primary mechanical properties of copper are hardness, strength and ductility.

Platinum is one of the most active metals and it has remarkable resistance to corrosion, even at high temperature. The physical properties of Pt show in **Table 2.2.** Pt catalysts have advantages of high surface area and surface-to-volume ratio, which would be beneficial for improving catalytic efficiency. The Pt nanoparticles with smaller size also have high surface energy, and easy to aggregate between interparticle, leading to poor stability. Thus, dispersion of small size Pt nanoparticle on suitable support material is one of the best ways of controlling and stabilization of Pt nanoparticle

Table 2.2 The Physical properties of Cu and Pt [16] metals.

Properties	Pt	Cu
Atomic number	78	29
Molecular weight (g/mol)	195.08	63.55
Density (g/cm^3)	21.45	8.96
Boiling point (ºC)	3825	2562
Electron configuration	[Xe]^{54} 4f^{14} 5d^9 6s^1	[Ar]^{18} 3d^{10} 4s^1

2.4.2 Titanium dioxide [17]

Titanium dioxide or titania is a naturally occurring oxide of the metal titanium with a chemical formula of TiO_2. Titanium dioxide exists in a both crystalline and amorphous forms and mainly exists in three crystalline, namely, anatase rutile and bookite, the structure as Illustrated in **Figure 2.4**. Anatase is considered the most important phase of titanium dioxide in terms of trade and rarely exists in nature in pure form. This phase is stable at temperature less than 600 ºC and change to rutile phase at temperature higher than 600 ºC. The bulk properties as show in **Table 2.3.** Titania shows unique characteristics such as non-toxicity, low cost, easy handling,

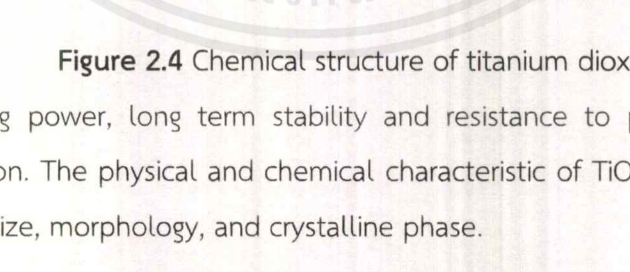


Figure 2.4 Chemical structure of titanium dioxide [18]

Strong oxidizing power, long term stability and resistance to photochemical and chemical erosion. The physical and chemical characteristic of TiO_2 can be controlled by its particle size, morphology, and crystalline phase.

Table 2.3 The bulk properties of TiO_2 [17]

Properties	Anatase	Rutile	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Density (kg/m^3)	3830	4240	4170
Dimension, nm			
a	0.3733	0.4584	0.5436
b	-	-	0.9166
c	0.9370	0.2953	0.5135

2.5 Incipient-wetness impregnation method [17]

Incipient wetness impregnation is the most widely used method for the preparation of heterogeneous catalysts. This method carried out in aqueous solution. It is the most common method for catalyst preparation. Metal salts that used as catalyst precursors are simply dissolved in the impregnating solution, the volume of which is made to match the pore volume of the support. The metal loading is controlled by the concentration of metal ion in solution. Incipient wetness impregnation is attractive because of its technical simplicity, low costs and limited amount of wastes.

2.6 Literature reviews

C. Zhang et.al [4] studied the catalytic performance supported of platinum over layer on nickel (Ni@Pt) and copper (Cu@Pt) catalysts in furfural hydrogenation. According to H_2 chemisorption and ethylene hydrogenation results showed weakened H_2 binding strength of both over layer catalysts compared to pure Pt,which results consistent with literature predictions. Cu@Pt showed higher TOFS of furfural hydrogenation compared to pure Pt and pure Cu. It is proposed that Cu@Pt catalyst can improved the catalytic activity of furfural hydrogenation by decreasing H_2 adsorption strength is decreased.

Á. O'Driscoll et.al. [19] studied the selective hydrogenation by using monometallic catalysts such as platinum, palladium, copper and nickel which prepared by wet impregnation. It was found that platinum was the most promising metal of those studied because it displayed higher selectivity to furfuryl alcohol.

B. A.T. Mehrabadi, et.al,[20] studied synthesis efficacy the preparation of Pt on different supports by impregnation, reductive deposition and colloidal methods gives larger particle size. The average particle size of the catalyst that was prepared by SEA is 1.5 nm for carbon, 1.8 nm for silica, and 2.9 nm for alumina. These are much smaller particles than those prepared by DI, 10.3, 10, and 10 nm, there is perhaps no method more effective than strong electrostatic adsorption (SEA). Finally, the best methods simply in terms of depositing high metal loadings are DI.

S. Bhogeswararao et.al.,[21] studied hydrogenation of furfural over γ-Al_2O_3 supported Pt and Pd catalysts. This difference in selectivity over Pd and Pt catalysts is also due to differences in the binding energies and orientation of adsorption of FAL on catalyst surfaces While the Pt catalysts were selective for C=O hydrogenation (yielding furfuryl alcohol) while Pd facilitated ring hydrogenation (producing tetrahydrofurfuryl alcohol) and Pd catalyst exhibited excellent decarbonylation activity forming furan.

H. Lou et.al.,[7] studied Nano-Pt and Nano-Pd particles were introduced to liquid-phase hydrogenation of farfural by using nano Pt and nano Pd supported multwalled carbon nanotubes which prepared via co-impregnation method. Different transition metal (Cr, Mn, Fe, Co, Ni) were added to modified on Pt and Pd-catalysts. Among the catalysts, Pt–Fe/MWNT (Pt: 0.5 wt%) showed highest conversion and selectivity to furfuryl alcohol (yield of 87.4%) while Pd–Ni/MWNT (Pd: 0.5 wt%) catalysts exhibited the best catalytic performance (83.3% yield of tetrahydrofurfuryl alcohol)

X. Chen, et.al.,[22] studied the catalytic hydrogenation of furfural to furfuryl alcohol either in gas phase and liquid phase by using Pt@TECN catalysts. When compared between liquid phase and gas-phase hydrogenation process of furfural, gas phase would result in higher amount of byproducts and need higher energy consumption owing to the necessity of vaporizing furfural while in liquid phase the Pt@TECN catalysts showed superior activity in the chemo selective hydrogenation of furfural toward furfuryl alcohol.

A. B. Merlo et.al.,[23] studied the bimetallic PtSn catalyst for the selective hydrogenation of furfural to furfuryl alcohol in liquid-phase. Tin-modified catalysts allowed obtaining higher conversions than the Pt/SiO_2 catalyst for the hydrogenation of furfural in the liquid-phase

CHAPTER 3

EXPEIMENTAL

3.1 Chemical and Substrates

The chemicals and substrates, purity, and the supplier that used in this research are summarized in **Table 3.1**.

Table 3.1 Chemical and substrates

	Chemical reagents	Grade of purity	Manufacturers
1	Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$)	Analytical	SIGMA-ALDRICH
2	Cupper (II) nitrate hexahydrate ($Cu(NO_3)_2$)	Analytical	CARLO ERBA
3	Titanium Dioxide (P25)	-	-
4	Deionized water	-	-
5	Furfural ($C_5H_4O_2$)	Analytical	SIGMA-ALDRICH
6	Butanol ($C_4H_{10}O$)	Analytical	CARLO ERBA
7	Air zero gas, zero grade	High purity (99.99%)	PRAXP
8	Hydrogen gas, high purity	High purity (99.99%)	RAXIR
9	Nitrogen gas, ultra-high purity	High purity (99.99%)	PRAXAIR

3.2 Instruments and apparatus

The instruments and apparatus which used to prepare and characterize all catalysts are illustrated as following:

- Beaker
- Dropper
- Burette clamp and stand
- Cylinder
- Wash bottle
- Desiccator
- Evaporating dish
- Forceps
- Oven
- Furnace
- X-ray powder diffractometer (XRD)
- X-ray fluorescence spectrometer (XRF)
- Temperature programmed reduction instrument (TPR, Mododel TCD_2-NIFED)
- BET surface area analyzer
- Transmission electron microscopy (TEM)

3.3 Preparation of monometallic Cu/TiO_2 Pt/TiO_2, and bimetallic Pt-Cu/TiO_2 catalysts by incipient wetness impregnation method

In this work, TiO_2-P25 was selected as the catalysts support. Prior to preparation of catalyst, TiO_2 was dried in the oven at 100 °C for 12 h. The pore volume of TiO_2 support was determined by adsorption of DI-water. Approximately, 3.0 g of dry TiO_2 was slowly dropped with DI-water until the TiO_2 powder became wet solid. The total pore volume of TiO_2 is equal to the total amount of adsorbed DI-water. These can be calculated from the different between initial and final volume of DI-water.

3.3.1 Preparation of monometallic 5%Cu/TiO_2 catalyst by incipient wetness impregnation method.

In this case, the desired amount of $Cu(NO_3)_2$. $6H_2O$ precursor (0.6001 g) which was 5.0 %wt. of Cu metal was dissolved in DI-water with equals pore volume of TiO_2

support. Then, the Cu solution was slowly dropped on TiO_2 support. The wet solid of Cu/TiO_2 was left to stand at room temperature for 6 h followed by drying in the oven at 100 °C 12 h. The dried Cu/TiO_2 sample was calcined in air at 450 °C with a heating rate 10 ° C/min for 3 h. Finally, we can get a monometallic 5.0 % Cu/TiO_2 catalyst.

3.3.2 Preparation of monometallic 0.5%Pt/TiO_2 catalyst by incipient wetness impregnation method.

For monometallic Pt/TiO_2 catalyst, 0.5 %wt. of Pt was deposited on TiO_2-P25 by using chloroplatinic acid hexahydrate as a Pt precursor. The desired amount of chloroplatinic acid hexahydrate (0.0398 g) was dissolved in DI-water with equals pore volume of TiO_2 support. After that, the solution was gradually dropped and mixed on TiO_2. Then, wet solid of Pt/TiO_2 sample was left to stand at room temperature for 6 h in order to assure the metal was adsorbed into the interpore of TiO_2. Afterward, the sample was dried in the oven at 100 °C for 12 h and then calcined in air at 450 °C with a heating rate 10 °C/min for 3 h. Finally, we can get a monometallic 0.5 % Pt/TiO_2 catalyst.

3.3.3 Preparation of a series of Pt-Cu/TiO_2 catalysts by incipient wetness impregnation method.

A series of bimetallic Pt-Cu/TiO_2 catalysts were prepared by sequential incipient wetness impregnation method with difference Pt/Cu ratios (0.5:0.5 and 0.5:5.0 %wt. /wt.). Various amount of Cu at 0.5 and 5.0 wt.% were impregnated on 0.5%Pt/TiO_2 catalyst that was prepared by incipient wetness impregnation method. The desired amount of $Cu(NO_3)_2.6H_2O$ precursor (0.5 and 5.0 wt.%) was dissolved in DI-water and then slowly dropped in 0.5%Pt/TiO_2 sample. After that, the wet solid of 0.5%Pt-x%Cu/TiO_2 catalyst was left to stand at room temperature for 6 h followed by drying in the oven at 100 °C 12 h. Then, the dried catalyst was calcined in air at 450 ° C with a heating rate 10 ° C/min for 3 h. Finally, we can get bimetallic 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2 catalysts.

3.4 Characterization of catalysts

3.4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is analytical technique used for crystalline phase identification of material. The patterns of TiO_2 support, Pt/TiO_2 catalysts and $Pt\text{-}Cu/TiO_2$ catalysts obtained using a D8 Advance Bruker AXS X-ray diffractometer and CuK_α radiation in scanning rage from 20 to 80 degree of 2-theta.

3.4.2 X-ray Fluorescence spectrometer (XRF)

X-ray Fluorescence spectrometer (XRF) is analytical technique to fine the chemical composition of the catalysts. The catalyst sample was weighed about 0.4 g and mixed together with boric and then compressed into alumina pan before analysis.

3.4.3 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) is a technique for the characterization of solid sample to find the efficient reduction condition and reduction temperature by percent metal loading of the catalysts. Approximately, 0.04-0.4 g of the catalysts were packed in a quartz tube reactor. The catalysts were pretreated with a N_2 flow (30 mL/min) at 200° C for 1 h and then cooled down to 35°C. Next step for TPR analysis, 30 mL/min of 10% H_2/Ar was introduce to sample and simultaneously raised up the temperature from 35 °C to 800 °C with a heating rate 10 °C/min.

Table 3.2 Amount of catalysts packed in TPR

Catalysts	Catalysts packed (g)
0.5%Pt/TiO_2	0.3805
5%Cu/TiO_2	0.0410
0.5%Pt-0.5%Cu/TiO_2	0.4319
0.5%Pt-5%Cu/TiO_2	0.1051

3.4.4 Brunauer Emmett Teller (BET)

The Brunauer Emmett Teller (BET) method is commonly applied to calculate the specific surface area on the basis of nitrogen adsorption isotherm measurements. Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. Nitrogen adsorption–desorption measurements surface area and porosity analyzer to determine the surface area, pore size distribution and structure, pore volume and the mean particle size.

3.4.5 Scanning Electron Microscopy (SEM) With Energy Dispersive X-Ray Spectroscopy (EDX)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Data are collected over a selected area of the surface of the sample

3.5 Liquid-phase selective hydrogenation of furfural alcohol

The liquid-phase selective hydrogenation of furfural was carried out in 100 mL stainless-steel batch reactor that the schematic diagram was illustrated in **Figure 3.1.** Prior to test the catalytic reaction, 0.1 g of catalyst was reduced in H_2 gas at 300 ° C for 2 h. After that, 0.05 g (50 mg) of catalyst was load in the stainless-steel batch reactor. Then, 50 μL of furfural mixed with 10 mL of butanol were added to stainless-steel batch reactor. After that, the reactor was heated up to 100 ° C and then 20 bar of H_2 gas was introduced. The solution was continuously stirred at 900 rpm for 2 h. After reaction, the liquid product was centrifuged in order to separate the solid catalyst and then the liquid sample was analyzed by GC.

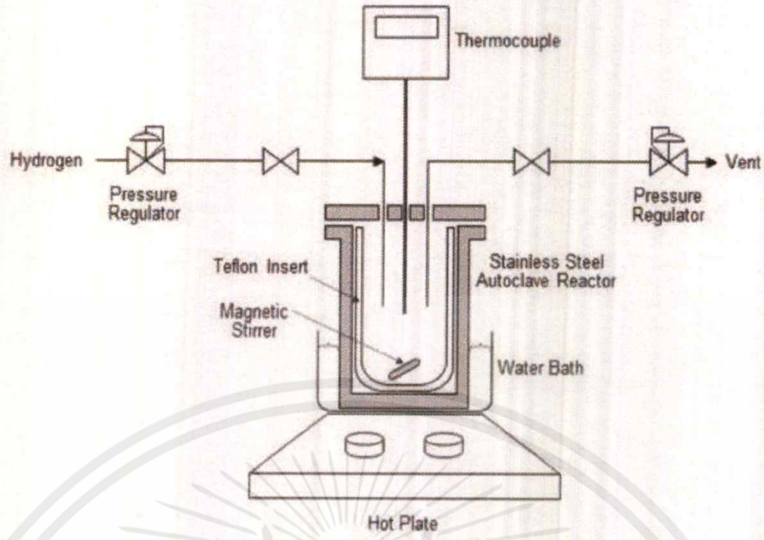


Figure 3.1 The schematic diagram of the liquid phase hydrogenation system

Table 3.3 Gas-Chromatography operating conditions

Gas chromatography (Shimadzu GC-2014)	Condition
Detector	FID
Packed column	Rtx-5
Carrier gas	Helium (99.99 vol.%)
Make-up gas	Air (99.99 vol. %)
Column temperature	110 °C
Injector temperature	260 °C
Detector temperature	270 °C
Time analysis	41.80 min

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalysts Characterizations

The characteristics of monometallic 5%Cu/TiO_2, 0.5%Pt/TiO_2 and bimetallic 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2 catalysts were investigated by various characterization techniques such as x-ray diffraction (XRD), X-ray fluorescence spectrometer (XRF), Temperature programmed reduction (H_2-TPR), Brunauer emmett teller (BET), and Scanning electron microscopy (SEM).

4.1.1 X-ray diffraction (XRD)

Figure 4.1 shows the XRD patterns of TiO_2 support and all catalysts. The TiO_2 support exhibited the characteristic peaks of mixed phase between anatase and rutile. Typically, the characteristic peaks of anatase TiO_2 are corresponding to 2θ = 25° (major), 37°, 48°, 55-56°, 62°, 71° and 75° whereas rutile TiO_2 are corresponding to 2θ= 28° (major), 36°, 42° and 57° [24]. For monometallic 0.5%Pt/TiO_2, the characteristic peaks of TiO_2 support were observed similar as the TiO_2 support, however, the characteristic peaks of PtO that should be appeared on around 2θ = 32° and 40° [36] were not detected. It is probably because of low among of Pt loading or high dispersion of PtO. Meanwhile for monometallic 5%Cu/TiO_2, the XRD patterns of CuO was found at 2θ =35.6°. Nevertheless, the characteristic peaks corresponding to PtO, CuO, or Pt-Cu alloy species did not observe on bimetallic 0.5%Pt-0.5%Cu/TiO_2 catalysts implied to both metals were highly dispersed on TiO_2 support. However, the characteristic peak of CuO species was detected on bimetallic 0.5%Pt-5%Cu/TiO_2 indicating to some agglomeration of CuO specie. [25]

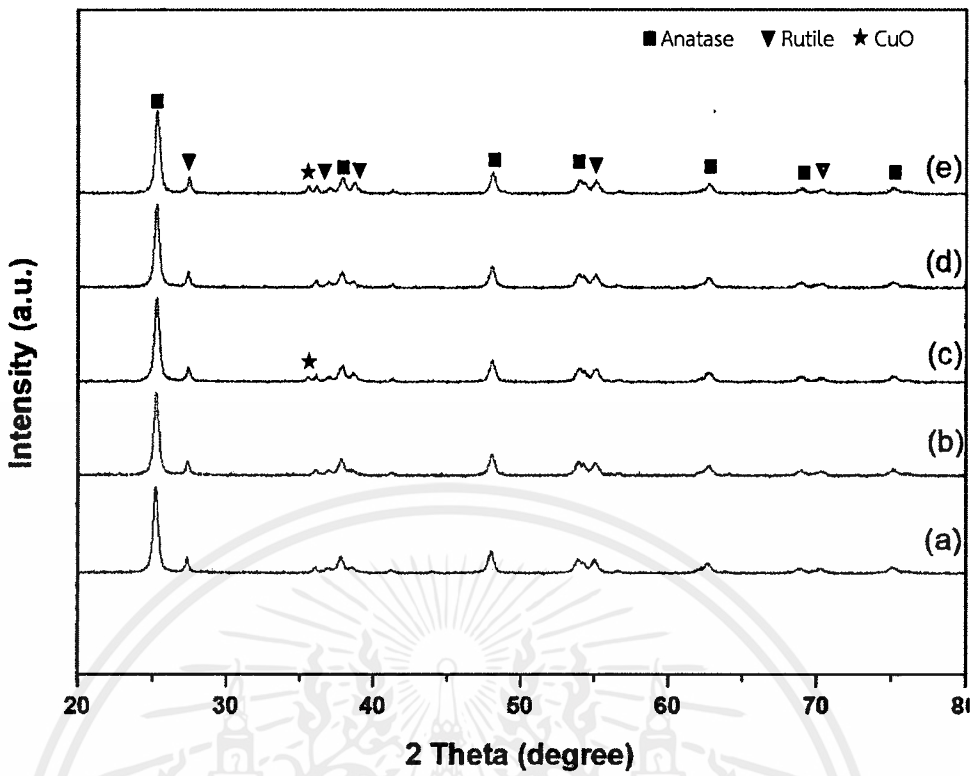


Figure 4.1 The XPD patterns of a) TiO_2, b) 0.5%Pt/TiO_2, c) 5%Cu/TiO_2, d) 0.5%Pt-0.5%Cu/TiO_2, and e) 0.5%Pt-5%Cu/TiO_2

4.1.2 X-ray fluorescence spectroscopy (XRF)

The metal composition of all catalysts was analyzed by X-ray fluorescence spectroscopy (XRF). **Table 4.1** summarized the elementals composition of 5%Cu/TiO_2, 0.5%Pt/TiO_2, 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%CuTiO_2 catalysts. For monometallic, the actual percentage of Cu on 5%Cu/TiO_2 catalysts was 5.04 %wt. which consisted of the desired amount of Cu loading at 5 %wt. While, for 0.5%Pt/TiO_2, the actual amount of Pt was found to be 0.63% wt. Which was higher than the desired amount of Pt loading at 0.5% wt. According to bimetallic catalysts, the actual amount of Pt was 0.5% and 0.47% wt. for 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2, respectively. Moreover, the actual amount of Cu loading was 0.53 and 4.74 %wt. for 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2, respectively. These could be said that the actual amount of Pt and Cu loading were accurate on both of bimetallic catalysts.

Table 4.1 Elementals composition of catalysts

Catalysts	wt.% Metal loading (XRF)		
	Cu	Pt	TiO_2
5%Cu/TiO_2	5.04%	-	94.0%
0.5%Pt-0.5%Cu/TiO_2	0.53%	0.50%	98.8%
0.5%Pt-5%Cu/TiO_2	4.74%	0.47%	93.4%
0.5%Pt/TiO_2	-	0.63%	99.1%

4.1.3 Temperature programmed reduction (TPR)

The reducibility and reduction behavior of the monometallic 5%Cu/TiO_2, 0.5%Pt/TiO_2 and bimetallic 0.5%Pt-0.5%Cu /TiO_2 and 0.5%Pt-5%Cu/TiO_2 catalysts were investigated by temperature programmed reduction technique (H_2-TPR). The results illustrate in **Figure 4.2**. The monometallic 0.5%Pt/TiO_2 shows a sharp reduction peak from 60-160 °C with a center peak at 101°C indicating to PtO specie was mostly reduced to metallic Pt^0 at 101 °C. However, the monometallic 5%Cu/TiO_2 catalyst shows two reduction peaks around 130 °C and 179 °C correspond to the reduction of different CuO species. Generally, large and crystallized CuO particles reduces at higher temperature than smaller CuO particles. Therefore, it can be noted that small and large crystallite CuO species were found on 5%Cu/TiO_2 [25]. For bimetallic catalysts, 0.5%Pt-0.5%Cu/TiO_2 gave a sharp reduction peak form 80-140 °C with a center peak at 115 °C corresponded to forming of Pt-Cu alloy while for bimetallic 0.5%Pt-5%Cu/TiO_2 catalysts two peaks at 133 °C and 214 °C, which similar the reduction peaks of 5%Cu/TiO_2 appeared in the range of 80-246 °C. These could be described that some of Cu adding was formed to Pt-Cu alloy and excess Cu loading could be formed high crystallite of CuO specie.

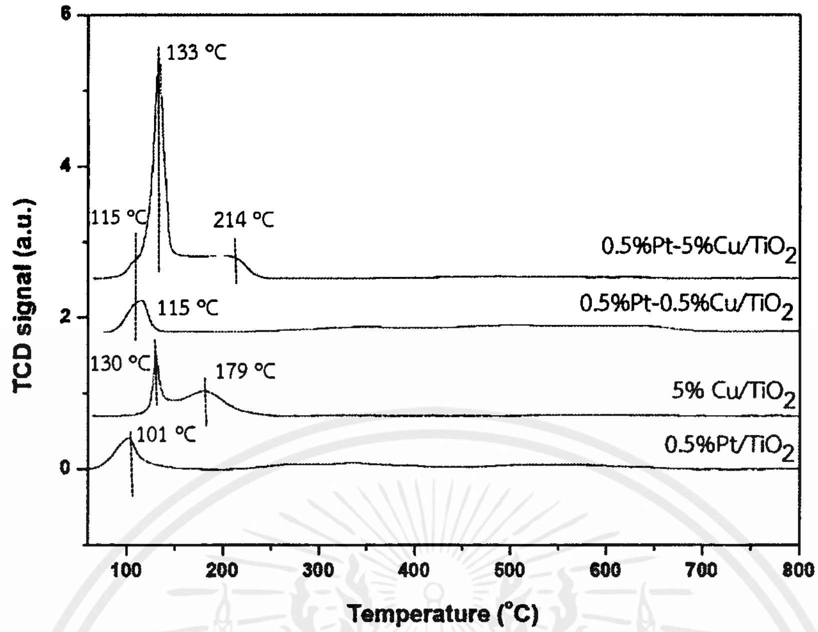


Figure 4.2 TPR profiles of 0.5%Pt/TiO_2, 5%Cu/TiO_2,0.5%Pt -0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2 catalysts

4.1.4 Brunauer Emmett Teller (BET)

The BET surface area, pore volume, and average pore diameters of all catalysts are reported in **Table 4.2**. The surface area of TiO_2 was 71.65 m^2/g and it decreased when Pt and Cu were impregnated. The surface area of monometallic 0.5%Pt/TiO_2 and 5%Cu/TiO_2 were 69.78 m^2/g and 64.90 m^2/g respectively which a bit decreased form TiO_2 support (71.65 m^2/g). For bimetallic catalysts, the surface area of 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2 were found to be 57.94% and 62.81%, respectively. However, the pore volume and average pore diameter of all samples were not significantly difference. Moreover, the isotherms of monometallic and bimetallic catalysts that show in **Figure 4.3** exhibited type IV of isotherms indicating to the characteristic of mesoporous materials. The mesoporous materials are defined as organized structures with pore diameters ranging between 2 nm to 50 nm [27].

Table 4.2 Physical properties of TiO_2, monometallic and bimetallic catalysts

Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
TiO_2	71.65	0.2405	2.150
5%Cu/TiO_2	64.90	0.3474	2.168
0.5%Cu-0.5%Pt/TiO_2	57.94	0.2269	2.182
5%Cu-0.5%Pt/TiO_2	62.81	0.2611	2.166
0.5%Pt/TiO_2	69.78	0.2552	2.169

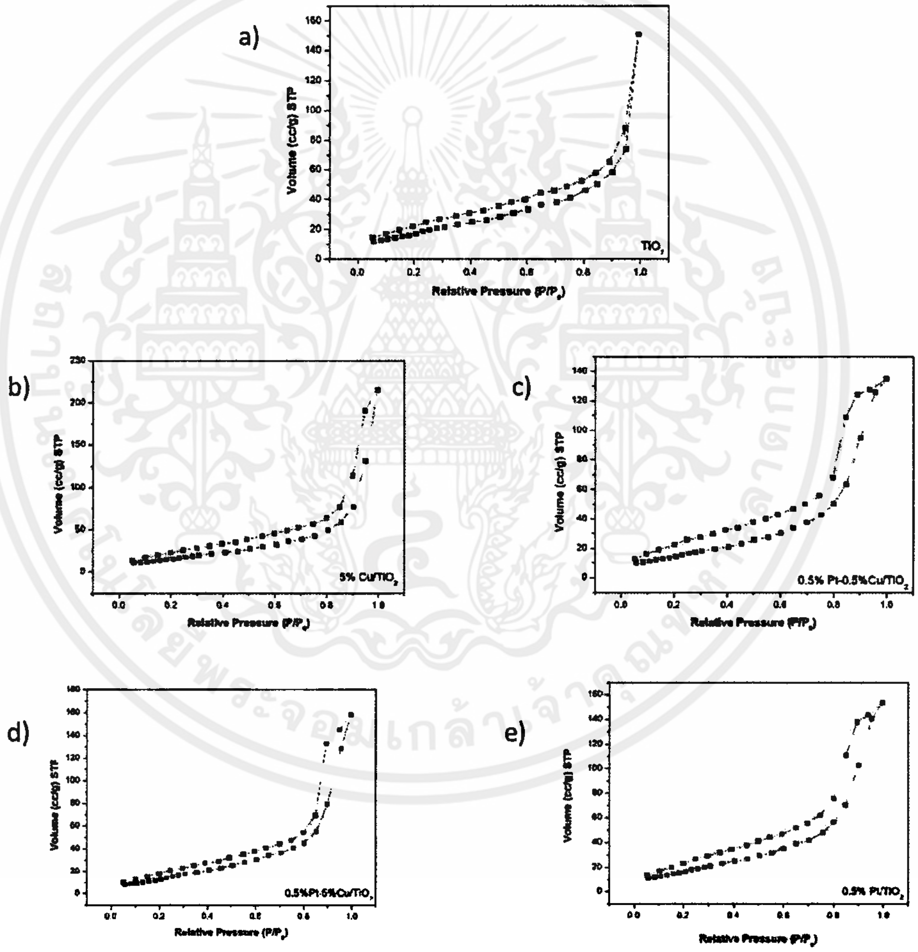


Figure 4.3. Desorption-adsorption isotherms of a) TiO_2, b) 5%Cu/TiO_2, c) 0.5%Pt -0.5%Cu/TiO2, d) 0.5%Pt-5%Cu/TiO_2 and e) 0.5%Pt/TiO_2 catalysts

4.1.5 Scanning Electron Microscopy (SEM)

The surface morphology and metal dispersions of all catalysts were investigated by SEM techniques. **Figure 4.4** shows the SEM images of monometallic 5%Cu/TiO_2, 0.5%Pt/TiO_2 and bimetallic 0.5%Pt-0.5%Cu/TiO_2, and 0.5%Pt-5%Cu/TiO_2 catalysts. All samples exhibited the similar morphologies as spheres and dense particles. In addition, the metals dispersion can be investigated by Elemental Dispersive X-ray (EDX) technique, which results illustrates in **Figure 4.5.** For monometallic 5%Cu/TiO_2 catalyst, most of Cu particles showed well dispersed on TiO_2 support however some Cu particles became agglomeration. In contrast for 0.5%Pt/TiO_2 catalyst, all Pt particles were highly dispersed on TiO_2 support and could not found an agglomeration of Pt particles. These results were good agreement with the XRD results. For bimetallic Pt-Cu/TiO_2 catalysts, highly dispersion of Pt metals were found on both 0.5%Pt-0.5%Cu/TiO_2, 0.5%Pt-5%Cu/TiO_2 catalysts whereas Cu dispersion were difference and were found to be depending on the amount of Cu loading. Low amount of Cu loading at 0.5%wt. gave highly dispersion of Cu metals whereas high amount of Cu loading at 5%wt. gave some agglomeration of Cu particles.

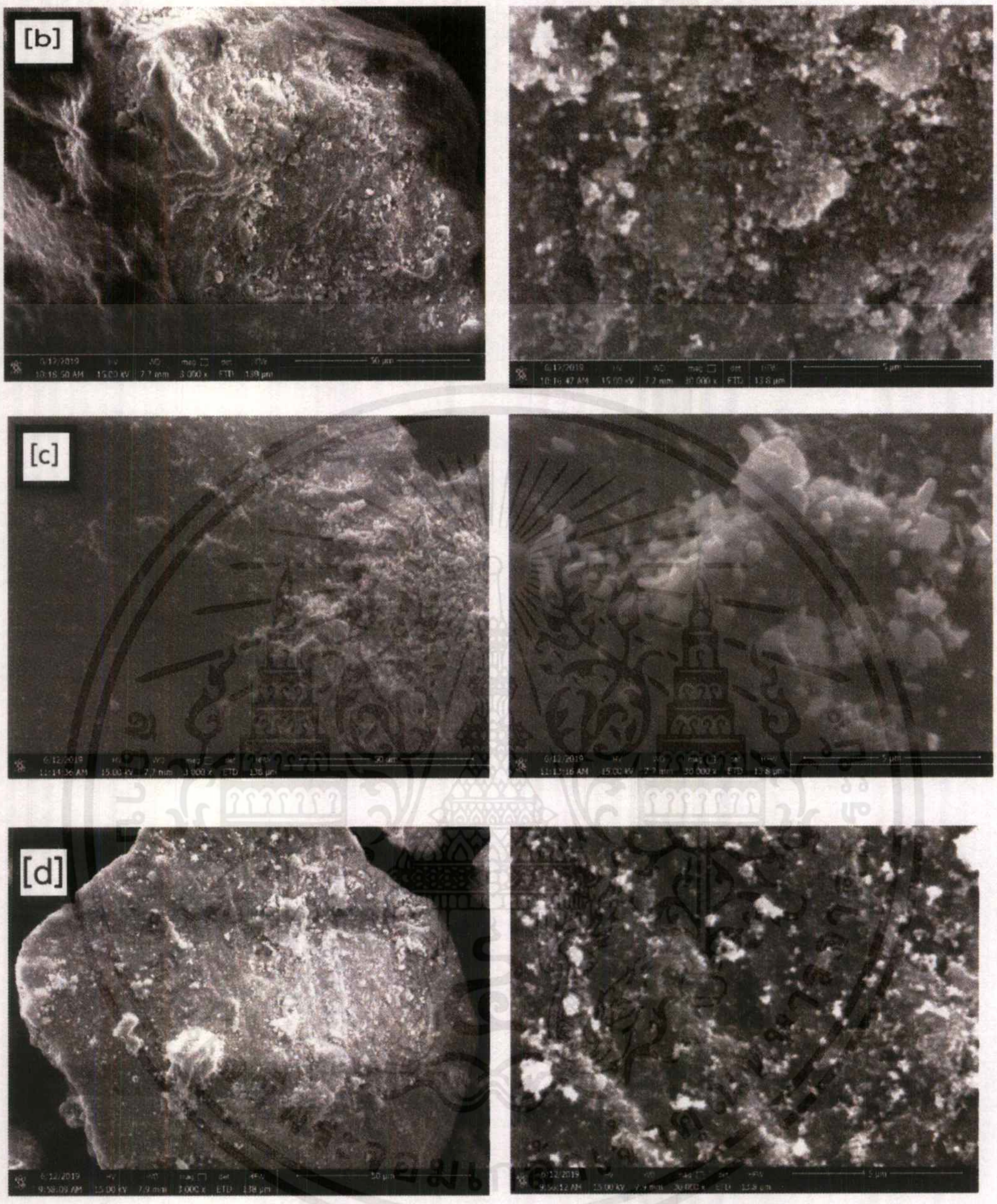


Figure 4.4 SEM images of a) 5%Cu/TiO_2, b) 0.5%Pt-0.5%Cu/TiO_2, c) 0.5%Pt-5%Cu/TiO_2, d) 0.5%Pt/TiO_2,

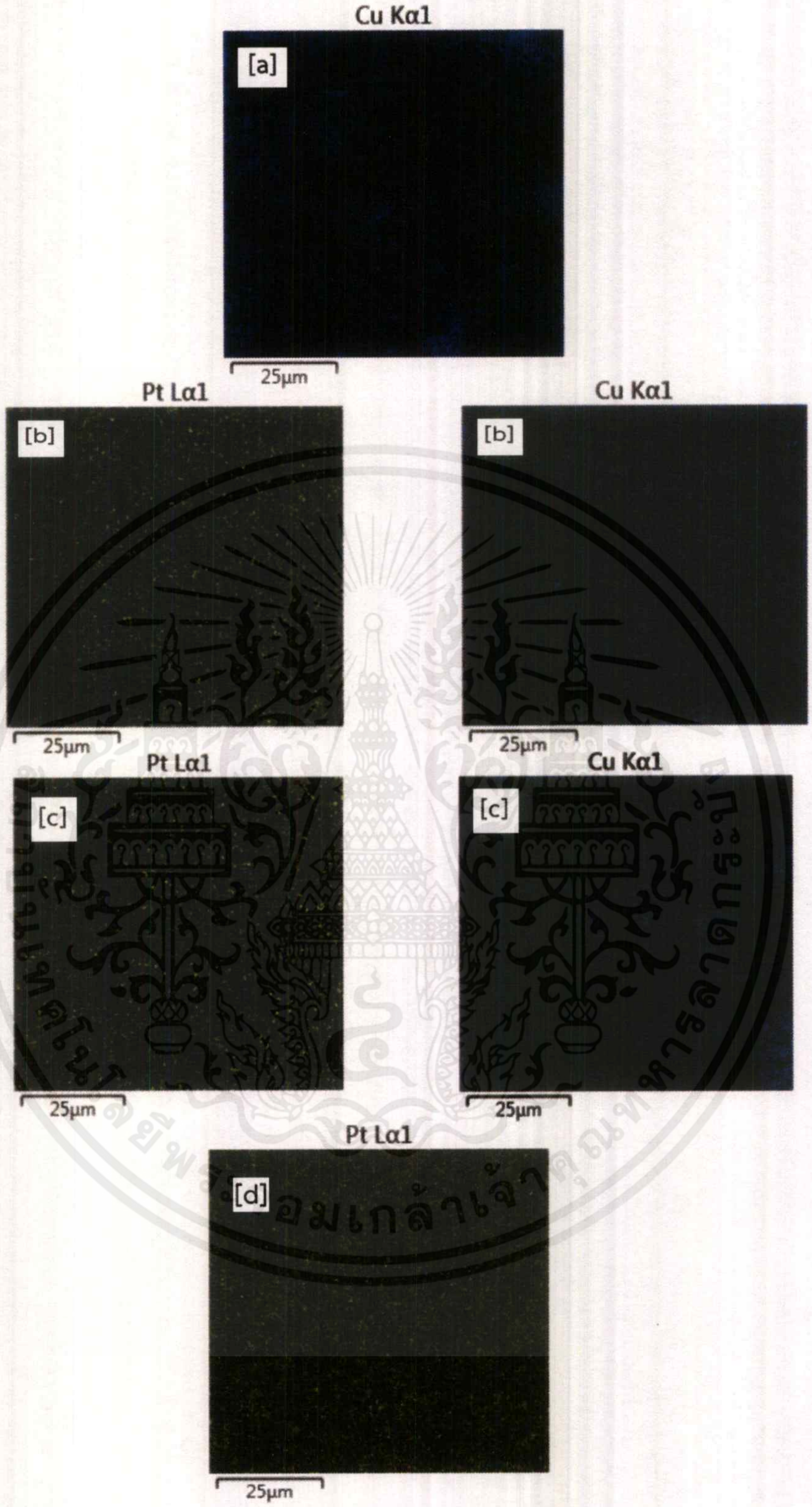


Figure 4.5 SEM-EDX images of (a) $5\%Cu/TiO_2$, (b) $0.5\%Pt$-$0.5\%Cu/TiO_2$, c) $0.5\%Pt$-$5\%Cu/TiO_2$, (d) $0.5\%Pt/TiO_2$,

4.2 Reaction study in liquid-phase selective hydrogenation of furfural to furfuryl alcohol

The catalytic performance of all catalysts was investigated in liquid-phase selective hydrogenation of furfural to furfuryl alcohol. **Table 4.3** exhibits the catalytic performances of monometallic 5%Cu/TiO_2, 0.5%Pt/TiO_2 and bimetallic 0.5%Pt-0.5%Cu/TiO_2 and 0.5%Pt-5%Cu/TiO_2 catalysts. Prior to test the reaction, hydrogenation was performed in batch reactor at the same condition for all catalysts but did not add catalyst in the reactor. The result showed that no conversion of furfural. It means hydrogenation did not occur without catalyst. Afterward the hydrogenation of all catalysts were tests. The conversion of 5%Cu/TiO_2 catalyst was 25.44% with 100% of selectivity to 2-furaldehyde dibutyl acetal, which was an undesired product that produced from acetalization between furfural and butanol. It was possibly due to TiO_x oxygen vacancy, which obtained from reduction of TiO_2, acted as the lewis acid site that promoted acetalization. The mechanism of acetalization of furfural and butanol could exhibit in **Scheme 1**. Moreover, rate of hydrogenation of Cu metal is known to be low when compared with other metal. Therefore, 0.5% wt. of Pt was added into 5%Cu/TiO_2 in order to improve the catalytic performance and then conversion of furfural for 0.5%Pt-5%Cu/TiO_2 decreased to 15.53% but the selectivity to furfuryl alcohol increased to 55.12% and did not found acetal product. However, butyl furfural ester produced from oxidative coupling reaction around 41.95% was found as other undesired product in **Scheme 2**. According to XRD and TPR results, 0.5%Pt-5%Cu/TiO_2 shows high dispersion of Pt-Cu alloy particles and some agglomerations of CuO particles. These might be resulted to low conversion of furfural but high selectivity to furfuryl alcohol. In addition, 0.5%Pt-5%Cu/TiO_2 catalyst was a bifunctional one that promoted hydrogenation and oxidative coupling reaction activity. To clarify the behavior of Pt and Cu metal on selective hydrogenation of furfural, 0.5%Pt-0.5%Cu/TiO_2, which expected to form completed Pt-Cu alloy, was studied and the conversion of furfural increased to 47.08% with selectivity to furfuryl alcohol only 16.18% whereas the selectivity of acetal enhanced to 77%. These results indicated that Pt-Cu alloy could improve hydrogenation conversion but did not improve the selectivity to furfuryl alcohol. The selectivity of furfuryl alcohol seem to depend on the proportion of reduced TiO_x and active metal loading. In this case when the amount of total active metal (Pt, Cu) decreased, the amount of TiO_x might be increased and could be promoted acetalization produced acetal as an undesired product resulting to lower selectivity to furfuryl alcohol. In addition, monometallic

0.5%Pt/TiO_2 catalyst was used to confirm the effect of Pt metal on the hydrogenation. Using 0.5%Pt/TiO_2 catalyst, highest conversion at 65.57% with highest selectivity to furfuryl alcohol at 76.40% was found. Moreover, decreasing of reaction temperature from 100 to 50°C was test for 0.5%Pt/TiO_2 catalyst. It was seen that, conversion of furfural increased whereas the selectivity of furfuryl alcohol was not significant changed. However, the oxidative coupling reaction to form ester were suppressed. Hence, it could be said that monometallic 0.5%Pt/TiO_2 was an excellence catalyst in liquid-phase selective hydrogenation of furfural to furfuryl alcohol. The result of 0.5%Pt/TiO_2 can be conclude when decreased temperature from 100 to 50°C the selective of 2-furaldehyde dibutyl acetal increases due to acetalization reaction is a thermodynamic control depend on a temperature but selective of furfuryl alcohol decrease as same as a selective of butyl furfural ester because hydrogenation and oxidative coupling reaction is a kinetic control depend on a concentration of furfural. Nevertheless, the catalytic performance of both bimetallic Pt-Cu/TiO_2 catalysts were better than 5%Cu/TiO_2 because they gave a higher yield of furfuryl alcohol than monometallic 5%Cu/TiO_2.

Table 4.3 the catalytic performance of monometallic Cu/TiO_2, Pt/TiO_2 and bimetallic Pt-Cu/TiO_2 catalysts

Catalysts	Temperature (°C)	Conversion (%)	Selective (%)			
			FA [a]	THFA [b]	Ester [c]	Acetal [d]
Blank	100	0.00	0.00	0.00	0.00	0.00
5%Cu/TiO_2	100	25.44	0.00	0.00	0.00	100
0.5%Pt-5%Cu/TiO_2	100	15.53	55.12	2.93	41.95	0.00
0.5%Pt-0.5%Cu/TiO_2	100	47.04	16.18	0.47	5.93	77.00
0.5%Pt/TiO_2	100	65.57	76.40	1.42	22.18	0.00
0.5%Pt/TiO_2	50	86.63	72.58	5.56	0.00	21.86

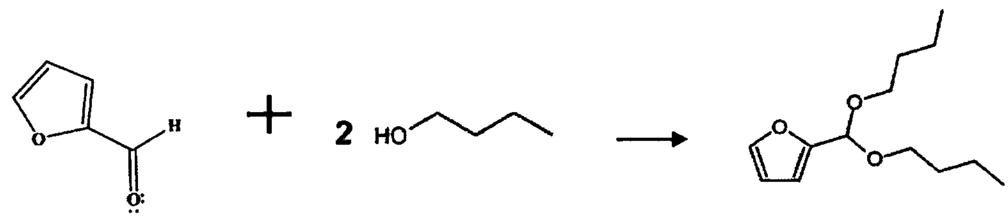
Reaction conditions: catalysts 50 mg, 50 μL furfural in 10 mL butanol under H_2 pressure 20 bar for 2 hours.

a FA: furfuryl alcohol

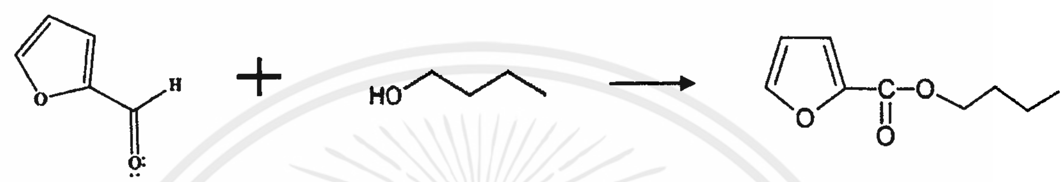
b THFA: tetrahydrofurfuryl alcohol

c Ester: butyl furfural ester

d Acetal: 2-furaldehyde dibutyl acetal



Scheme 1 Oxidative coupling reaction of furfural and butanol to form butyl furfural ester



Scheme 2. Acetalization reaction of furfural and butanol to form 2-furaldehyde dibutyl acetal

The effect of solvents to product distribution in liquid-phase selective hydrogenation of furfural to furfuryl alcohol was investigated and the results were summarized in **Table 4.4**. In this case, methanol, butanol and acetronitrile were selected to comparatively study with 0.5%Pt/TiO_2 catalyst at the temperature 50 °C H_2-pressure 20 bar. When using methanol as a solvent, the furfural conversion is the highest (98.66%) but the selective of furfuryl alcohol is the lowest (11.99%) because almost of product was 2-furaldehyde dimethyl acetal, which produced from acetalization between furfural and methanol. It could be note that acetalization was easy to occur more than hydrogenation when using small molecule alcohol. However, when using butanol (higher molecule alcohol as a solvent, the furfural conversion slightly decreased to 86.63% but gave high selectivity of furfuryl alcohol (72.58%). It might be because of higher alcohol occupied a long chain hydrocarbon and more steric hindrance than a small one. It is difficult to occur acetalization. However, when using acetonitrile as a solvent, the conversion of furfural became lowest at 22.29% with a selectivity to furfuryl alcohol around 72.57%. The lowest conversion for acetonitrile might be because of C☰N in acetonitrile could competitive adsorbed with furfural causing a low conversion of furfural. Therefore, the suitable solvent for liquid-phase selective hydrogenation of furfural to furfuryl alcohol in this case was butanol because it gave a high conversion of furfural with high selectivity of furfuryl alcohol

Table 4.4 The effect of solvents on the catalytic performance of 0.5%Pt/TiO_2 catalyst.

Solvent	Conversion (%)	Selectivity (%)			
		FA [a]	THFA [b]	Acetal [c]	Other
Methanol	98.66	11.99	0	88.01[c1]	0
Butanol	86.63	72.58	5.56	21.86[c2]	0
Acetronitrile	22.29	72.57	0	0	27.42

Reaction conditions: catalyst 50 mg, 50 μL of furfural, 10 mL of solvent temperature 50 °C, H_2 pressure 20 bar after 2 hours

[a] FA: furfuryl alcohol

[b] THFA: tetrahydrofurfuryl alcohol

[c1] Acetal: 2-furaldehyde dimethyl acetal

[c2] Acetal: 2-furaldehyde dibutyl acetal

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusions

The bimetallic 0.5%Pt-5%Cu/TiO_2 give a good catalytic performance in liquid-phase selective hydrogenation than monometallic 5%Cu/TiO_2 because it occupied highly dispersion of Pt-Cu alloy with a suitable proportion reduced TiO_x and the total amount of active metals. However, the monometallic 0.5%Pt/TiO_2 is the best catalyst in this reaction because it gave the highest furfural conversion and highest furfuryl alcohol selective.

5.2 Suggestions

1. Pt/TiO_2 catalyst should be calcined at temperature 550 °C for decomposition Cl^-.

2. Incipient wetness impregnation method should be done at low metal loading because it can be a good dispersion catalyst.

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APPENDIX

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

A.1 The calculation shown below for 0.5%Cu/TiO_2 prepared by incipient wetness impregnation method

Precursor:

Cupper (II) nitrate hexahydrate (Cu $(NO_3)_2$) MW. = 241.57 g/mol

Calculation

TiO_2 100-5 = 95 g

Cu 5 = 5 g

For TiO_2 3 g

Cu required $= \frac{(3\ g \times 5\ g)}{95\ g} = \mathbf{0.158\ g}$

Cupper (II) nitrate hexahydrate dissolved in DI water, the pore volume of the TiO_2 is 1.8 ml in silica 3 g. which Cu precursor was stock in solution form.

$$\text{Cu required in stock solution} = \frac{\text{weight of Cu required} \times \text{MW. Cu }(NO_3)_2}{\text{MW. Cu}}$$

$$= \frac{0.158\ g \times 241.57\ g/mol}{63.55\ g.\ Pt}$$

$$= 0.6001\ g\ \text{precursor}$$

A.2 The calculation shown below for 0.5%Pt/TiO_2 prepared by incipient wetness impregnation method

Precursor:

Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) MW. = 517.90 g/mol

Calculation

TiO_2 100-0.5 = 99.5 g

Pt 0.5 = 0.5 g

For TiO_2 3 g

Pt required $= \frac{(3\ g \times 0.5\ g)}{99.5\ g} = \mathbf{0.015\ g}$

Chloroplatinic acid hexahydrate dissolved in DI water, the pore volume of the TiO_2 is 1.8 ml in silica 3 g. which Pt precursor was stock in solution form

$$\text{Pt required in stock solution} = \frac{\text{weight of Pt required} \times \text{MW. } H_2PtCl_6.6H_2O}{\text{MW. Pt}}$$

$$= \frac{0.015 \text{ g} \times 517.9 \text{ g/mol}}{195.078 \text{ g. Pt}}$$

$$= 0.0398 \text{ g precursor}$$

Calculation of 0.5%Cu on 0.5%Pt/TiO_2 by incipient wetness impregnation method.

1. Prepared 0.5%Pt/TiO_2

Precursor:

Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) MW. = 517.90 g/mol

Cupper (II) nitrate hexahydrate ($Cu (NO_3)_2$) MW. = 241.57 g/mol

Calculation

TiO_2 100-0.5 = 99.5 g

Pt 0.5 = 0.5 g

For TiO_2 3 g

$$\text{Pt required} = \frac{\mathbf{(3 \text{ g} \times 0.5 \text{ g})}}{\mathbf{99.5 \text{ g}}} = \mathbf{0.015 \text{ g}}$$

$$\text{Pt required in stock solution} = \frac{\text{weight of Pt required} \times \text{MW. } H_2PtCl_6.6H_2O}{\text{MW. Pt}}$$

$$= \frac{0.015 \text{ g} \times 517.9 \text{ g/mol}}{195.078 \text{ g. Pt}}$$

$$= 0.0398 \text{ g precursor}$$

2. Dissolved 0.5%Cu concentration solution

Calculation

TiO_2 100-0.5 = 99.5 g

Cu 0.5 = 0.5 g

For TiO_2 3 g

$$\text{Cu required} = \frac{\mathbf{(3 \text{ g} \times 0.5 \text{ g})}}{\mathbf{99.5 \text{ g}}} = \mathbf{0.015 \text{ g}}$$

$$\text{Cu required in stock solution} = \frac{\text{weight of Cu required} \times \text{MW. } Cu (NO_3)_2}{\text{MW. Cu}}$$

$$= \frac{0.015 \text{ g} \times 241.57 \text{ g/mol}}{63.55 \text{ g. Pt}}$$

$$= 0.057 \text{ g precursor}$$

3. Dropped 0.5%Cu solution on 0.5Pt/TiO_2 based

Calculation

0.5%Pt/TiO_2	99.5 g	has Cu metal	0.5 g
0.5%Pt/TiO_2	2.8 g	has Cu metal	$\frac{0.5\ g \times 2.8\ g}{99.5\ g} = 0.0141\ g$

Cu metal 63.55 g $Cu(NO_3)_2 \cdot 3H_2O$ = 241.57 g

Cu metal 0.0141 g $Cu(NO_3)_2 \cdot 3H_2O = \frac{241.57\ g \times 0.0141\ g}{63.55\ g}$

= 0.0536 g precursor

Other concentration catalysts do as same as this calculation

APPENDIX B

CATALYST CHARACTERIZATION

B.1 X-ray diffraction (XRD)

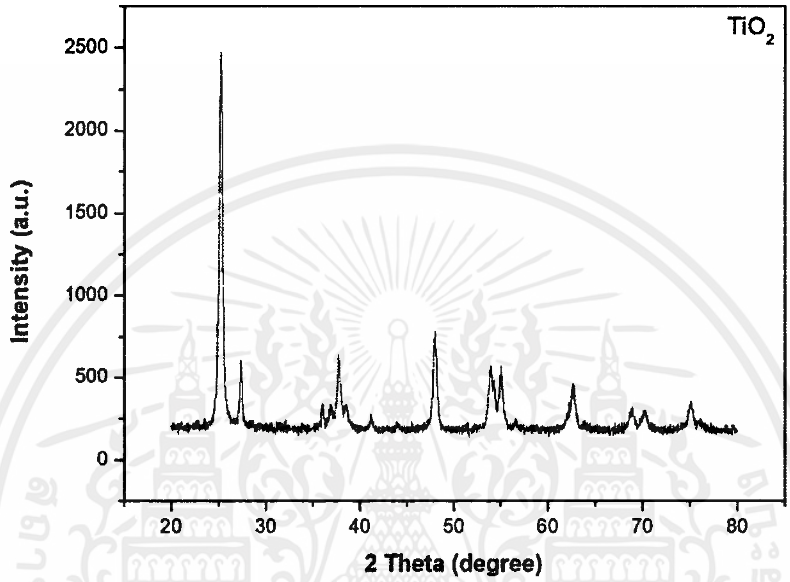


Figure B1 The XRD patterns of TiO_2 support.

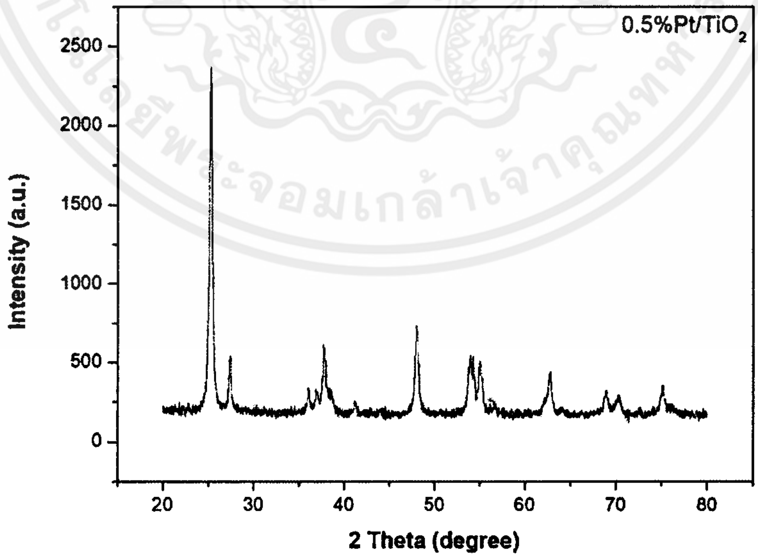


Figure B2 The XRD patterns of 0.5%Pt/TiO_2 catalyst.

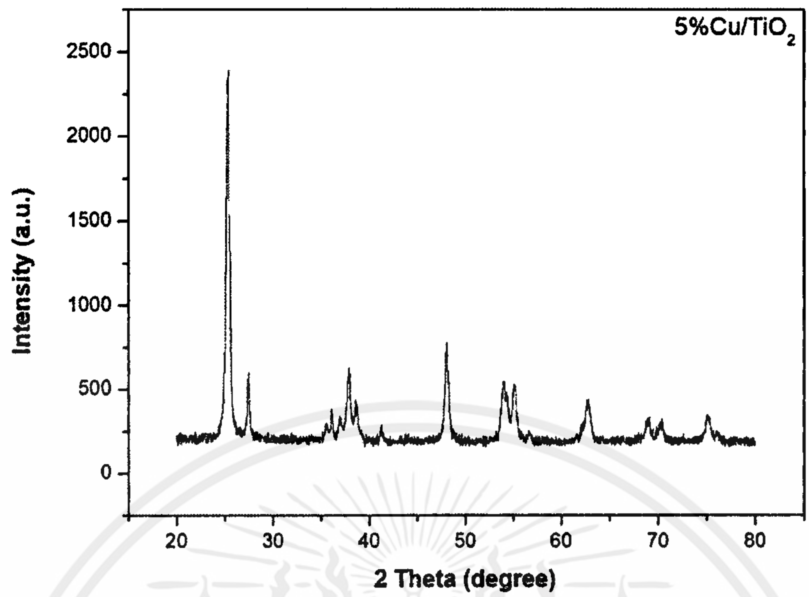


Figure B3 The XRD patterns of 5%Cu/TiO_2 catalyst.

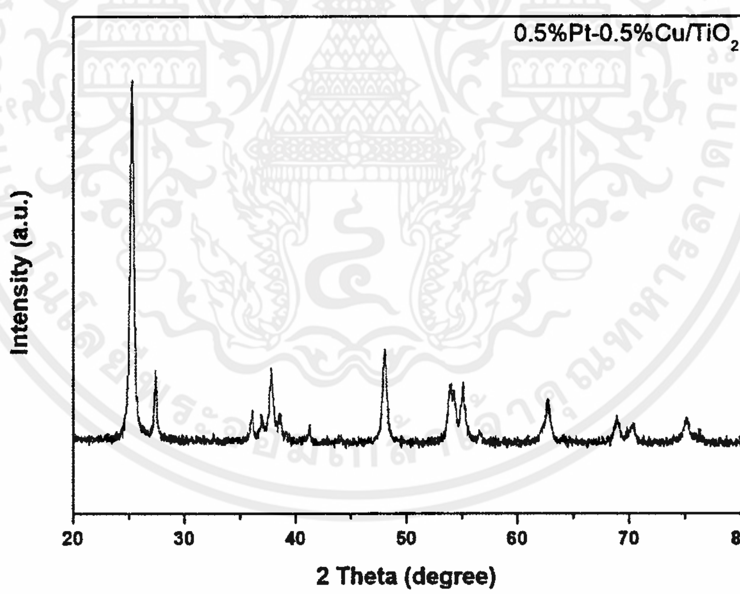


Figure B4 The XRD patterns of 0.5%Pt-0.5%Cu/TiO_2 catalyst.

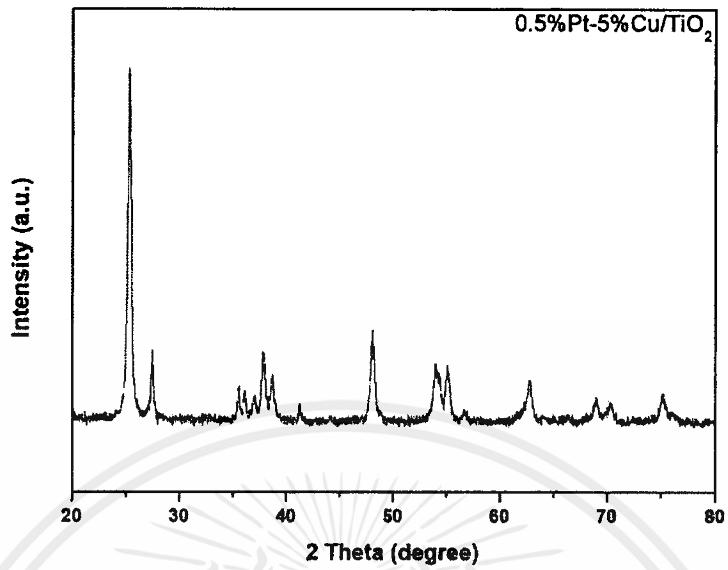


Figure B5 The XRD patterns of 0.5%Pt-5%Cu/TiO_2 catalyst.

B.2 X-ray fluorescence spectrometer (XRF)

Table B1 The Results Amount of metal of Pt/TiO_2, Cu /TiO_2 and Pt-Cu/TiO_2 catalysts.

Catalysts	Pt (%)	Cu (%)	TiO_2 (%)
5%Cu /TiO_2	-	5.04	94.0
0.5%Cu-0.5%Pt/TiO_2	0.50	0.53	98.80
5%Cu-0.5%Pt/TiO_2	0.47	4.74	93.40
0.5%Pt/TiO_2	0.63	-	99.10

B.3 Temperature program reduction (TPR)

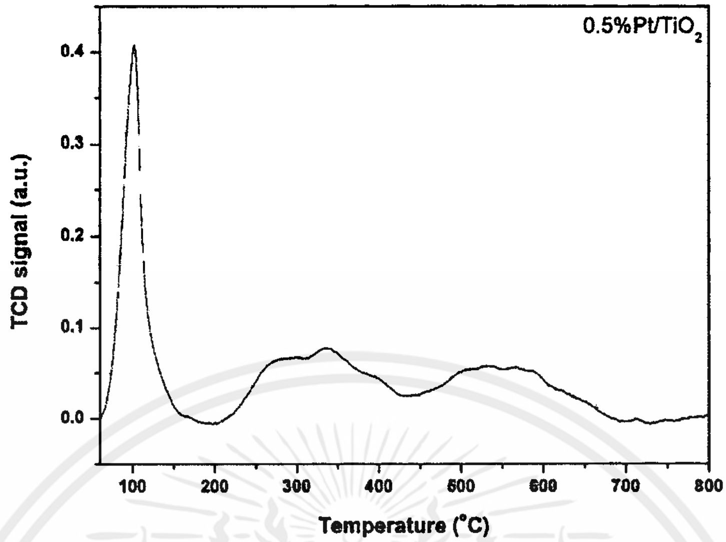


Figure B6 TPR profiles of 0.5%Pt/TiO_2 catalyst.

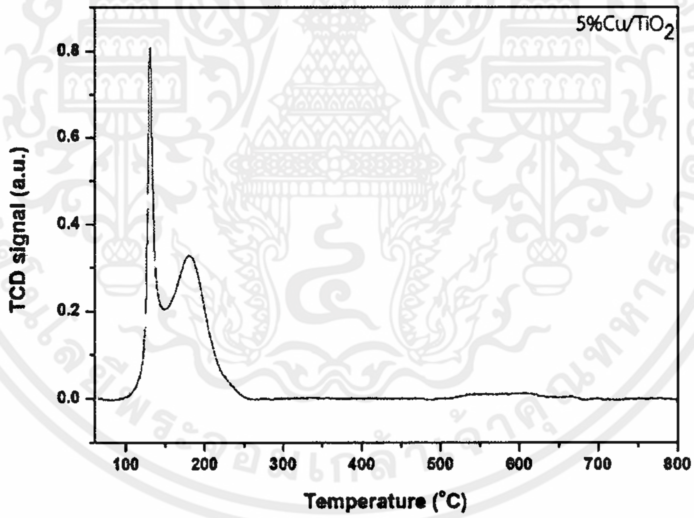


Figure B7 TPR profiles of 5%Cu/TiO_2 catalyst.

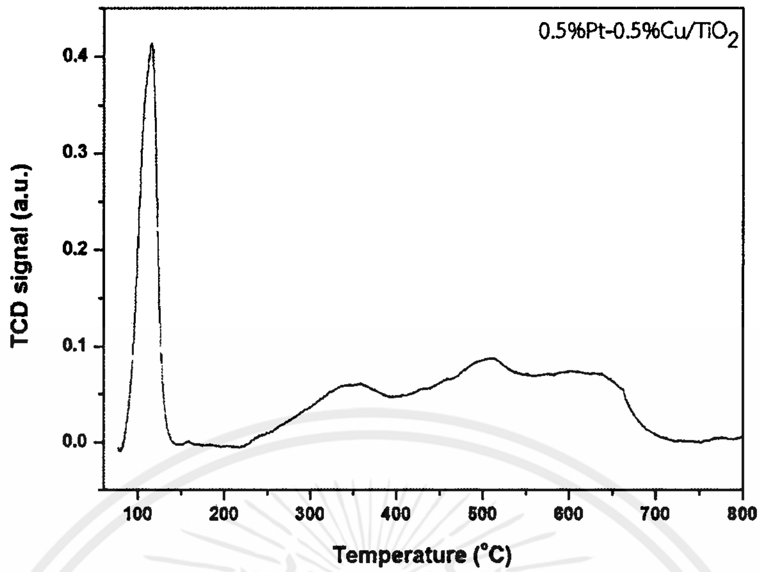


Figure B8 TPR profiles of 0.5%Pt-0.5%Cu/TiO_2 catalyst.

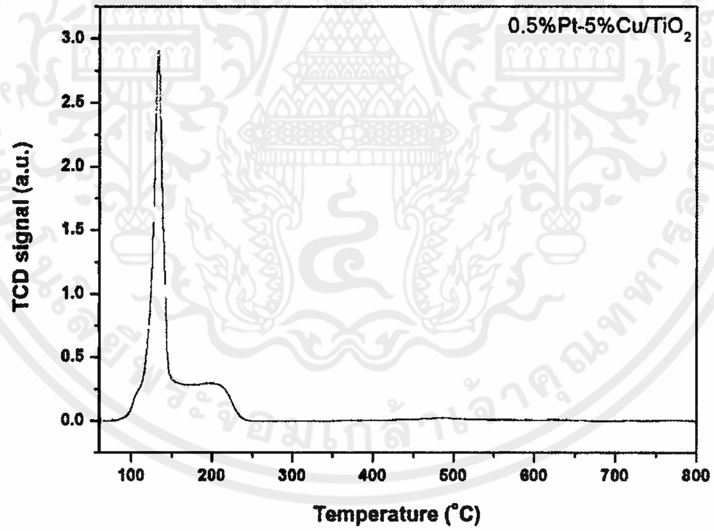


Figure B9 TPR profiles of 0.5%Pt-5%Cu/TiO_2catalyst.

B.4 Scanning electron microscope (SEM)

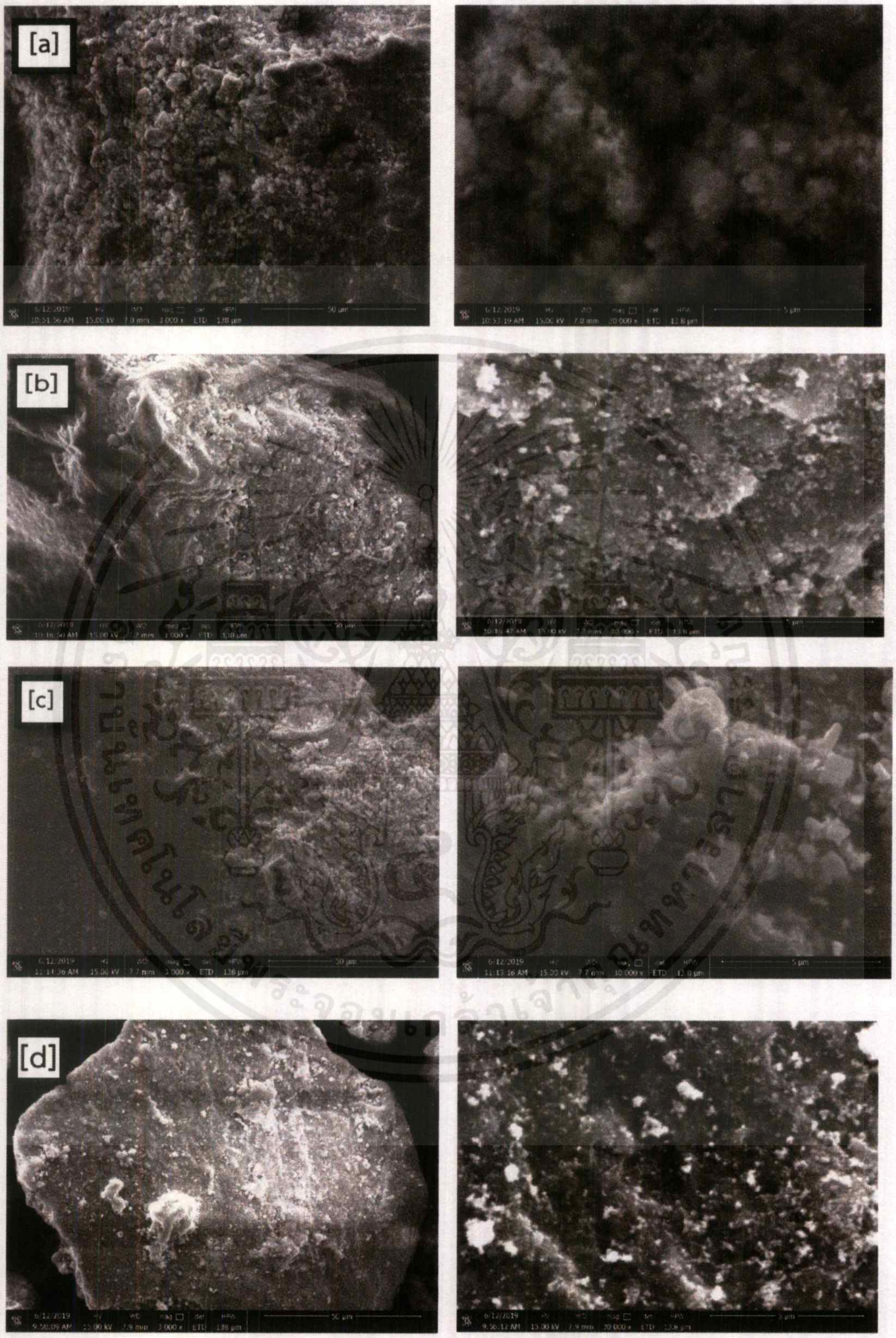


Figure B10 SEM images of (a) 5%Cu/TiO_2, (b) 0.5%Pt-0.5%Cu/TiO_2 c) 0.5%Pt-5%Cu/TiO_2, (d) 0.5%Pt/TiO_2,

Energy dispersive X-ray spectroscopy (EDX)

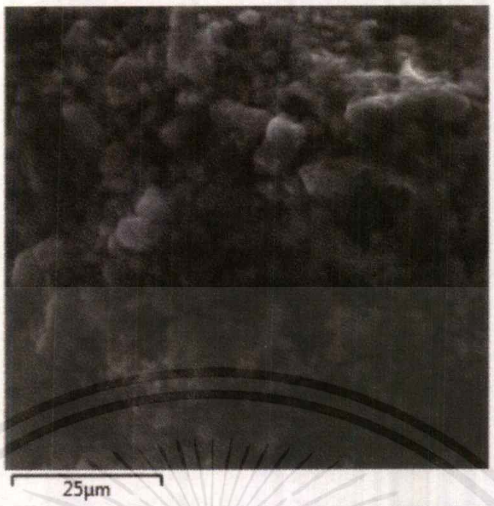
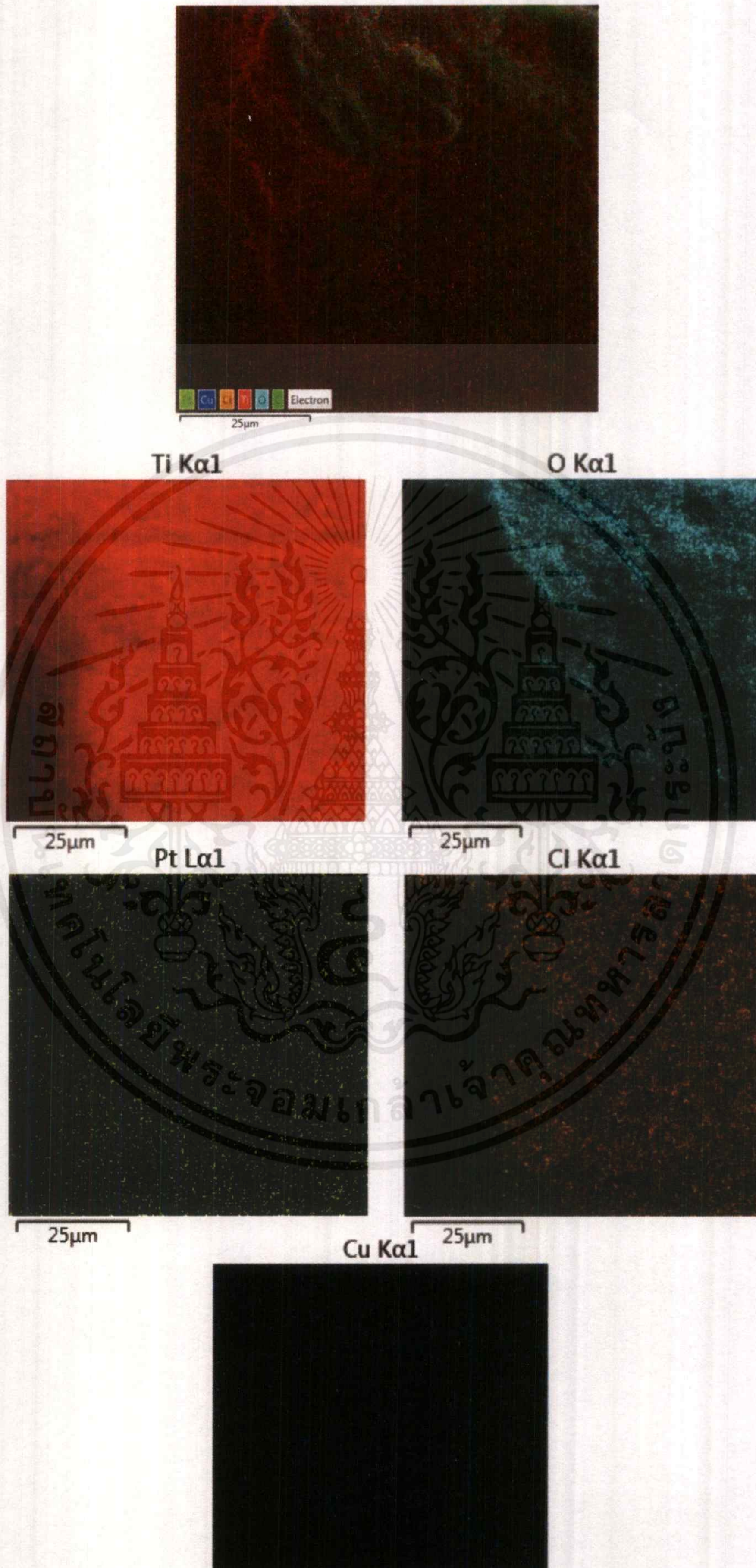


Figure B11 EDX images and map sum spectrum of 5%Cu/TiO_2 catalyst.

Table B2 Sum spectrum of 5%Cu/TiO_2 catalyst

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
C	K series	1.65	0.01653	4.04	0.12	8.71	-
O	K series	13.98	0.04706	37.52	0.23	60.64	-
Ti	K series	67.66	0.67661	51.76	0.20	27.94	Ti
Cu	K series	7.90	0.07896	6.67	0.06	2.72	Cu
Total				100.00		100.00	


Cu
Cl
Ti
O
Electron
25µm
Ti Kα1
O Kα1
25µm
25µm
Pt Lα1
Cl Kα1
25µm
25µm
Cu Kα1
25µm

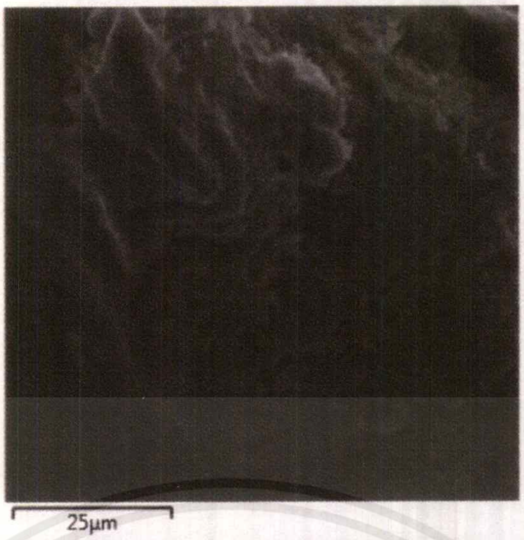


Figure B12 EDX images and map sum spectrum of 0.5%Pt-0.5%Cu/TiO_2 Catalyst

Table B3 Sum spectrum of 0.5%Pt-0.5%Cu/TiO_2 Catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt.%	Wt.% Sigma	Atomic %	Standard Label
C	K series	7.43	0.07425	14.72	0.17	25.18	-
O	K series	18.86	0.06346	44.79	0.21	57.54	-
Cl	K series	0.15	0.00130	0.10	0.01	0.06	-
Ti	K series	51.94	0.51943	39.86	0.16	17.10	Ti
Cu	K series	0.34	0.00336	0.28	0.02	0.09	Cu
Pt	L series	0.25	0.00245	0.25	0.07	0.03	Pt
Total				100.00		100.00	


Electron
25μm
Ti Kα1
25μm
O Kα1
25μm
Cu Kα1
25μm
Pt Lα1
25μm

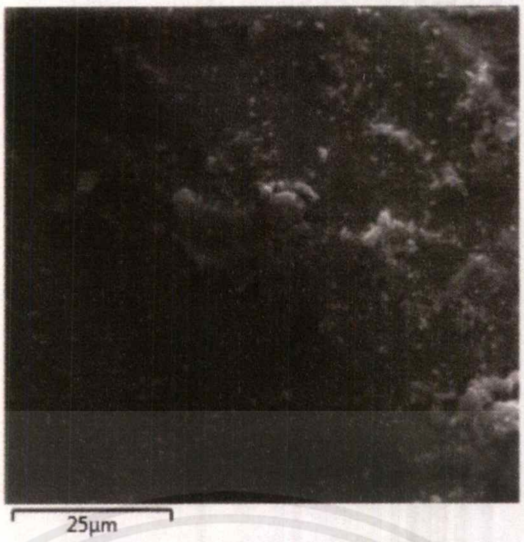


Figure B13 EDX images and map sum spectrum of 0.5%Pt-5%Cu/TiO_2 Catalyst

Table B4 Sum spectrum of 0.5%Pt-5%Cu/TiO_2 Catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt.%	Wt.% Sigma	Atomic %	Standard Label
C	K series	2.36	0.02362	6.88	0.19	12.46	-
O	K series	17.35	0.05840	50.31	0.24	68.36	-
Cl	K series	0.16	0.0138	0.15	0.02	0.09	-
Ti	K series	39.42	0.39421	40.15	0.20	18.22	Ti
Cu	K series	2.25	0.02246	2.51	0.05	0.86	Cu
Pt	L series	0.00	0.0000	0.00	0.10	0.00	Pt
Total				100.00		100.00	

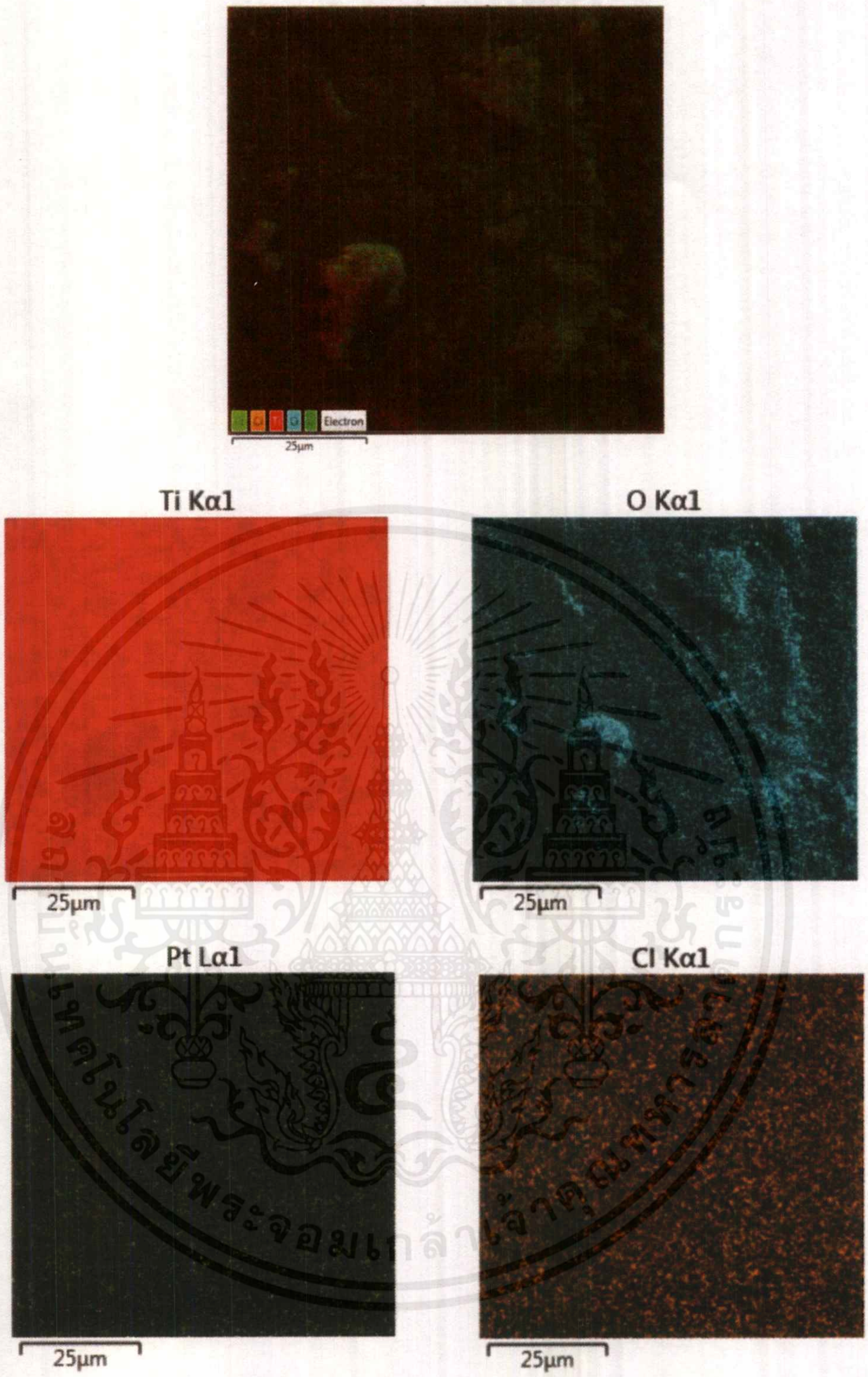

Electron
25μm
Ti Kα1
O Kα1
25μm
25μm
Pt Lα1
Cl Kα1
25μm
25μm

Figure B14 EDX images and map sum spectrum of 0.5%Pt/TiO_2 catalyst.

Table B5 Sum spectrum of 0.5%Pt/TiO_2 catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
O	K series	54.24	0.18253	44.99	0.14	66.21	TiO_2
Ti	K series	202.32	2.0232	49.68	0.13	24.42	Ti
Pt	L series	1.41	0.0140	0.45	0.06	0.05	Pt
Cl	K series	0.82	0.00721	0.19	0.01	0..13	-
C	K series	6.72	0.06719	4.69	0.09	9.20	-
Total				100.00		100.00	

APPENDIX C

REACTION DATA

Table C1. The area of all product of hydrogenation of furfural

Catalysts	Area					
		Product				
	Feed	Furfural	FA [a]	THFA [b]	Ester [c]	Acetal [d]
5%Cu /TiO_2	798941.9	681033.8	0.00	0.00	9695.5	325159.3
0.5%Pt-5%Cu/TiO_2	738709.5	546230.1	61710.65	3282.7	46968	29927.9
0.5%Pt-0.5%Cu/TiO_2	738709.5	427158.3	104963.2	3062.8	38485.2	502236.1
0.5%Pt/TiO_2	773716.2	361109.1	187817	3500	54515	0.00

Reaction conditions: based on 50 mg of catalyst, 50 μL of furfural, 10 mL of butanol, P_{H2} = 20 bar, T = 100 °C and t = 2 h.

[a] FA: Furfuryl alcohol

[b] THFA: Tetrahydrofurfuryl alcohol.

[c] Ester: butyl furfural ester.

[d] Acetal: 2-furaldehyde dibutyl acetal

Table C2. The area of all product of hydrogenation of furfural

Catalysts	Area					
		Product				
	Feed	Furfural	FA [a]	THFA [b]	Ester [c]	Acetal [d]
0.5%Pt/TiO_2	738709.5	92521.65	425415.8	32618.8	0.00	128116.4

Reaction conditions: based on 50 mg of catalyst, 50 μL of furfural, 10 mL of butanol, P_{H2} = 20 bar, T = 50 °C and t = 2 h.

[a] FA: Furfuryl alcohol

[b] THFA: Tetrahydrofurfuryl alcohol.

[c] Ester: butyl furfural ester.

[d] Acetal: 2-furaldehyde dibutyl acetal

Table C3. The area of all product of hydrogenation of furfural

Solvents	Area					
		Product				
	Feed	Furfural	FA [a]	THFA [b]	Acetal [c]	other
Methanol	772388.15	9796.0	114463.3	1055.9	812252.9 [c1]	0.00
Butanol	738709.5	92521.65	425415.8	32618.8	128116.4 [c2]	0.00
Acetronitrile	619151.4	481094.8	71418.35	0.00	0.00	26982.9

Reaction conditions: based on 50 mg of 0.5%Pt/TiO_2 catalyst, 50 µL of furfural, 10 mL of solvents, P_{H2} = 20 bar, T = 50 °C and t = 2 h.

[a] FA: Furfuryl alcohol

[b] THFA: Tetrahydrofurfuryl alcohol.

[c1] Acetal: 2-furaldehyde dimethyl acetal

[c2] Acetal: 2-furaldehyde dibutyl acetal

Calculation of furfural conversion, furfuryl alcohol selectivity and reaction yield

Calculation of conversion. Conversion can be calculated from the following equation:

$$\text{Conversion (\%)} = \frac{\text{(Area feed of FF/IS feed)} - \text{(Area product of FF/IS)} \times 100}{\text{(Area feed of FF/IS)}}$$

IS: Internal Standard

For example;

FF Conversion (%) of 0.5%Pt/TiO_2 at temperature 100 °C

$$\text{FF Conversion (\%)} = \frac{(97529.6/33581.0) - (361109.1/45515.5)}{(97529.6/33581.0)} \times 100 = 65.57\%$$

Calculation of Yield

Calculate the percent yield of each component in sample as follow:

$$\text{\% Yield in each product} = \frac{\text{(Area product/IS)}}{\text{(Area feed of FF/IS)}} \times \text{Response factor} \times 100$$

For example;

FA yield (%) of 0.5%Pt/TiO_2 at temperature 100 °C

$$\text{\% Yield of FA} = \frac{(187817/45515.5) \times 100}{(97529.6/33581.0) \times 0.773} = 23.17\ \%$$

Calculation of selectivity

% Selectivity can be obtained from the following equation:

$$\text{\%Selectivity in each product} = \frac{\text{Area product}}{\text{Total area of total product}} \times 100$$

For example;

FA selectivity (%) of 0.5%Pt/TiO_2 at temperature 100 °C

$$\text{\% Selectivity of FA} = \frac{187817}{(187817+3500+43515)} \times 100 = 76.40\ \%$$

Table C4. Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol (yield at 100° C)

Catalyst	Yield (%)			
	FA [a]	THFA [b]	Ester [c]	Acetal [d]
5%Cu /TiO_2	0.00	0.00	0.00	36.60
0.5%Pt-5%Cu/TiO_2	12.39	0.34	7.26	0.00
0.5%Pt-0.5%Cu/TiO_2	16.82	0.25	0.38	62.27
0.5%Pt/TiO_2	23.17	0.22	5.20	0.00

Table C5. Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol (100° C)

Catalyst	Conversion (%)	Selectivity (%)			
		FA [a]	THFA [b]	Ester [c]	Acetal [d]
5%Cu /TiO_2	25.44	0.00	0.00	0.00	100.00
0.5%Pt-5%Cu/TiO_2	15.53	55.12	2.93	41.95	0.00
0.5%Pt-0.5%Cu/TiO_2	47.04	16.18	0.47	5.93	77.41
0.5%Pt/TiO_2	65.57	76.40	1.42	22.18	0.00

Reaction conditions: Catalyst 50 mg, 50 μL of furfural, 10 mL of butanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

[a] FA: Furfuryl alcohol

[b] THFA: Tetrahydrofurfuryl alcohol.

[c] Ester: butyl furfural ester.

[d] Acetal: 2-furaldehyde dibutyl acetal

Table C6 Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol (Yield at 50° C)

Catalyst	Yield (%)			
	FA [a]	THFA [b]	Ester [c]	Acetal [d]
0.5%Pt/TiO_2	79.55	3.16	0.00	18.52

Table C7. Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol. (50° C)

Catalyst	Conversion (%)	Selectivity (%)			
		FA [a]	THFA [b]	Ester [c]	Acetal [d]
0.5%Pt/TiO_2	86.63	72.58	5.56	0.00	21.86

Reaction conditions: Catalyst 50 mg, 50 μL of furfural, 10 mL of butanol, Hydrogen pressure 20 bar, Temperature at 50 °C and Stirring speed of 900 rpm with reaction time 2 hours.

[a] FA: Furfuryl alcohol

[b] THFA: Tetrahydrofurfuryl alcohol.

[c] Ester: butyl furfural ester.

[d] Acetal: 2-furaldehyde dibutyl acetal

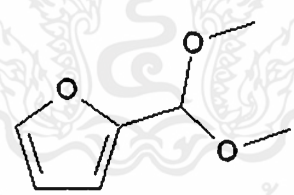


Figure C1 Structure of 2-furaldehyde dimethyl acetal [28]

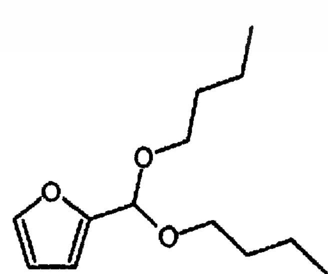


Figure C2 Structure of 2-furaldehyde dibutyl acetal