CATALYTIC PERFORMANCE STUDY OF BIMETALLIC Ni-Cu/SiO_2 CATALYSTS FOR LIQUID PHASE SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL

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Title	Catalytic Performance Study of Bimetallic Ni-Cu/SiO_2 Catalysts for Liquid Phase Selective Hydrogenation of Furfural to Furfuryl Alcohol		
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Faculty of Science, King Mongkut's Institute of Technology Ladkrabang (KMITL), has approved this special project submitted in partial fulfillment of requirements for the degree of Bachelor of Science (Industrial Chemistry) in academic year 2018.

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บทคัดย่อ

โครงงานพิเศษนี้ศึกษาประสิทธิภาพของตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัวรองรับซิลิกาสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟูรอลเป็นเฟอร์ฟูริวแอลกอฮอล์ โดยตัวเร่งปฏิกิริยา 2 เปอร์เซ็นต์โดยน้ำหนักของนิกเกิลบนตัวรองรับซิลิกาเตรียมด้วยวิธีการดูดซับแบบไฟฟ้าสถิตย์ที่แข็งแรง (strong electrostatic adsorption, SEA) ในขณะที่ตัวเร่งปฏิกิริยา 2 เปอร์เซ็นต์โดยน้ำหนักของคอปเปอร์บนตัวรองรับซิลิการเตรียมด้วยวิธีจุ่มชุบ (incipient wetness impregnation, IM) หลังจากนั้นตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัวรองรับซิลิกาที่อัตราส่วนระหว่างนิกเกิลและคอปเปอร์ (2ต่อ2 และ 2ต่อ5 เปอร์เซ็นต์โดยน้ำหนัก) ถูกเตรียมด้วยวิธีการดูดซับแบบไฟฟ้าสถิตย์ที่แข็งแรง (SEA) ตามด้วยวิธีจุ่มชุบ (IM) จากการวิเคราะห์ตัวเร่งปฏิกิริยาด้วยเทคนิคการกระเจิงรังสีเอกซ์ (X-ray diffraction, XRD) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (Scanning electron microscopy, SEM) พบว่าตัวเร่งปฏิกิริยา 2 เปอร์เซ็นต์โดยน้ำหนักของนิกเกิลบนตัวรองรับซิลิกาที่เตรียมด้วยวิธีการดูดซับแบบไฟฟ้าสถิตย์ที่แข็งแรง (SEA) แสดงการกระจายตัวที่ดีของนิกเกิลที่มีขนาดเล็กและเท่ากัน ในขณะที่ตัวเร่งปฏิกิริยา 2 เปอร์เซ็นต์โดยน้ำหนักของคอปเปอร์บนตัวรองรับซิลิการที่เตรียมด้วยวิธีจุ่มชุบ (IM) จะแสดงการรวมกลุ่มของโลหะคอปเปอร์ โดยเปรียบเทียบกับตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัว

รองรับซิลิกาที่อัตราส่วน 2 ต่อ 2 เปอร์เซ็นต์โดยน้ำหนักแสดงการกระจายตัวของนิกเกิลและคอปเปอร์ที่ดี ในขณะที่ตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัวรองรับซิลิกาที่อัตราส่วน 2 ต่อ 5 เปอร์เซ็นต์โดยน้ำหนักพบว่ามีการรวมกลุ่มของคอปเปอร์บางส่วน จากผลการทดลองตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัวรองรับซิลิกาทั้ง 2 อัตราส่วนมีประสิทธิภายในการเร่งปฏิกิริยาที่สูงกว่าตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับซิลิกาและคอปเปอร์บนตัวรองรับซิลิกาโดยตัวเร่งปฏิกิริยาของโลหะผสมสองชนิดระหว่างนิกเกิลและคอปเปอร์บนตัวรองรับซิลิกาที่อัตราส่วน 2 ต่อ 5 เปอร์เซ็นต์โดยน้ำหนักแสดงประสิทธิภาพในการเร่งปฏิกิริยาสูงที่สุดซึ่งให้ค่าการแปรผันของเฟอร์ฟูรอลเท่ากับ 94.34 เปอร์เซ็นต์และค่าการเลือกเกิดของเฟอร์ฟูริวแอลกอฮอล์ที่ 63.60 เปอร์เซ็นต์ การเติมโลหะคอปเปอร์ในปริมาณที่เหมาะสมลงบนตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับซิลิกาที่เตรียมด้วยวิธีการดูดซับแบบไฟฟ้าสถิตย์ที่แข็งแรง (SEA) สามารถที่จะปรับปรุงประสิทธิภาพในการเร่งปฏิกิริยาได้เนื่องจากการเกิดอัลลอยด์ของโลหะผสมนิกเกิลและคอปเปอร์จะยับยั้งการเกิดปฏิกิริยาไฮโดรจิเนชันที่มากเกินไป อัตราส่วนที่เหมาะสมระหว่างโลหะนิกเกิลและคอปเปอร์สำหรับปฏิกิริไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟูรอลเปลี่ยนเป็นเฟอร์ฟูริวแอลกอฮอล์ คือ 2 ต่อ 5 เปอร์เซ็นต์โดยน้ำหนัก

คำสำคัญ : ตัวเร่งปฏิกิริยานิกเกิลคอปเปอร์บนตัวรองรับซิลิกา เฟอร์ฟูรอล เฟอฟูริวแอลกอฮอล์ ปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลว การดูดซับแบบไฟฟ้าสถิตย์ที่แข็งแรง การจุ่มชุบ

Title	Catalytic performance study of bimetallic Ni-Cu/SiO_2 catalysts for liquid phase selective hydrogenation of furfural to furfuryl alcohol
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Academic Year	2018
Advisor	Dr. Patcharaporn Weerachawanasak
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Abstract

This special project studied the catalytic performance of bimetallic Ni-Cu/SiO_2 catalysts in liquid phase selective hydrogenation of furfural to furfuryl alcohol. The monometallic 2%Ni/SiO_2 catalyst was prepared by strong electrostatic adsorption (SEA) method whereas 2%Cu/SiO_2 catalyst was prepared by incipient wetness impregnation (IM) method. Afterward, bimetallic Ni-Cu/SiO_2 catalysts with various Ni/Cu ratios (2:2 and 2:5 wt.%/wt.%) were prepared by SEA followed by IM method. According to X-ray diffraction (XRD) and Scanning electron microscopy (SEM) results, monometallic 2%Ni/SiO_2 [SEA] shows small and uniform Ni particles size with well dispersion while 2%Cu/SiO_2 [IM] shows some agglomeration of Cu metal. In comparison, the bimetallic 2%Ni-2%Cu/SiO_2 [SEA-IM] shows uniform dispersion of Ni and Cu metal whereas 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts found some Cu agglomeration. As the reaction results, both of bimetallic Ni-Cu/SiO_2 catalysts gave higher catalytic performances than monometallic Ni/SiO_2 and Cu/SiO_2 catalysts. The 2%Ni-5%Cu/SiO_2 [SEA-IM] exhibited the highest catalytic performance, which a furfural conversion 94.34% and furfuryl alcohol selectivity 63.60%.

Adding suitable Cu metal onto Ni/SiO_2 [SEA] could be improved the catalytic performances since Ni-Cu alloy forming suppressed over hydrogenation. The suitable Ni/Cu ratio for liquid phase selective hydrogenation of furfural to furfuryl alcohol was found to be 2:5 wt.%/wt.%.

Keywords : Ni-Cu/SiO_2 catalyst, furfural, furfuryl alcohol, liquid phase selective hydrogenation, strong electrostatic adsorption method, incipient wetness impregnation method.

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Pacharaporn Kraemanee
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CHAPTER 1

INTRODUCTION

1.1 Rationale

Furfuryl alcohol is one of the most important chemical intermediates for a wide range of applications in polymer industries and fine chemicals. It is widely used as an intermediate in the production of thermostatic resins, fiber glass, polymer concrete and liquid resins for galvanic bath tub. Moreover, it is also employed as a chemical intermediate for synthesis of lysine, vitamin C, lubricants, dispersing agents, binders and adhesives. [1-2] Generally, furfuryl alcohol is derived from a simple hydrogenation of furfural in the presence of suitable catalysts. However, hydrogenolysis of C=O bond or decarboxylation is possible to occur during the hydrogenation of furfural, thus various products such as tetrahydrofuran, tetrahydrofurfuryl alcohol, 2-methylfuran, or furan, etc. [3] can be obtained. The major product is mainly depended on the kind of catalysts that affect to control the reaction mechanism pathways. The catalytic hydrogenation of furfural to furfuryl alcohol is generally carried out either in the gas phase or in the liquid phase. In comparison between liquid phase and gas phase hydrogenation, gas phase hydrogenation would result in higher amounts of byproducts and require higher energy consumption to the necessity of vaporizing furfural. The liquid phase chemistry is possibly preferred for compatibility with the upstream production. Therefore, it is attractive to explore an efficient catalytic system for furfural hydrogenation to furfuryl alcohol in the liquid phase. [4]

Nowadays, liquid phase selective hydrogenation of furfural to furfuryl alcohol has been extensively studied using both of noble metals and non-noble metals catalysts. Various precious metals such as Ni, Cu, Co, Pt, Ru, or Pd catalysts have been investigated in this reaction. [5-6] Conventional production of furfuryl alcohol via the selective hydrogenation of furfural usually performs by copper chromite catalyst. The main problem of copper chromite catalyst is toxicity and non-environmentally friendly from chromium oxides. Furthermore, it typically gives the moderate activity in conversion of furfural. Therefore, many researches are interested in designing environmentally friendly catalysts for high conversion and high selectivity of furfural to furfuryl alcohol. [1] Various noble metal catalysts such as Pd/SiO_2 [5], Pd/TiO_2 [6], Pt/C [7], Ir/SiO_2 [8] have been reported to be active and selective in the liquid phase hydrogenation of furfural to furfuryl alcohol. However, using these catalysts tend to high cost of furfuryl alcohol production. Thus, non-noble metal catalysts are intensive attention to develop the efficient and economically catalysts for this reaction. Among these catalysts, Ni and Cu-based catalysts such as Ni/CNT [9], Ni/TiO_2 [10], Ni-Al_2O_3 [11], Ni/SiO_2 [12], Cu/SiO_2 [13], Cu/TiO_2 [14] catalysts have been known to be high catalytic activity in hydrogenation. In case of furfural hydrogenation, Ni and Cu base catalysts can give high furfural conversions with a moderate to low selectivity of furfuryl alcohol. Tetrahydrofurfuryl alcohol obtained as a major product for Ni-catalysts whereas furan can be obtained when using Cu catalysts. Moreover, the ring opening products such as butanal, butanol and butane were found over using Ni/SiO_2 catalyst. Therefore, to improve the catalytic activity and selectivity for furfural hydrogenation for Ni catalysts, bimetallic catalyst or adding a second metal with high metal dispersion is one of the good alternatives. The second metal or promoter can improve the activity or/and the selectivity, by increasing the surface area or acting as Lewis acid site to polarize the C=O bond.

Furthermore, one of the key issues to achieve high catalytic performance is high dispersion of metal active species which obtain from various preparation methods. Many preparation methods have been used to improve the metal dispersion such as co-precipitation, wet impregnation, incipient wetness impregnation, sol-immobilization, or strong electrostatic adsorption, etc. In this work, we are interested in strong electrostatic adsorption (SEA) because SEA gives a monolayer adsorption of metal complexes on the support surface by electrostatic adsorption which provides higher metal dispersion compared to other conventional methods. The metal solution at suitable pH will be electrostatically adsorbed onto the support surface, well dispersed particles with a tight particle size distribution can be obtained. However, the bimetallic Ni-Cu/SiO_2 catalyst has never been used in liquid phase selective hydrogenation of furfural to furfuryl alcohol and the suitable ratio of Ni/Cu to this reaction has never been discussed. Therefore, this work aims to synthesize an effective bimetallic Ni-Cu/SiO_2 catalyst for liquid phase selective hydrogenation of furfural to furfuryl alcohol. The suitable Ni/Cu ratio to obtain an effective Ni-Cu/SiO_2 catalyst will be determined.

1.2 Objectives of research

1.2.1 To synthesize a series of bimetallic Ni-Cu/SiO_2 catalysts and determine the suitable Ni/Cu ratio for liquid phase selective hydrogenation of furfural to furfuryl alcohol.

1.2.2 To study the characteristics and catalytic properties of bimetallic Ni-Cu/SiO_2 catalysts compared with monometallic Ni/SiO_2 and Cu/SiO_2 catalysts in liquid phases selective hydrogenation of furfural to furfuryl alcohol.

1.3 Research scope

1.3.1 Monometallic Ni/SiO_2 catalyst was prepared by strong electrostatic adsorption method (SEA) whereas Cu/SiO_2 catalyst was prepared by incipient wetness impregnation method (IM).

1.3.2 A series of bimetallic Ni-Cu/SiO_2 was prepared by strong electrostatic adsorption (SEA) following by incipient wetness impregnation (IM) method. Nickle solution (1400 ppm) has been loaded on SiO_2 by SEA method and denoted as Ni/SiO_2 (SEA). Then adding second metal, various amount of copper at (2, 5 wt.%) was deposited on Ni/SiO_2 (SEA) by incipient wetness impregnation method (IM). The catalysts were denoted as *x*%Ni-*y*%Cu/SiO_2 catalyst. (x and y are percentage of metal loading).

1.3.3 The characteristics of Ni/SiO_2, Cu/SiO_2 and a series of Ni-Cu/SiO_2 catalysts will be characterized by following techniques

- Temperature program reduction (TPR)
- X-ray diffraction (XRD)
- X-ray fluorescence (XRF)
- Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX)
- Surface area, pore size, and pore volume analyzer by Brunauer-Emmett-Teller (BET).

1.3.4 The catalytic properties of all catalysts will be investigated in liquid phase selective hydrogenation of furfural to furfuryl alcohol using bath type reactor.

1.4 Benefits of the study

1.4.1 To obtain highly efficient bimetallic Ni-Cu/SiO_2 catalysts that is an economically and environmentally friendly for liquid phase selective hydrogenation of furfural to furfuryl alcohol.

1.4.2 To understand the catalytic mechanism of liquid phase selective hydrogenation of furfural to furfuryl alcohol over Ni-Cu/SiO_2 catalysts.

CHAPTER 2

THEORY AND LITERATUE REVIEWS

2.1 Furfural [15-16]

Furfural is an organic compound which consists of formyl group attach on furan ring. The empirical formula is $C_5H_4O_2$ and the chemical structure illustrates in **Figure 2.1** Pure furfural is colorless liquid. However, the color usually turn to brown when it is prolonging exposure 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 and chemical properties of furfural are summarized in **Table 2.1**. Furfural may be obtained by the acid catalyzed dehydration of 5-carbon sugars (pentoses), particularly xylose. These sugars may be obtained from hemicellulose present in lignocellulosic biomass such as bagasse, corn cob, wheat bran and rice husk. These feedstocks are part of a sustainable productive process in nature and they do not destroy the environment. Moreover, the production of some important furfural derivatives such as furfuryl alcohol and tetrahydrofurfuryl alcohol have a great importance in industrial process.

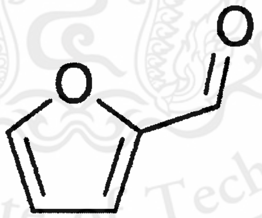


Figure 2.1 Chemical structure of furfural. [16]

2.2 Furfuryl alcohol [17]

Furfuryl alcohol is a colorless organic compound containing a furan substituted with a hydroxymethyl group. The empirical formula of furfuryl alcohol is $C_5H_6O_2$ and the chemical structure illustrates in **Figure 2.2** and the chemical properties are summarized in **Table 2.1**. Furfuryl alcohol is manufactured industrially by hydrogenation of furfural, which is itself typically produced from waste biomass such as corncobs or sugar cane bagasse. So that, furfuryl alcohol may be considered a green chemical. Furfuryl alcohol has been used in a variety applications especially employing as a chemical intermediate for production of polymer, resin and pharmaceutical product. In the decade, the demand of furfuryl alcohol all over the world trends to increase in every year.

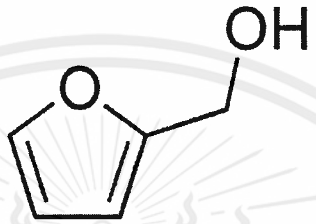


Figure 2.2 Chemical structure of furfuryl alcohol. [17]

Table 2.1 The physical and chemical properties of furfural and furfuryl alcohol. [17-18]

Properties	Furfural	Furfuryl Alcohol
Molecular weight (g/mol)	96.08	98.10
Boiling point (°C)	161.7	170
Freezing point (°C)	−36.5	-29
Density at 25 °C	1.16	1.13
Critical pressure Pc (MPa)	5.50	5.35
Critical temperature Tc (°C)	397	359
Solubility in water, wt% (25 °C)	8.3	∞
Heat of vaporization (liquid), (kJ/mol)	42.8	50.1
Viscosity, mPa·s, 25 °C	1.49	4.62
Heat of combustion at 25 °C (kJ/mol)	234.4	254.8
Enthalpy of formation (kJ/mol)	−151	-218.9

2.3 Hydrogenation pathways of furfural [15, 19]

The derivatives of furfural, some of which are outlined in **Figure 2.3** include furfuryl alcohol, tetrahydrofuran, 2-methylfuran, furoic acid, hydroxymethylfurfural, furylidene, furan and resins. Many of these products are formed via furfural hydrogenation with a variety of additional reactions including furfural decarbonylation and oxidation also possible. It is therefore of great importance to choose a catalyst which is selective to the desired reaction route.

Furfural can be hydrogenated at two positions, that are carbonyl group (C=O) at the exocyclic of furan ring and unsaturated bond in furan ring. If the carbonyl group is hydrogenated, furfuryl alcohol will be obtained the main product whereas if unsaturated bond in furan ring is hydrogenated tetrehydrofurfural will be obtain as the main product. In addition, many products are formed via furfural hydrogenation with a variety of additional reactions including furfural decarbonylation and oxidation also possible. For the purpose of this research, furfuryl alcohol is the desired product that can be produced by the selective hydrogenation of furfural.

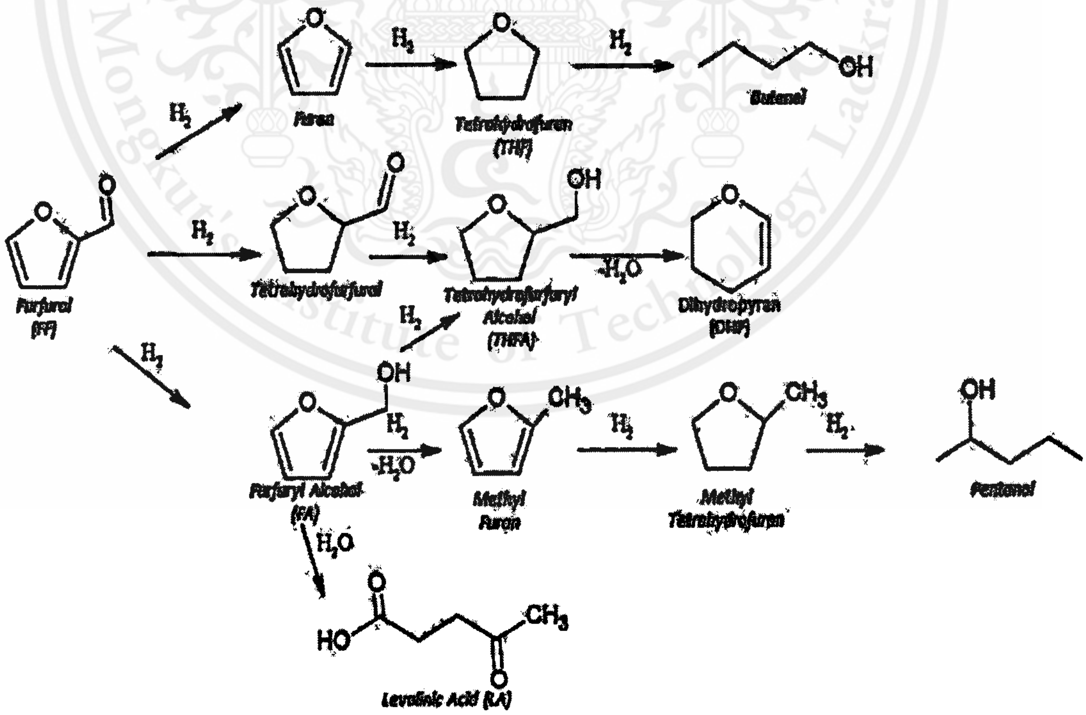


Figure 2.3 Hydrogenation pathways of furfural. [19]

2.4 Catalysts

2.4.1 Nickel and Copper metals [20]

Several studies have been reported that Ni catalyst produces high conversion of furfural but low selective to furfuryl alcohol, due to a strong interaction with the furan ring, which weakens the C=O bond enough to open the ring. In contrast, Cu catalyst produces low conversion of furfural but high selectivity to furfural alcohol, due to Cu catalysts are always more selective in the hydrogenation of the C=O bond in conversion of aldehydes containing C=O and C=C bonds than other metal catalysts. Therefore, using Ni and Cu so that the catalysts have both high conversion and high selectivity in alloy Ni-Cu catalysts. The properties of Ni and Cu metals are shown in **Table 2.2, 2.3**. Both metal can use as the active metal catalysts because Ni and Cu are low cost, and possess high activity for many reaction.

Table 2.2 Properties of nickel metal (Ni). [21]

Properties of Nickel	
Symbol of Element	Ni
Atomic Number	28
Atomic Mass	58.6934 amu
Melting Point	1453.0 °C - 1726.15 °K
Boiling Point	2732.0 °C - 3005.15 °K
Density (@293 K)	8.902 g/cm^3
Color	Silvery

Table 2.3 Properties of copper metal (Cu). [22]

Properties of Copper	
Symbol of Element	Cu
Atomic Number	29
Atomic Mass	63.546 amu
Melting Point	1083.0 °C - 1356.15 °K
Boiling Point	2567.0 °C - 2840.15 °K
Density (@293 K)	8.96 g/cm^3
Color	red / orange / brown

2.4.2 Silicon dioxide (SiO_2) [23]

"Silicon dioxide" or "silica" is most commonly found in nature which comprises more than 10% by mass of the earth's crust. The structure of silicon dioxide is a tetrahedral arrangement with silicon as the central atom and surrounded by atoms of oxygen as illustrated in **Figure 2.4**. Due to the tetrahedral structure, the melting point of silicon dioxide is very high. The strong silicon-oxygen covalent bonds get broken at very high temperatures, close to 1700 °C. Also, silicon dioxide is very hard and rigid, and this is again due to the strong covalent bond between silicon and oxygen. Due to the absence of free electrons within the molecular structure, silicon dioxide is a very bad conductor of electricity and acts as an insulator. Silicon dioxide is insoluble in water and in all organic solvents. However, it is soluble in alkalies and hydrofluoric acid. From the properties of silicon dioxide mentioned, It is used in structural materials, microelectronics (as an electrical insulator) and as components in the food and pharmaceutical industries. In addition, Silicon dioxide is a common support for metal catalysts because it has the good physical and chemical properties such as high surface area, high porosity and stability resistant with chemical and high thermal.

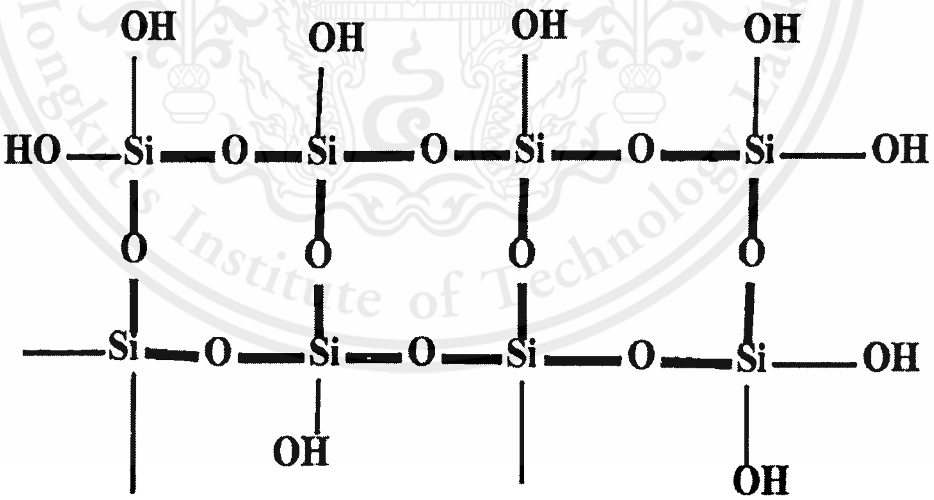


Figure 2.4 Chemical structure of silica. [24]

2.5 Strong Electrostatic Adsorption method (SEA) [25-26]

"Strong Electrostatic Adsorption" or "SEA" is an interesting method that recently applied for catalysts preparation because it can give a high metal dispersion with a uniform metal particle size. The principle of SEA is electrostatic adsorption between metal and support via a special case of wet impregnation. The electrostatic adsorption will be occurred when adjusted the pH of impregnating solution above or below point of zero charge (PZC) of the support with the solution of acid or base that enough to charge the surface of the support and creating coulomb interaction between the support surface and the precursor. **Figure 2.5** shows the mechanism of electrostatic adsorption. Typically, an oxide surface contains terminal hydroxyl groups that can be protonated or deprotonated, depending on the acidity of the impregnating solution. The pH at which the hydroxyl groups are neutral is termed the point of zero charge (PZC). Below this pH (pH<PZC), the hydroxyl groups are protonated and become positively charge and this positively surface can adsorb anionic metal complexes such as hexachloroplatinate $[PtCl_6]^{-2}$. On the other hand, above the PZC (pH>PZC), the hydroxyl groups are deprotonated and become negatively charge and the surface can adsorb cationic metal complexes such as platinum tetraamine $[(NH_3)_4Pt]^{+2}$. The PZC and suitable metal complexes for various supports are summarized in **Table 2.4**.

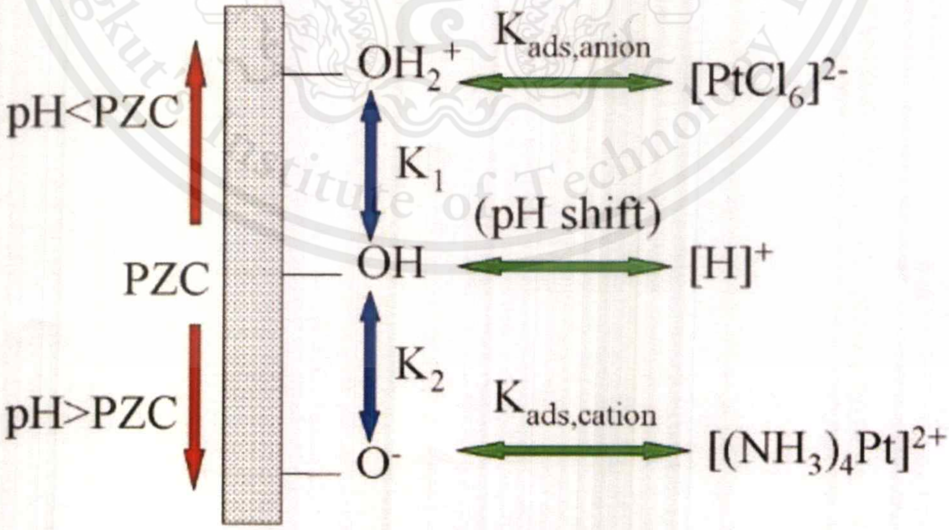


Figure 2.5 Mechanism of electrostatic adsorption. [25]

Table 2.4. The PZCs and suitable metal complexes for common supports. [26]

Support	PZC	Surface area	Precursor
Silica (Aerosil 300)	4.0	330 m^2/g	$[Pt(NH_3)_4]^{2+}$ and
Oxidized Vulcan-XC72 (oxC)	2.0	170 m^2/g	$[Pd(NH_3)_4]^{2+}$ (PTA and
PtO_2	1.0	104 m^2/g	PdTA)
PdO	4-7	118 m^2/g	PTA, PdTA, PHC and PdTC
γ-Alumina (VGL-25)	8.5	277 m^2/g	$[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$
Carbon (Vulcan-XC72)	8.9	254 m^2/g	(PHC and PdTC)

2.6 Literature reviews

In 2017, Zhaolin Fu, et al. [11] studied The conversion of furfural to 2-methylfuran over Ni-Cu/Al_2O_3 catalyst with formic acid as a hydrogen donor. Two monometallic catalysts, Ni/Al_2O_3 and Cu/Al_2O_3, and the bimetallic Ni-Cu/Al_2O_3 were investigated with formic acid as a hydrogen donor. It was found that mono Ni catalyst had a catalytic activity both in decarbonylation and hydrogenation, making the product system complex. Contrarily, a mono Cu catalyst showed a moderate catalytic activity but a high selectivity for the hydrogenation of carbonyl. The Ni-Cu/Al_2O_3 bimetallic catalyst exhibited an integrated performance of the both mono metal catalysts. The suitable Ni/Cu content at 5:10 %wt. in Ni-Cu/Al_2O_3 gave the highest Selectivity of furfural. The synergic effect of Ni-Cu alloy effect to increase affinity for carbonyl and repulsion for furan ring.

In 2013, M.M.Villaverde, et al. [13] studied Selective liquid phase hydrogenation of furfural to furfuryl alcohol over Cu-based catalysts. Reported Cu-based catalysts free of Cr are active for the liquid phase hydrogenation of furfural with 100% selectivity to furfuryl alcohol. In particular, a CuMgAl catalyst, prepared by the coprecipitation method was more active for this reaction than a copper chromite traditional catalyst. Solid catalyst formed by small copper particles is more active and stable in the liquid phase hydrogenation of furfural than when it is mainly constituted by large metal copper particles. This is clearify by the comparison of Cu/SiO_2 catalysts prepared by precipitation–deposition and impregnation methods. However, metal-support interaction can also play a very important role in modifying the activity of metal copper.

In 2016, Á. O'Driscoll, et al. [19] studied the influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol. They found that 1.9%Pd/SiO_2 and 1.4%Pt/SiO_2 were identified as promising catalysts for the liquid phase hydrogenation of furfural. Of a series of supports investigated (SiO_2, Al-SBA-15, β-zeolite and TiO_2), SiO_2 was the superior support as it gave the best furfuryl alcohol selectivity. The furfural conversion and furfuryl alcohol selectivity results may indicate the importance of the acidity of the supports on the overall catalyst activity. The presence of aluminium in the beta zeolite and the Al-SBA-15 makes these supports acidic in nature and both of these catalysts presented the highest furfural conversions. However, although these acidic supports resulted in the promotion of furfural conversion, they presented low furfuryl alcohol selectivity. This may be a result of furfural acetalization which is a non-catalytic reaction facilitating the conversion of furfural due to the presence of ethanol. Alternatively, the low furfuryl alcohol selectivity may be due to etherification with ethanol as the Bronsted acid supports can influence the direction of the reaction while Lewis acid supports such as TiO_2 facilitate furfuryl alcohol etherification via the Meerwein-Pondorf-Verley reaction whereby the carbonyl group and the alcohol coordinate to a Lewis acid metal centre and a hydride transfer from the alcohol to the carbonyl occurs. Subsequent comparisons to commercial palladium catalysts found that palladium presents good furfural conversion but was not selective to furfuryl alcohol. In order to investigate the influence of the solvent on furfural conversion, 1.9%Pd/SiO_2 and 1.4%Pt/SiO_2 were hydrogenated using ethanol (EtOH) and toluene (Tol) as solvents. Found that two undesired products were formed, 2-furaldehyde diethyl acetal and difurfuryl ether when ethanol was used as the solvent. The production of these undesirable products was significantly reduced or eliminated when toluene was employed as solvent. Platinum based catalysts presented high selectivity to furfuryl alcohol. A variety of weight loadings in the range of 0.5–2 %wt. were tested and 1%Pt/SiO_2 was selected for further research of bimetallic catalysts. From the bimetallic catalysts studied, Pt-Sn was the most active for the hydrogenation of furfural to furfuryl alcohol.

In 2011, Surapas Sitthisa and Daniel E. Resasco. [20] studied the hydrodeoxygenation of furfural over three different metal catalysts, Cu, Pd and Ni supported on SiO_2 on a continuous-flow reactor under atmospheric presdsure of hydrogen in the 210–290 °C temperature range. The distribution of products is a strong function of the metal catalyst used High selectivity to furfuryl alcohol is obtained over Cu/SiO_2 with the formation of only small amounts of 2-methyl furan at the highest reaction temperature studied. In contrast to Cu catalyst, the conversion of furfural over Pd/SiO_2 mainly produces furan by decarbonylation. Furan can further react with hydrogen to form tetrahydrofuran (THF). Finally, on Ni/SiO_2 catalysts ring opening products (butanal, butanol and butane) can be obtained in significant amounts. The different product distributions are explained in terms of the strength of interaction of the furan ring with the metal surface and the type of surface intermediates that each metal is able to stabilize. In summary, the very different distributions of products observed on silica-supported Cu, Pd and Ni catalysts can be explained in terms of the extent of molecular interactions with the metal surface as follows: a) Cu mainly produces furfuryl alcohol via hydrogenation of the carbonyl group. This behavior is explained in terms of the preferred adsorption mode on Cu, η^1 (O)-aldehyde, since the interaction of Cu with C=C bond is very weak. No products involving the activation of the furan ring are observed b) Pd yields decarbonylation products due to the favorable formation of acyl surface species. It also generates products of ring hydrogenation and they are the result of a strong interaction of Pd with the ring. c) While Ni has a product distribution similar to that of Pd, furan is not as abundant because it can further react with hydrogen, thus forming ring opening products, due to the interaction of the ring with the surface that is even stronger than on Pd.

In 2008, Ling Jiao and John R. Regalbuto [25] studied the correlation between strong electrostatic interaction during impregnation and the high dispersion of reduced metals. A series of silica-supported noble and base metal catalysts prepared by strong electrostatic adsorption (SEA) was compared with the traditional incipient wetness impregnation (IWI) method. Metal ammine complexes $[Pd(NH_3)_4]^{+2}$, $[Cu(NH_3)_4]^{+2}$, $[Co(NH_3)_6]^{+3}$, $[Ru(NH_3)_6]^{+2}$, $[Ru(NH_3)_6]^{+3}$ and $[Ni(NH_3)_6]^{+2}$ were adsorbed onto amorphous silica at various pHs. In this work, It was found that over silica support, the pH range of optimal interaction appears to be in the range of 11–12 for all metals. Therefore, the results showed that the SEA method can be applied for many ammine complexes to synthesize well-dispersed metals over amorphous silica. In addition, SEA method appears to be a rational procedure for the cheap, simple, and scalable preparation of highly dispersed supported catalysts, even at relatively high metal loadings.

In 2012, Yoshinao Nakagawa, et al. [27] studied total hydrogenation of furfural over a silica-supported nickel catalyst prepared by the reduction of a nickel nitrate precursor. Investigated gas-phase hydrogenation of furfural was performed over SiO_2-supported Ni catalysts with various particle sizes. There have been many reports regarding Ni/SiO_2 catalysts, and two types of supporting methods have been the most widely used; impregnation and deposition-precipitation. The average metal size is, notably, dependent on the choice of preparation method and the atmosphere (oxidizing or reducing) of thermal treatment for the decomposition of precursor. Although higher dispersion is generally obtained by using a deposition-precipitation method, they chose an impregnation method because the deposition-precipitation method gives stronger SiO_2-metal interactions, which also affect the catalytic performance of the metal particles. They found higher performances in the production of THFA over highly dispersed Ni/SiO_2 catalysts, which were prepared by reduction of SiO_2-supported nickel nitrate at a lower temperature than over the catalysts with larger Ni particles. The hydrogenation of FOL to THFA was especially enhanced by high Ni dispersion, which shows high turnover frequency (TOF) values based on the number of surface metal sites. From the studied, Total hydrogenation of furfural to tetrahydrofurfuryl alcohol (THFA) can be achieved with a 94% yield in the gas phase over a Ni/SiO_2 catalyst prepared by the reduction of $Ni(NO_3)_2$ supported on SiO_2 and clearly total hydrogenation of furfural to THFA proceeds in two separate steps: furfural to furfuryl alcohol (FOL) and FOL to THFA. Moreover, In the conversion of furfural to FOL, the TOF value is almost constant for different average sizes of Ni metal particles of Ni/SiO_2 catalysts prepared by the reduction of $Ni(NO_3)_2$ supported on SiO_2. And in the conversion of FOL to THFA, the reaction rate is intrinsically higher than that for furfural to FOL. However, the adsorption of furfural onto the catalyst surface is much stronger than that of FOL, and furfural hydrogenation takes precedence over FOL hydrogenation in the presence of furfural. The conversion of FOL to THFA is sensitive to the structure of the catalyst. Ni particles with a smaller size give higher TOF values.

In 2016, Marimuthu Manikandan, et al. [28] studied role of surface synergistic effect on the performance of Ni-based hydrotalcite catalyst for highly efficient hydrogenation of furfural. They found that the selective vapor phase hydrogenation of furfural at ambient pressure has been investigated using a facile and robust hydrotalcite derived Ni containing mixed oxide catalyst. The systematic characterization results conferred that the difficulty in the reduction of Ni species due to the strong interaction between Ni and support, which facilitated from the homogeneous distribution of hydrotalcite structure. It was also found that the structure and catalytic performance of the catalysts were greatly influenced by Ni loading. Through fine-tuned surface elemental sites and reaction conditions, furfural conversion of 98% with 95% of furfuryl alcohol selectivity was achieved over a MAN-2 catalyst containing two molar ratio of Ni. The results have demonstrated that the incorporation of Mg significantly enhances the Ni-support interaction, Ni dispersion and catalytic performance. The high efficiency of the Ni-based hydrotalcite derived catalyst was mainly attributed to the surface synergistic interaction between the catalytically active metallic Ni sites and the strong basic sites, which furnished an eco-benign and sustainable catalyst for the selective hydrogenation of furfural. Furthermore, the spent catalyst analysis substantiated that no significant difference in the catalyst phase was observed even after 48 hours of reaction stream.

In 2011, Surapas Sitthisa, et al. [29] studied kinetics and mechanism of hydrogenation of furfural on Cu/SiO_2 catalysts. They examine both mechanisms for the case of furfural on Cu surfaces, which has not been previously investigated. They have investigated the kinetics and reaction pathways of furfuraldehyde hydrogenation over a silica-supported Cu catalyst. These studies have been complemented with DFT calculations of adsorbed furfural on Cu (111) and Cu (110) planes, as well as DRIFTS analysis of adsorbed furfural species conducted on unsupported Cu metal powder, to avoid adsorption on the support that masks the signal from the metal. DFT calculations and DRIFTS have helped them identify the type of adsorbed species on the Cu surface and explore the reaction pathways involved in the conversion of furfural. The results were found that the conversion of furfural on Cu/SiO_2 yields mainly furfuryl alcohol from hydrogenation of the carbonyl, with only small amounts of 2-methylfuran, obtained from a subsequent cleavage of the C-O bond in furfuryl alcohol. A kinetic model for furfuraldehyde conversion has been developed based on a Langmuir–Hinshelwood model. Moreover, the heat of adsorption of furfural agrees with the adsorption energy predicted by the DFT calculations using a Cu (110) surface (7.3 kcal/mol). The DRIFTS and DFT results demonstrate that the adsorption of furfural takes place preferentially in a η^1 (O)-aldehyde (perpendicular) binding mode. Two possible mechanisms for furfuraldehyde hydrogenation have been compared, based on the order of the first H atom attack to the carbonyl group, resulting in two possible surface intermediates adsorbed on the Cu surface. The activation energy barrier for the first H addition to the O carbonyl group to form adsorbed hydroxyalkyl intermediates was found to be lower than when the first addition of H is to the carbonyl C forming an alkoxide intermediate (i.e., 7.6 kcal/mol compared to 10.8 kcal/mol). These results suggest that the presence of the aromatic furan ring helps stabilizing the hydroxylalkyl intermediate, lowering the energy barrier for this path.

In 2019, Hong Du, et al. [30] studied catalytic furfural hydrogenation to furfuryl alcohol over Cu/SiO_2 catalysts: A comparative study of the preparation methods. Thay found that the effect of preparation methods of silica supported copper catalysts on the structure and performance was investigated by means of ICP, N_2 physisorption, ex-situ/in-situ XRD, in-situXPS, FT-IR, H_2-TPR, TEM, N_2O titration, TG as well as furfural hydrogenation. The results indicated that the different catalyst synthesis strategies led to the diverse copper species in the calcined samples and disparate Cu^0 surface area as well as different molar ratio of $Cu^+/(Cu^+ + Cu^0)$ in the fresh samples. The performance of impregnation derived sample was poorer than that of commercial CuCr-Strem catalyst. The catalysts prepared by deposition precipitation and ion exchange exhibited similar performance to the CuCr-Strem. The ammonia evaporation derived catalyst (Cu/SiO_2-EA) showed superior performance in the activity, selectivity and stability among all the studied catalysts. The excellent performance was related to the highest surface area of Cu^0, smallest copper particle size, large surface area and pore volume as well as appropriate higher $Cu^{+}/(Cu^{+} + Cu^{0})$ ratio. Furthermore, all the copper catalysts went through deactivation, which was caused by carbon deposition, during the reaction. Owing to the largest amount of Cu^{0} sites and large S_{BET}, the Cu/SiO_2-EA exhibited the slowest deactivation rate.

In 2017, Jun Wu, et al. [31] studied Efficient of CuNi alloy nanocatalysts for the selective hydrogenation of furfural. They found that the bimetallic CuNi catalyst showed obviously higher activity compared to the monometallic Cu and Ni which further demonstrated the important role of synergistic effect between Cu and Ni in these two reaction systems. The bimetallic nanocatalysts could also realize efficient production of furfuryl alcohol from the selective hydrogenation of furfural at its aldehyde group. Moreover, the bimetallic nanocatalysts showed good recyclability in the liquid phase hydrogenation. efficient and versatile CuNi alloy nanocatalysts not only provide promising candidates for effective upgrading of furfural but also broaden the application of non-noble bimetallic nanocatalysts for hydrogenative transformations.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals and substrates

The details of chemicals and substrates that used in this work were summarized in **Table 3.1**. The manufacturers or supplier of all chemicals also illustrated.

Table 3.1 Chemicals and substrates which used in this study.

	Chemical reagents	Grade of purity	Manufacturers
1.	Silicon dioxide (SiO_2)	99.8%	SIGMA-ALDRICH
2.	30% Ammonium hydroxide solution (NH_4OH)	30%	CARLO ERBA
3.	Nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$)	Analytical	CARLO ERBA
4.	Deionized water	-	-
5.	Acetone ($(CH_3)_2CO$)	-	-
6.	Hexa-aminenickel (II) chloride ($[Ni(NH_3)_6]Cl_2$)	-	-
7.	Copper (II) nitratetrihydrate ($Cu(NO_3)_2{\cdot}3H_2O$)	Analytical	CARLO ERBA
8.	Methanol (CH_3OH)	Analytical	MERCK
9.	Furfural ($C_5H_4O_2$)	Analytical	SIGMA-ALDRICH
10.	Air zero gas, zero grade	High purity (99.99%)	UIG
11.	Hydrogen gas, high purity	High purity (99.99%)	PRAXAIR
12.	Nitrogen gas, high purity	High purity (99.99%)	UIG

3.2 Instruments and apparatus

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

- Laboratory glassware
- Balances
- pH conductivity meter (OHAUS Corporation, USA, Model STARTER3100)
- Shaker (GALLENKAMP)
- Buchner funnel filtration
- Oven
- Calcination furnace
- Sieve (U.S.A standard sieve, Model AASHO M-92)
- Gas Chromatograph (SHIMADZU, Model GC-2014)
- Temperature program reduction Instrument (Model TCD2-NIFED)
- X-ray diffractometer (BRUKER, Model D5000)
- X-ray fluorescence spectrometer (Wavelength Dispersive, Philips, Model PW2400) and (Energy Dispersive, Oxford, Model ED-2000)
- Scanning electron microscope (USA Instrument, Model Quanta 250)
- Energy dispersive x-ray spectrometer (Oxford Instrument, X-MaxN, College of Advanced Manufacturing Innovation, KMITL)
- Surface area, pore size, and pore volume distribution analyzer (BET)

3.3 Preparation of monometallic Ni/SiO_2, Cu/SiO_2, and bimetallic Ni-Cu/SiO_2 catalysts.

In this section, hexaamine nickel (II) chloride $[Ni(NH_3)_6]Cl_2$ was synthesized in order to use as a nickel precursor for preparation of Ni/SiO_2 catalyst. The synthesis procedure is exhibited in section 3.3.1. Then, monometallic Ni/SiO_2 was prepared by SEA method. The procedure is illustrated in section 3.3.2. Moreover, Cu/SiO_2 catalyst was prepared by IM method that procedure is explained in section 3.3.3. A series of bimetallic Ni-Cu/SiO_2 catalysts was prepared by SEA following IM method and the procedure is illustrated in section 3.3.4.

3.3.1 Synthesis of hexaamminenickel (II) chloride ([Ni $(NH_3)_6$] Cl_2).

Approximately 6.00 g of nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) was dissolved in 10 mL of deionized water, then continuously stirred with a glass rod until got the clear green nickel solution. Afterthat, 20 mL of cool 30% ammonium hydroxide solution (30%NH_4OH) was slowly added dropwise into the nickel solution and then continuously stirred in iced bath until observed the violet crystals precipitation. The color of solution will change from green to blue and violet. The precipitation solution was filtrated by vacuum filtration and then washed with 6 mL of cool 30% NH_4OH followed with 5 mL of acetone. The precipitation powder was dried in the oven at 80°C for 10 min.

3.3.2 Preparation of Ni/SiO_2 catalyst by strong electrostatic adsorption method (SEA).

Prior catalyst preparation, SiO_2 support was dried in oven at 90 °C overnight. The 1400 ppm of $[Ni(NH_3)_6]Cl_2$ solution was prepared in 250 mL of volumetric flask. Approximately 0.35 g of $[Ni(NH_3)_6]Cl_2$ was dissolved with deionized water and then adjusted pH to 12 by using 30% NH_4OH solution. Afterthat, 100 mL of solution was pipetted into 0.5 g of SiO_2 support, and continuously shake for 1 hour. Then, the solution was filtrated by vacuum filtration and washed with 30 mL of deionized water at pH 12. The powder was dried in the oven at 110°C overnight. Finally, Ni/SiO_2 catalyst was calcined in air flow (60 mL/min) at 450 °C for 3 hours with a heating rate 2 °C/min to remove the organic ligands.

3.3.3 Preparation of Cu/SiO_2 catalyst by incipient wetness impregnation method (IM).

The 2 wt.% of Cu was used for preparation of Cu on SiO_2 by incipient wetness impregnation method. The copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) was dissolved in deionized water. Then aqueous solution of copper (II) nitrate trihydrate were slowly impregnated on to SiO_2 surface. The impregnated catalyst was left to stand for 6 hours to assure adequate distribution of metal complex. After the impregnation, the catalyst was dried in the oven at 110°C overnight. The dried impregnation catalyst was calcined in air at 450°C for 3 hours with a heating rate 10°C /min.

3.3.4 Preparation bimetallic Ni-Cu/SiO_2 catalysts by strong electrostatic adsorption followed incipient wetness impregnation method (SEA-IM).

The amount of Ni was 2 wt.% for each catalysts which was prepared from SEA method. Then, 2%Ni/SiO_2 catalyst was used for preparation of *x*%Ni-*y*%Cu/SiO_2 catalysts by impregnation method. The 2%Ni/SiO_2 catalyst was impregnated with copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) that was dissolved in deionized water. The impregnated catalysts were left to stand for 6 hours to assure adequate distribution of metal complex. After the impregnation, the catalysts were dried in the oven at 110 °C. The dried impregnation catalysts were calcined in air at 450 °C for 3 hours with a heating rate 10 °C /min.

The catalysts are prepared by incipient wetness impregnation method as 2%Ni-2%Cu/SiO_2 and 2%Ni-5%Cu/SiO_2 catalysts, respectively.

3.4 Catalyst characterizations

The crystal structure, elemental compositions, morphology, surface area, pore size distribution, pore volume, the reduction temperature and physical properties of monometallic Ni/SiO_2, Cu/SiO_2, and bimetallic Ni-Cu/SiO_2 catalysts will be investigated by several techniques such as TPR, XRD, XRF, SEM, EDX, and BET etc. The details of all techniques are descripted as following.

3.4.1 Temperature program reduction (TPR)

Temperature program reduction (TPR) provides information on the active site species of the catalysts by monitoring their reducibility and determine the % metal loading of the catalysts. Temperature-programmed reduction (TPR) was measured using thermal conductivity detector (TCD). The sample weighed 100 mg was placed into a quartz tube reactor, which was located inside a temperature-regulated furnace. Prior to the H_2-TPR, each sample was heated to its activation temperature in air zero (30 ml/min). After that, the heating rate of 10 °C/min, 20 ml/min of 10%H_2/Ar was applied for TPR analysis. Water production during the reduction process was removed in a U-shape tube trap before entering the TCD.

3.4.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) data provides information on the structures of crystalline solid to determine the bulk phase of catalyst. XRD patterns were carried out ex-situ by using X-ray diffractometer (SIEMENS XRD D5000). X-ray diffractometer connected to a personal computer with diffract A T version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using CuKα radiation with Ni filter in the 2θ range of 20° to 80° and resolution 0.02°.

3.4.3 X-ray fluorescence (XRF)

The chemical compositions of catalyst are determined by X-ray fluorescence spectroscopy (XRF). Approximately, 0.5 g of catalyst sample was mixed with 4.5 g of boric acid and then sample was compressed into alumina pan before measurement.

3.4.4 Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscopy (SEM) was used to observe the morphology of catalyst and the metal dispersion on silica. The sample must be conductive prevent charging by coating with gold particle by ion sputtering device. Sample was analyzed by JEOL JSM-6400 scanning electron microscopy. Energy dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample which was analyzed by ISIS Series 300 program at scientific instruments center, KMITL

3.4.5 Surface area, pore size and pore volume analyzer (BET)

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. Nitrogen adsorption–desorption measurements (BET) surface area and porosity analyzer to determine the surface area, pore size distribution and structure, pore volume and the mean particle size. The surface area was determined according to the standard Brunaur–Emmett–Teller (BET) method and the pore diameter distributions were calculated based on the desorption isotherms by the Barrett–Joyner–Halenda (BJH) method.

3.5 Liquid phase selective hydrogenation of furfural to furfuryl alcohol

The liquid phase hydrogenation of furfural was carried out in a 100 ml stainless steel autoclave equipped with a mechanical stirrer as show in the **Figure 3.1**. Prior to test the reaction, catalyst was reduce at 450 °C flowing H_2 50 mL/min for 2 hours by using tube furnace. Approximately 0.2 g of catalyst was packed in to 0.6 mm innerdiameter quartze tube than set up in to furnace. The reactor was loaded with approximately 0.2 g of catalyst, 50 µL of furfural and 10 mL of methanol (solvent) and 0.2 g of catalyst, 200 µL of furfural and 10 mL of methanol (solvent). Then purged with H_2 gas (around 3 bar) to remove air for three times. The reaction was carried out isothermally at 100 °C at 20 bar of H_2 with stirring speed 900 rpm using magnetic stirrer for 2 hours. After the reaction, the reactor was cooled down to room temperature in ice baht and then carefully depressurized. The liquid products was separated from the solid catalysts by centrifugal. All liquid product will be analyzed by FID gas chromatograph using Rtx-5 capillary column. The operating condition of gas chromatography is illustrated in **Table 3.2**.

Table 3.2 Operating conditions of gas chromatography for selective hydrogenation of furfural to furfuryl alcohol.

Gas chromatography	SHIMADZU GC-2014
Detector	FID
Packed column	Rtx5
Carrier gas	He
Carrier gas flow rate (ml/min)	9.7
Injector temperature (°C)	260
Detector temperature (°C)	270
Initial column temperature (°C)	40
Final column temperature (°C)	160
Analyzed gas	H_2

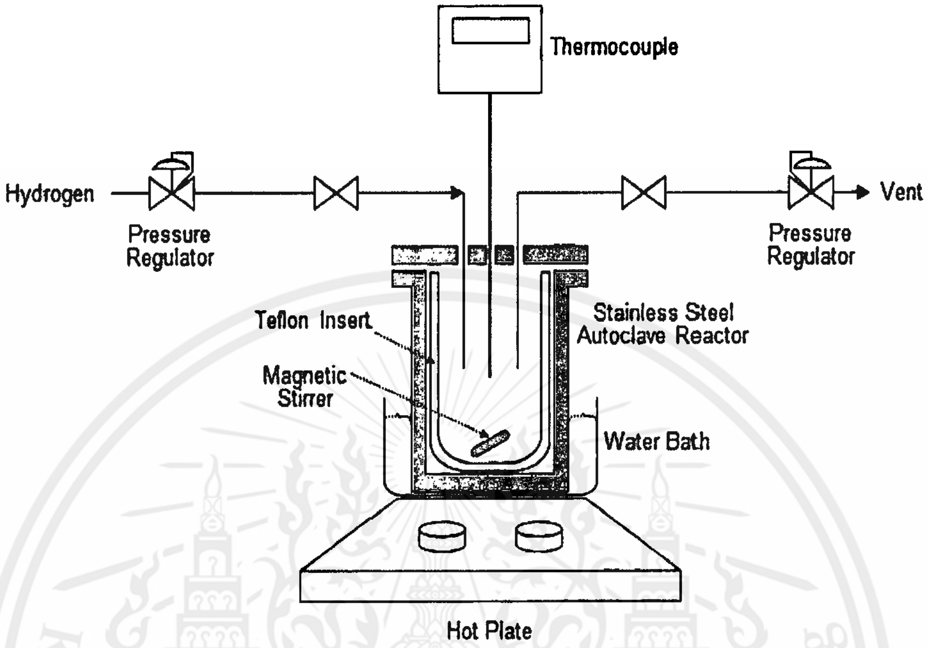


Figure 3.1 The schematic diagram of the liquid phase hydrogenation system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Ni/SiO_2, Cu/SiO_2 and $Ni-Cu/SiO_2$ catalysts

In this section, the characteristics and catalytic properties of monometallic Ni/SiO_2, Cu/SiO_2 and bimetallic $Ni-Cu/SiO_2$ catalysts were characterized by Temperature program reduction (TPR), X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and Brunauer-Emmett-Teller (BET) surface area , pore size and pore volume analyzer techniques. In this work, there are four catalysts prepared by strong-electrostatic adsorption (SEA) and incipient wetness impregnation (IM) method which were denoted as 2%Ni/SiO_2 [SEA], 2%Cu/SiO_2 [IM], 2%Ni-2%Cu/SiO_2 [SEA-IM] and 2%Ni-5%Cu/SiO_2 [SEA-IM].

4.1.1 Temperature Program Reduction (TPR)

The reducibility and reduction behavior of Ni/SiO_2, Cu/SiO_2 and $Ni-Cu/SiO_2$ catalysts were investigated by temperature program reduction technique. **Figure 4.1** exhibits the TPR profiles of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM]. Since SiO_2 is non-reducible metal oxide, therefore the present of reduction peaks can be attributed to the reduction process of different Ni and Cu species existed in catalysts. The monometallic 2%Ni/SiO_2 [SEA] catalyst shows a board reduction peak in a board range of 260-720 °C with a center around 475 °C. assigned to reduction temperature of metallic Ni^0 specie. For 2%Cu/SiO_2 [IM] catalyst, one reduction peak appeared in the range of 180-370 °C with a center around 320 °C, which was the reduction temperature of Cu specie. [29] For bimetallic 2%Ni-2%Cu/SiO_2 [SEA-IM], Two reduction peaks were observed at 200 and 570 °C. Peaks at 200 °C and 570 °C attributed to the reduction of Cu and nicklesilicate, respectively. For bimetallic 2%Ni-5%Cu/SiO_2 [SEA-IM], Two reduction peaks were observed 225 °C and 530 °C. The peaks at 220 °C and 530 °C attributed to the reduction of Cu species and nicklesilicate, respectively. [32] These peaks can be attributed to reduction of Ni-Cu alloy because the maximum temperature shift to lower reduction temperature of metallic Ni^0 and Cu^0 species which should be around 475 and 320 °C respectively.

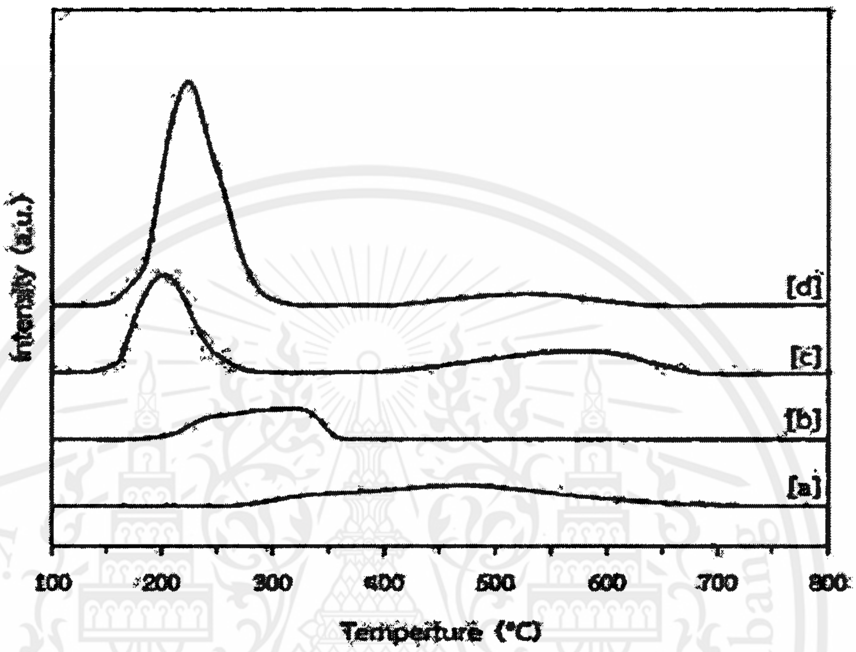


Figure 4.1 TPR profiles of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM] Catalysts.

4.1.2 X-ray diffraction (XRD)

The crystal structures and chemical phase compositions of monometallic Ni/SiO_2, Cu/SiO_2 and bimetallic Ni-Cu/SiO_2 catalysts were characterized by X-ray diffraction technique. **Figure 4.2** shows XRD patterns of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts. Which were reduce at 450 °C for 2 hours. For monometallic 2%Ni/SiO_2 [SEA] catalyst, it cannot be observed the characteristic peaks of metallic Ni which should be appeared at 2θ = 44.5°, 51.6°, and 76.4° for crystal plan of metallic Ni (111), (200), and (220), respectively. It's because of high dispersion of Ni metal or low amount of Ni loading. Meanwhile for 2%Cu/SiO_2 [IM] catalyst, three characteristic peaks were observed at 2θ = 43.3°, 50.4°, 74.1° which corresponding to crystal plan of Cu^0 (111), (200), and (220), respectively. For bimetallic Ni-Cu/SiO_2 catalysts, 2%Ni-2%Cu/SiO_2 [SEA-IM] and 2%Ni-5%Cu/SiO_2 [SEA-IM], three characteristic peaks at 2θ = 43.5°, 50.6° and 74.4° which were similar as the characteristic of metallic Cu^0 but small shift to higher degree that could be ascribed to Ni-Cu alloy species. [11] However, these peaks became more intense when increased amount of Cu loading from 2 to 5 wt.%. since the Ni-Cu alloy exhibited the behavior similar as metallic Cu^0.

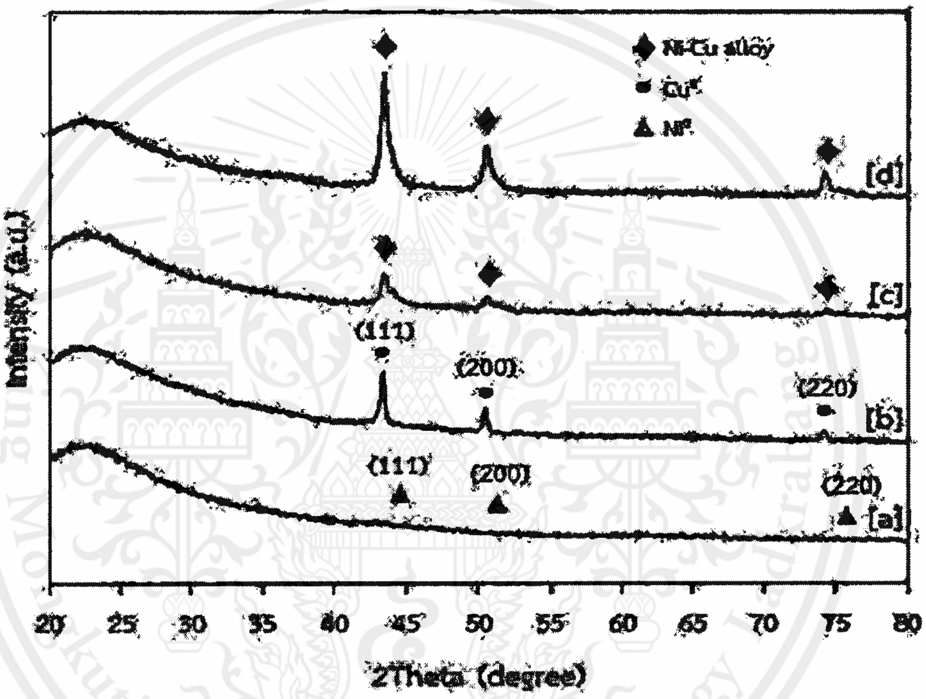


Figure 4.2 The XRD patterns of Catalysts (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM].

4.1.3 The elemental compositions of the catalysts by the XRF

The elemental compositions of all catalysts were analyzed by the X-ray fluorescence (XRF) as the results are summarized in **Table 4.1**.

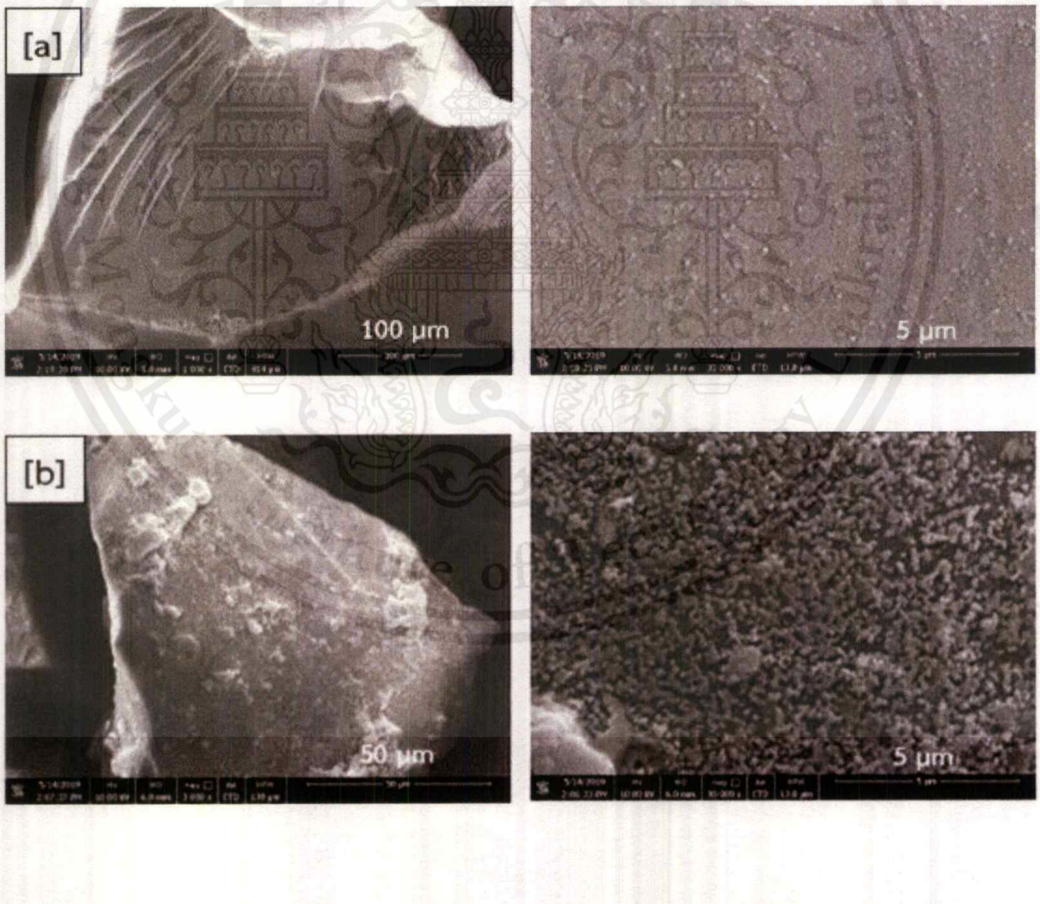
Table 4.1 Elemental compositions of Ni/SiO_2, Cu/SiO_2 and Ni-Cu/SiO_2 catalysts.

Catalysts	Amount of metal (wt.%)		
	Ni	Cu	SiO_2
(a) 2%Ni/SiO_2 [SEA]	2.67	-	95.60
(b) 2%Cu/SiO_2 [IM]	-	1.62	97.80
(c) 2%Ni-2%Cu/SiO_2 [SEA-IM]	2.67	1.71	92.80
(e) 2%Ni-5%Cu/SiO_2 [SEA-IM]	2.18	4.77	91.00

For Ni/SiO_2 [SEA] catalysts, the actual percentage of Ni was 2.67 wt.% which was lower than the maximum adsorption of Ni on SiO_2 (3.5 wt.%) while the actual percentage of Cu on Cu/SiO_2 [IM] catalyst was 1.62 wt.% which was less than the desired amount of Cu loading at 2 wt.% For bimetallic Ni-Cu/SiO_2 catalysts, Cu was different added from 2 wt.% to 5wt.% onto 2%Ni/SiO_2 [SEA]. Adding 2 wt.% of Cu metal into 2%Ni/SiO_2 [SEA] by incipient wetness impregnation method can be obtained a close Cu loading at around 1.71 wt.%. Whereas adding 5 wt.% of Cu into 2%Ni/SiO_2 [SEA] by incipient wetness impregnation method gave Ni loading around 2.18% by weight but gave a Cu loading around 4.77wt.% which inconsistent with desired amount of Cu metal.

4.1.4 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscopy (SEM) is a tool for observing the morphology and metal dispersion of monometallic and bimetallic Ni/SiO_2, Cu/SiO_2 and Ni-Cu/SiO_2 catalysts. The amount of metals dispersion were analyzed by Energy-Dispersive X-ray spectroscopy (EDX) technique. **Figure 4.3** illustrated the SEM images of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts. Form the pictures, the morphologies of monometallic 2%Ni/SiO_2 and 2%Cu/SiO_2 catalysts were difference. The morphology of 2%Ni/SiO_2 catalyst was smooth and dense surface on a large particle while 2%Cu/SiO_2 catalyst had rough surface and seem to agglomeration into small particles size. It could be remark that metal loading by strong-electrostatic adsorption gave a uniform metal dispersion than incipient wetness impregnation method. For bimetallic Ni-Cu/SiO_2 catalysts, adding 2% Cu onto 2%Ni/SiO_2 [SEA] changed the morphologies to more roughness and less dense. Moreover, adding 5% Cu onto 2%Ni/SiO_2 [SEA] gave a similar morphology as 2%Ni-2%Cu/SiO_2 [SEA-IM] catalyst but intense roughness. The metal dispersion can be investigated by EDX technique as the results were exhibited in **Figure 4.4**. It was seen that high dispersion of small Ni particle size was found on all catalysts. These results confirm that the strong electrostatic adsorption method gave high metal dispersion with a uniformly dispersed. On the other hand, adding of Cu metal by incipient wetness impregnation method, the agglomeration of Cu metal were found on 2%Cu/SiO_2 [IM] and 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts, except 2%Ni-2%Cu/SiO_2 catalyst. This could be remarked that ratio of Ni/Cu had a significantly effect to the high metal dispersions. Adding Cu metal more than 2wt%. by incipient wetness impregnation affect to an agglomeration of Cu particles.



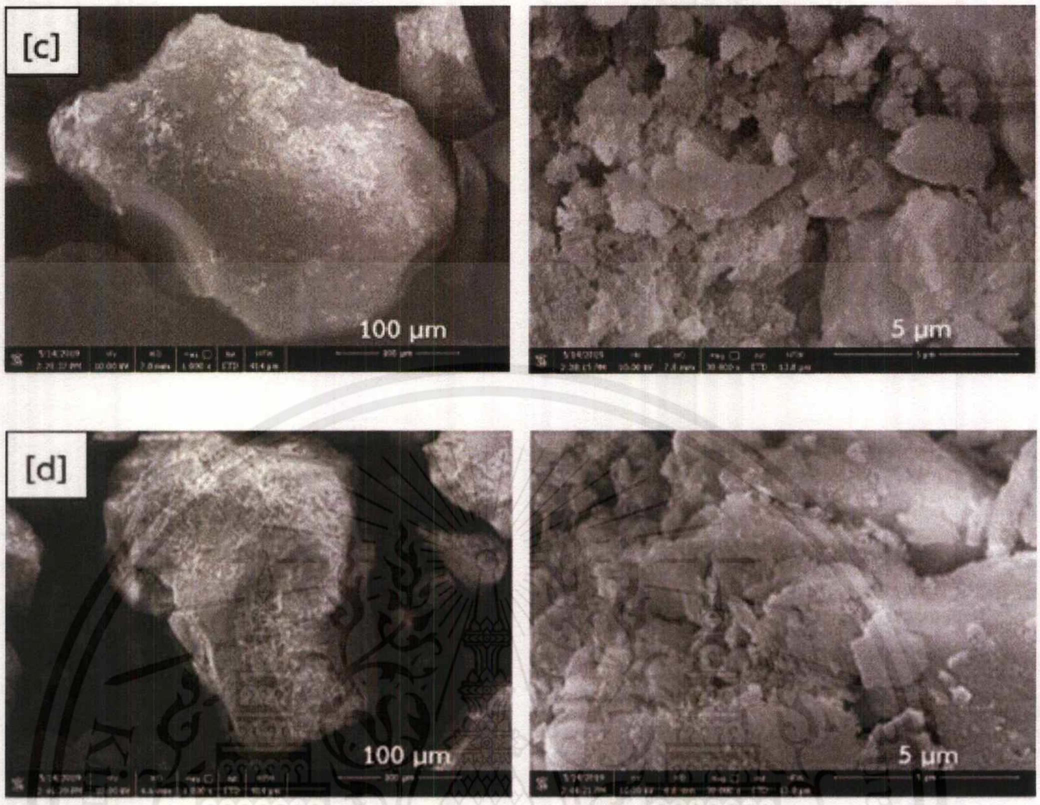


Figure 4.3 SEM images of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni- 2%Cu/SiO_2 [SEA-IM] and (d) 2.0%Ni-5.0%Cu/SiO_2 [SEA-IM] Catalysts.

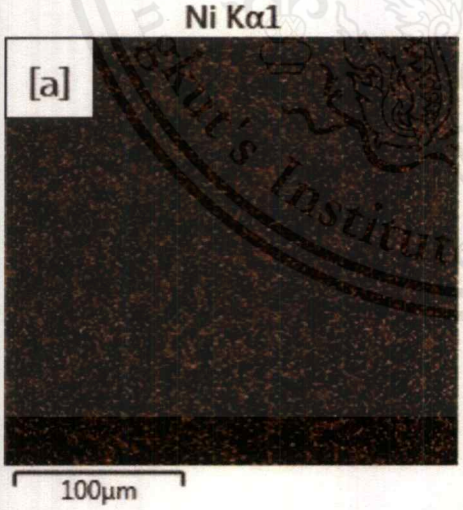


Figure 4.4 EDX images of (a) 2.0%Ni/SiO_2 [SEA], (b) 2.0%Cu/SiO_2 [IM], (c) 2.0%Ni-2.0%Cu/SiO_2 [SEA-IM] and (d) 2.0%Ni-5.0%Cu/SiO_2 [SEA-IM] Catalysts.

4.1.5 Surface area, pore size and pore volume analyzer (BET)

The specific surface area, pore size and pore volume of the catalyst are summarized in **Table 4.2**. The specific surface area of SiO_2 was 330 m^2/g. Ni and Cu metal loading effect to decrease SiO_2 surface area because metal was covered on the SiO_2 surface. **Figure 4.5** presents the isotherm of N_2 adsorption-desorption of all catalysts. All samples exhibited type IV isotherm, which were mesopores materials. Considering pore volume, monometallic 2%Ni/SiO_2 gave higher pore volume (0.96 cm^3/g) than 2%Cu/SiO_2 (0.77 cm^3/g) even though the amount of metal loading was the same. It was an evidence for highly dispersed of Ni more than Cu on the SiO_2 surface. In addition, pore volume of both bimetallic Ni-Cu/SiO_2 [SEA-IM] catalysts decreased when compared with 2%Ni/SiO_2 [SEA] catalyst indicating to Cu was added into the interpore of catalysts. However, increasing the amount of Cu loading from 2% to 5wt%. effected to decreasing of pore volume.

Table 4.2 Surface area, pore size and pore volume analyzer (BET)

Catalyst	Surface Area (m^2/g)	Pore Size (°A)	Pore Volume (cm^3/g)
2%Ni/SiO_2 [SEA]	304.19	123.49	0.96
2%Cu/SiO_2 [IM]	302.79	123.54	0.77
2%Ni-2%Cu/SiO_2 [SEA-IM]	304.88	123.52	0.84
2%Ni-5%Cu/SiO_2 [SEA-IM]	308.20	123.62	0.79

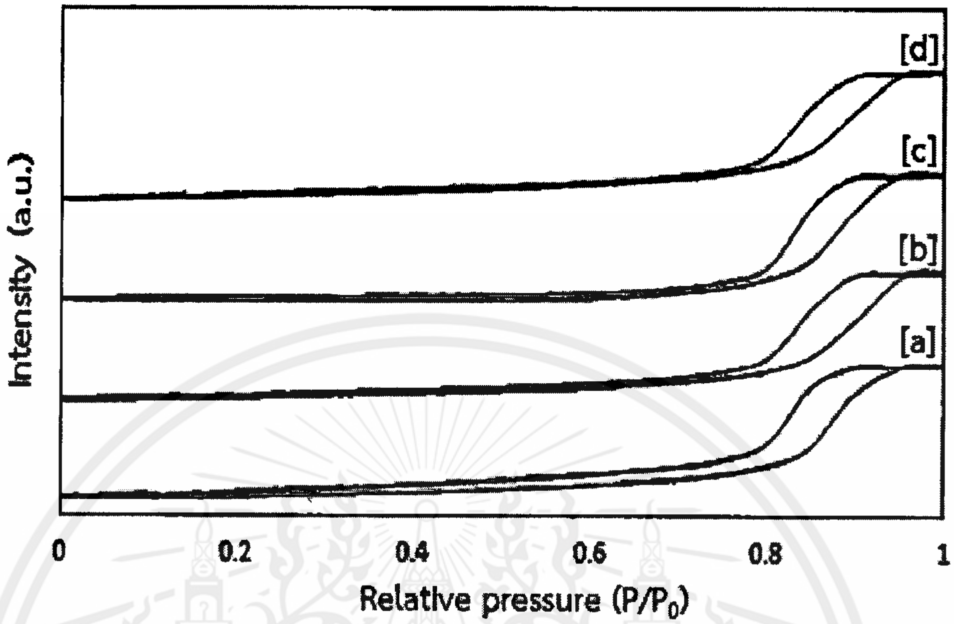


Figure 4.5 N_2 adsorption-desorption isotherms of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts.

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

In order to investigate the influence of the solvent on furfural conversion, furfural was mixed with 10 mL of methanol without the catalyst. The result of this test is displayed in (blank) **Table 4.3**, which shows the conversion of furfural at 55.95% and the selectivity at 100.00% to the 2-furaldehyde dimethyl acetal as the solvent product. From this study, it is observed that hydrogenation reaction cannot occur if there is no catalyst. Therefore, when using the monometallic 2%Ni/SiO_2 [SEA] catalyst, it is observed that occur the good hydrogenation reaction due to the catalyst reduced to occur the solvent product lead to high furfural conversion, high furfuryl alcohol selectivity as shows in the furfuryl alcohol yield at 9.05% and tetrahydrofurfuryl alcohol appeared a little because there is excess furfural that no occurred over hydrogenation. And, compared with the monometallic 2%Cu/SiO2 [IM] catalyst that Cu selective to furfuryl alcohol more than Ni, which shows the furfuryl alcohol yield at 27.72%. Then, in order to study the catalytic behavior of monometallic (Ni/SiO_2, Cu/SiO_2) compared with bimetallic (Ni-Cu/SiO_2) catalysts, four catalysts have been tested in liquid-phase hydrogenation of furfural by various furfural/catalyst ratios. **Table 4.3** and **Table 4.4** presents the catalytic performances of all catalysts. According to high furfural/catalyst ratio (**Table 4.3**), the conversion of furfural decreased in the order of 2%Cu-5%Ni/SiO_2 [SEA-IM] (62.75%) > 2%Cu-2%Ni/SiO_2 [SEA-IM] (57.67%) > 2%Ni/SiO_2 [SEA] (32.04%) > 2%Cu/SiO_2 [IM] (13.80%) while the yield of furfuryl alcohol were in the order of 2%Cu-5%Ni/SiO_2 [SEA-IM] (47.67%) > 2%Cu-2%Ni/SiO_2 [SEA-IM] (33.05%) > 2%Cu/SiO_2 [IM] (27.72%) > 2%Ni/SiO_2 [SEA] (9.05%), respectively. These could be noted that both of bimetallic Ni-Cu/SiO_2 catalysts gave higher conversion and yield of furfuryl alcohol than monometallic catalysts. Moreover, increasing of Cu loading gave a beneficial effect to enhance the conversion and of furfural. Generally, Ni-based catalysts have preferential occurred total hydrogenation via η^2 (C, O aldehyde) adsorption (**Figure 4.6**) then produced other byproducts such as tetrahydrofurfuryl alcohol and tetrahydrofuran. Meanwhile, Cu-based catalysts has been occurred hydrogenation of furfural via η^1 (O, aldehyde) adsorption, hence it was selectively to furfuryl alcohol product. The pathways of furfural hydrogenation by using bimetallic Ni-Cu/SiO_2 catalysts could be clearly confirmed when decreased the furfural/catalysts ratio (**Table 4.4**). At low feed, furfural was mixed with 10 mL of methanol without the catalyst that shows furfural transforms into total solvent product without the hydrogenation reaction as same as high feed, 2.0%Ni/SiO_2 [SEA] catalyst shows the highest furfural conversion at 100% with the lowest furfuryl alcohol selectivity at 35.21% because it has small Ni particles size and high dispersion of Ni metal on the SiO_2 supports. However, tetrahydrofurfuryl alcohol appeared as a dominant product indicating to 2%Ni/SiO_2 [SEA] catalyst preferred to occurred hydrogenation via η^2 (C,O aldehyde), the consecutive hydrogenation of furfural to furfuryl alcohol and then furfuryl alcohol occurred over hydrogenation to tetrahydrofurfuryl alcohol, respectively. For 2%Cu/SiO_2 [IM] catalyst, the conversion of furfural was 66.43% with the highest selectivity of furfuryl alcohol 94.41%. It is evidence to confirm Cu metal is very selectively to furfuryl alcohol product but low initial rate of hydrogenation. However, after adding Cu as a second metal, bimetallic 2%Ni-5%Cu/SiO_2 [SEA-IM] catalyst showed a high furfural conversion around 94.34% with a high furfuryl alcohol selectivity at 63.60%. This could be because of it occupies the high amount of small Ni-Cu alloy particles which found by TPR technique. Suitable combination of Ni and Cu alloy can promote the hydrogenation activity to get high conversion (reach to 100%) as a monometallic Ni/SiO_2 whereas Cu is very facilitating to high selectivity of furfuryl alcohol by suppressed the over hydrogenation of furfural. It can be remarked that 2%Ni-5%Cu/SiO_2 [SEA-IM] is one of a good catalyst for liquid-phase selective hydrogenation of furfural to furfuryl alcohol. Summary, properties of Ni-Cu alloy for good catalyst are suitable rate hydrogenation that no occur the over hydrogenation same Ni, on the other hand, it has not to low rate hydrogenation same Cu and important must have high furfuryl alcohol selectivity.

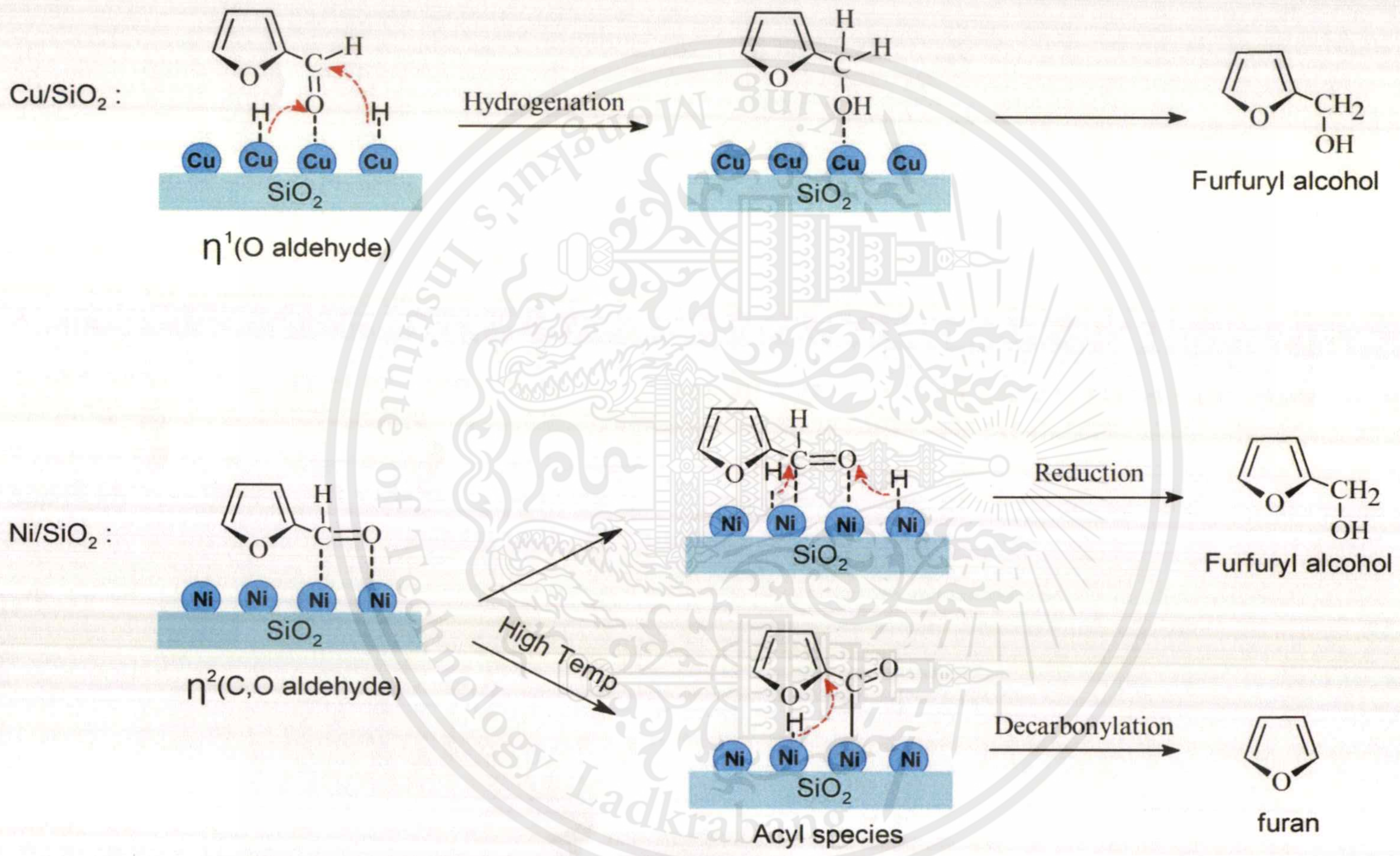


Figure 4.6 The possible reaction pathways of furfural over Cu/SiO_2 and Ni/SiO_2 catalysts.

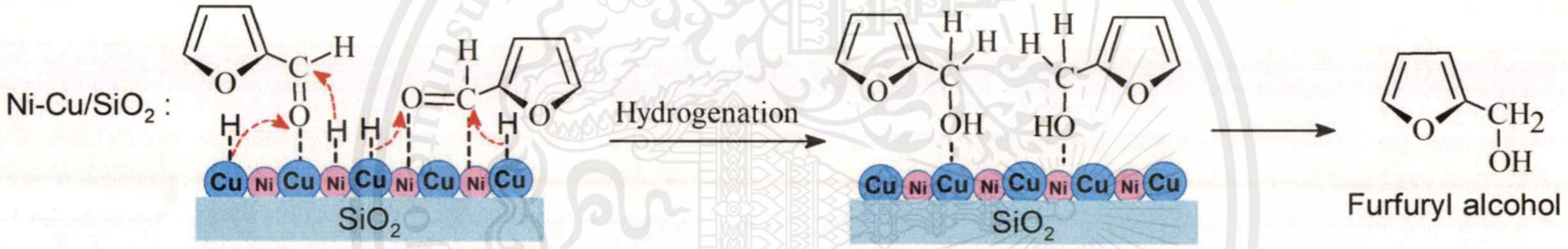


Figure 4.7 The possible reaction pathways of furfural over Bimetallic Ni-Cu/SiO$_2$ catalysts.

Table 4.3 Catalytic performance of Ni/SiO$_2$ [SEA], Cu/SiO$_2$ [IM], and bimetallic Ni-Cu/SiO$_2$ [SEA-IM] catalysts in liquid phase selective hydrogenation of furfural to furfuryl alcohol.[a]

Catalyst	Conversion (%)	Yield	Selectivity (%)			
		Furfuryl alcohol (%)	Furfuryl alcohol (FA)	Tetrahydrofurfuryl alcohol (THFA)	2-furaldehyde dimethyl acetal	Ethanone, 1-(2-furanyl)
Blank	55.95	0.00	0.00	0.00	100.00	0.00
2%Ni/SiO$_2$ [SEA]	32.04	9.05	77.75	10.20	3.46	8.60
2%Cu/SiO$_2$ [IM]	13.80	27.72	46.40	0.00	53.44	0.16
2%Ni-2%Cu/SiO$_2$ [SEA-IM]	57.67	33.05	47.00	5.94	44.59	2.47
2%Ni-5%Cu/SiO$_2$ [SEA-IM]	62.75	47.67	68.49	3.74	26.90	0.88

[a] Reaction conditions: Catalyst 0.2 g, 200 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

Table 4.4 Catalytic performance of Ni/SiO_2 [SEA], Cu/SiO_2 [IM], and bimetallic Ni-Cu/SiO_2 [SEA-IM] catalysts in liquid phase selective hydrogenation of furfural to furfuryl alcohol.[b]

Catalyst	Conversion (%)	Yield	Selectivity (%)			
		Furfuryl alcohol (%)	Furfuryl alcohol (FA)	Tetrahydrofurfuryl alcohol (THFA)	2-furaldehyde dimethyl acetal	Ethanone, 1-(2-furanyl)
Blank	80.72	0.00	0.00	0.00	100.00	0.00
2%Ni/SiO_2 [SEA]	100.00	47.88	35.21	61.66	3.13	0.00
2%Cu/SiO_2 [IM]	66.43	30.30	94.41	0.00	5.04	0.55
2%Ni-2%Cu/SiO_2 [SEA-IM]	85.71	36.94	65.02	21.83	10.25	2.90
2%Ni-5%Cu/SiO_2 [SEA-IM]	94.34	50.34	63.60	24.03	10.81	1.56

[b] Reaction conditions: Catalyst 0.2 g, 50 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

1. The bimetallic Ni-Cu/SiO_2 catalysts which prepared by SEA and IM method shows higher catalytic performance in liquid-phase selective hydrogenation of furfural to furfuryl alcohol than both monometallic Ni/SiO_2 and Cu/SiO_2 catalysts.

2 The suitable Ni/Cu ratio in liquid phase selective hydrogenation of furfural to furfuryl alcohol was 2:5 that give the highest yield of furfuryl alcohol at 50.34% with high conversion and high selectivity.

3. Formation of Ni-Cu alloy has a beneficially effect to the catalytic performance of liquid-phase selective hydrogenation of furfural to furfuryl alcohol.

5.2 Suggestions

1. The synergetic effect and dispersion of NiCu alloy should be confirmed by advanced characterization such as XPS, or EXANE techniques.

2. The reaction condition should be studied for the example; increasing of reaction temperatures, reaction time, and H_2 pressure.

3. The other second metal such as Sn, Fe, Co should be comparatively studied to improve the conversion and selectivity furfuryl alcohol

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

The calculation shown below for 2%Ni/SiO_2 prepared by strong electrostatic adsorption method (SEA), 2%Cu/SiO_2 prepared by incipient wetness impregnation method (IM), 2%Ni-2%Cu/SiO_2 and 2%Ni-5%Cu/SiO_2 catalysts prepared by strong electrostatic adsorption method - incipient wetness impregnation method (SEA-IM).

Calculation the weight of $[Ni(NH_3)_6]Cl_2$ at different concentrations in 250 mL volume.

The 2%Ni/SiO_2 catalyst prepared by strong electrostatic adsorption method (SEA)

$$\text{Weight of } [Ni(NH_3)_6]Cl_2 = \frac{\text{volume of stock solution X weight of Ni complex in 1000 mL}}{\text{1000 mL}}$$

For concentration of $[Ni(NH_3)_6]Cl_2$ at 1400 ppm in 250 mL

$$\text{Weight of } [Ni(NH_3)_6]Cl_2 = \frac{\text{250 mL X 1400 mg}}{\text{1000 mL}} = 0.3500 \text{ g}$$

Calculation of Cu/SiO_2 and Ni-Cu/SiO_2 by incipient wetness impregnation method (IM).

2%Cu/SiO_2 prepared by incipient wetness impregnation method (IM),

The 2%Ni/SiO_2 catalyst from SEA was used for preparation of 2%Ni-2%Cu/SiO_2 and 2%Ni-5%Cu/SiO_2 by incipient wetness impregnation method (IM).

The pore volume of the silica is 7.2 ml in silica 3 g. (M.W. of $Cu(NO_3)_2{\cdot}3H_2O$ = 241.6 g/mol and M.W. of Cu metal = 63.546 g/mol)

For weight of Cu complex for 2%Cu/SiO_2 catalyst prepared by IM:

SiO_2 98 g has Cu metal = 2 g

SiO_2 3 g has Cu metal = $\frac{2\text{ g} \times 3\text{ g}}{98\text{ g}}$ = 0.0612 g

Cu metal 63.546 g $Cu(NO_3)_2{\cdot}3H_2O$ = 241.6 g

Cu metal 0.0612 g $Cu(NO_3)_2{\cdot}3H_2O$ = $\frac{241.6\text{ g} \times 0.0612\text{ g}}{63.546\text{ g}}$ = 0.2328 g

APPENDIX B

CATALYST CHARACTERIZATION

1. Temperature program reduction (TPR)

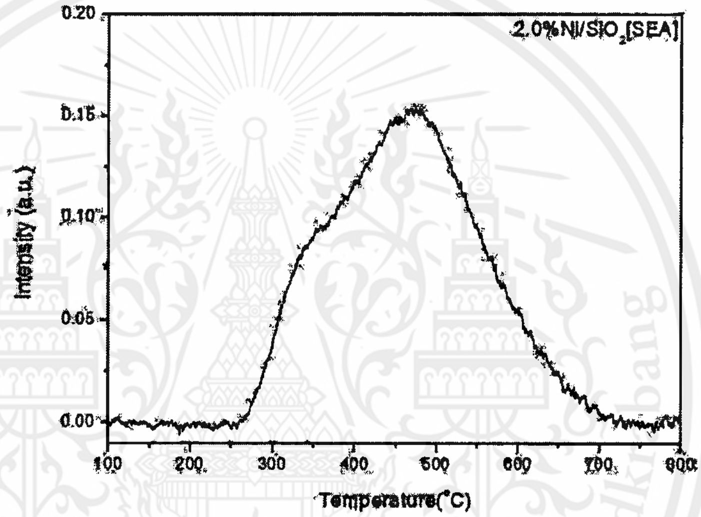


Figure B1 TPR profile of 2%Ni/SiO$_2$ [SEA] catalyst.

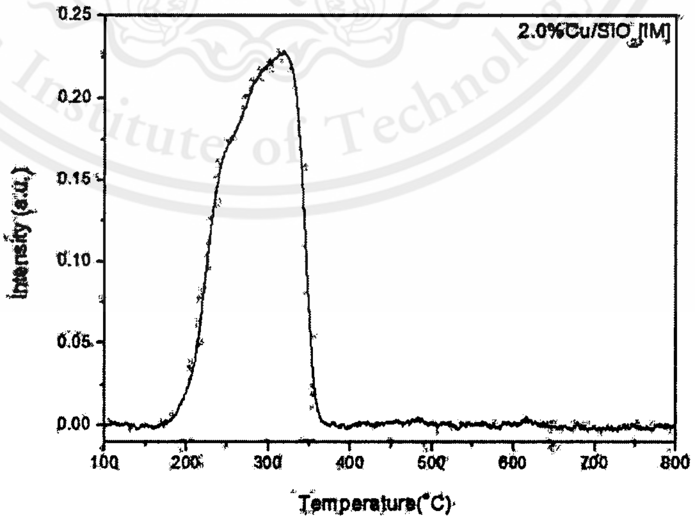


Figure B2 TPR profile of 2%Cu/SiO$_2$ [IM] catalyst.

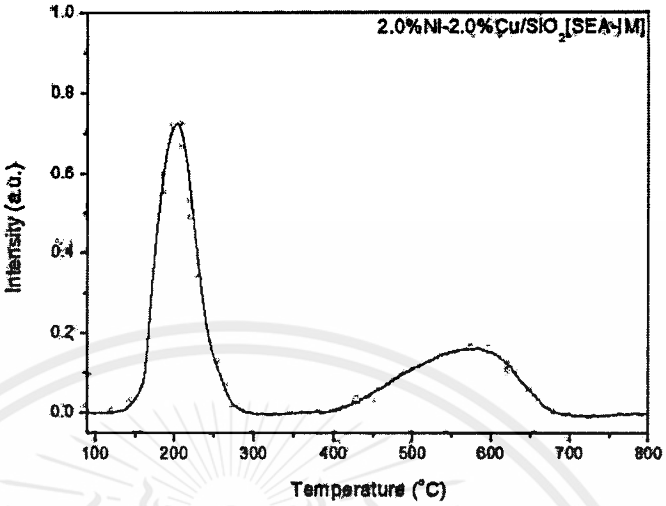


Figure B3 TPR profile of 2%Ni-2%Cu/SiO$_2$ [SEA-IM] catalyst.

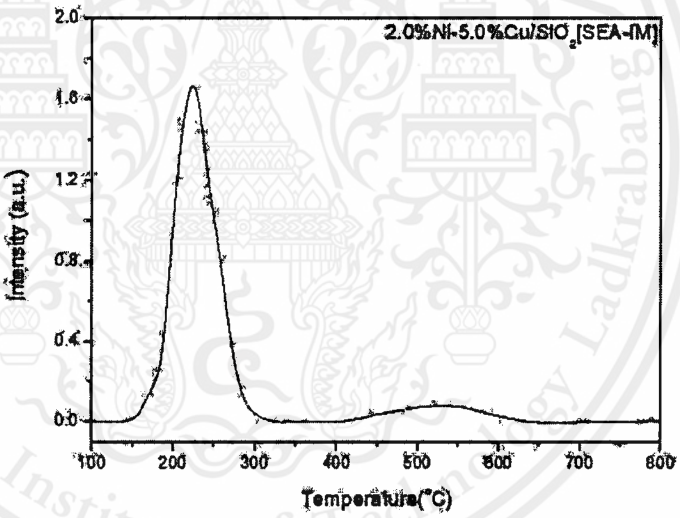


Figure B4 TPR profile of 2%Ni-5%Cu/SiO$_2$ [SEA-IM] catalyst.

2. X-ray diffraction (XRD)

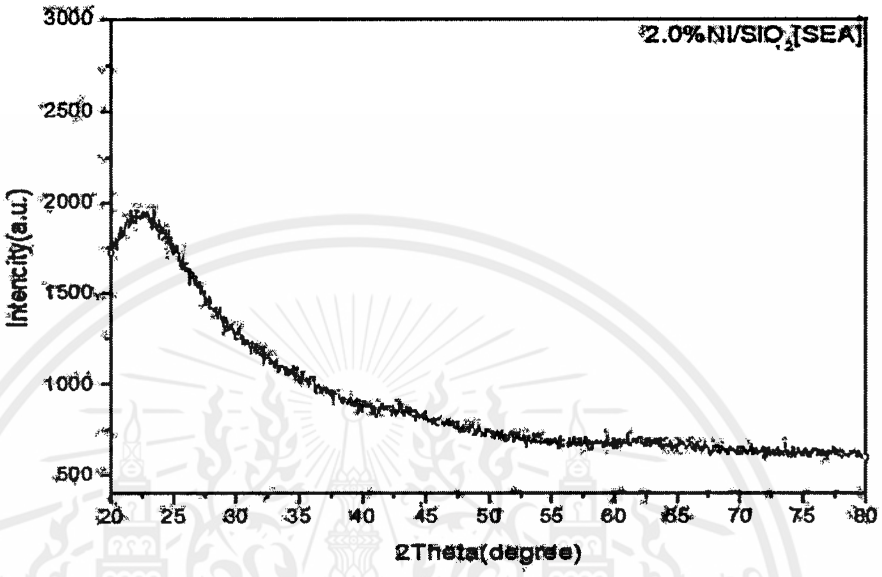


Figure B5 The XRD pattern of 2%Ni/SiO$_2$ [SEA] Catalyst.

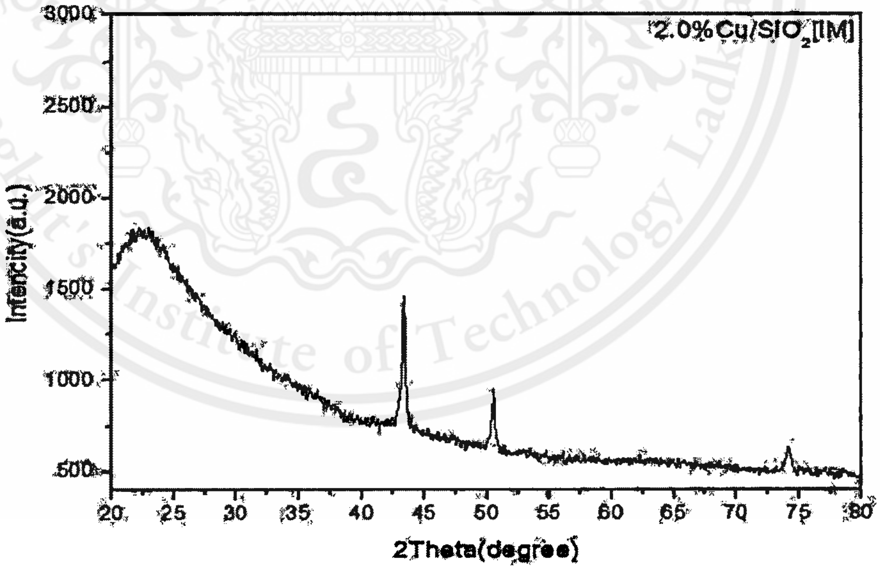


Figure B6 The XRD pattern of 2%Cu/SiO$_2$ [IM] Catalyst.

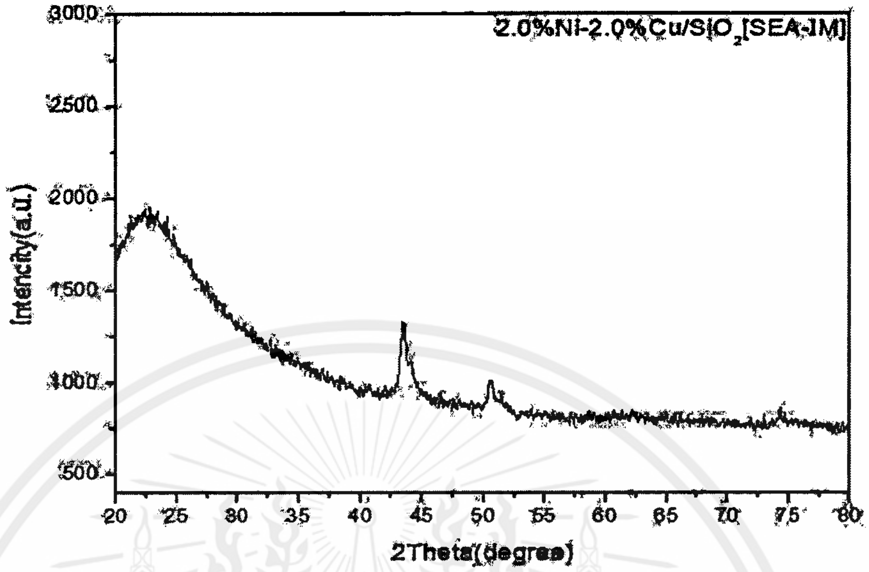


Figure B7 The XRD pattern of 2%Ni-2%/SiO$_2$ [SEA-IM] Catalyst.

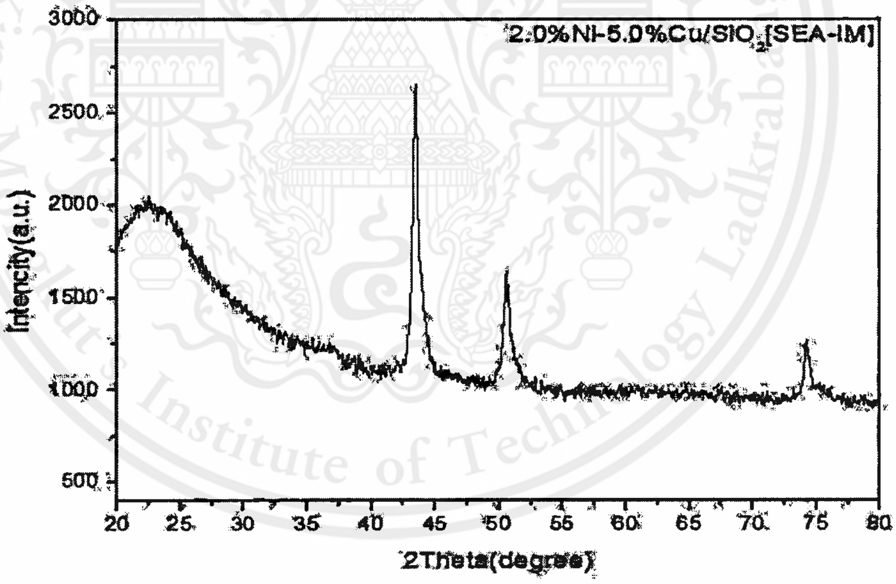


Figure B8 The XRD pattern of 2%Ni-5%/SiO$_2$ [SEA-IM] Catalyst.

3. X-ray fluorescence spectrometer (XRF)

Table B1 The Results Amount of metal of Ni/SiO_2, Cu/SiO_2 and Ni-Cu/SiO_2 catalysts.

Catalysts	Ni (%)	Cu (%)	SiO_2 (%)
2%Ni/SiO_2 [SEA]	2.67	-	95.60
2%Cu/SiO_2 [IM]	-	1.62	97.80
2%Ni-2%Cu/SiO_2 [SEA-IM]	2.67	1.71	92.80
2%Ni-5%Cu/SiO_2 [SEA-IM]	2.18	4.77	91.00

Table B2 The Results Amount of metal oxide of Ni/SiO_2, Cu/SiO_2 and Ni-Cu/SiO_2 catalysts.

Catalysts	NiO (%)	CuO (%)	SiO_2 (%)
2%Ni/SiO_2 [SEA]	3.40	-	95.60
2%Cu/SiO_2 [IM]	-	2.03	97.80
2%Ni-2%Cu/SiO_2 [SEA-IM]	3.40	2.14	92.80
2%Ni-5%Cu/SiO_2 [SEA-IM]	2.78	5.97	91.00

4. Scanning electron microscope (SEM)

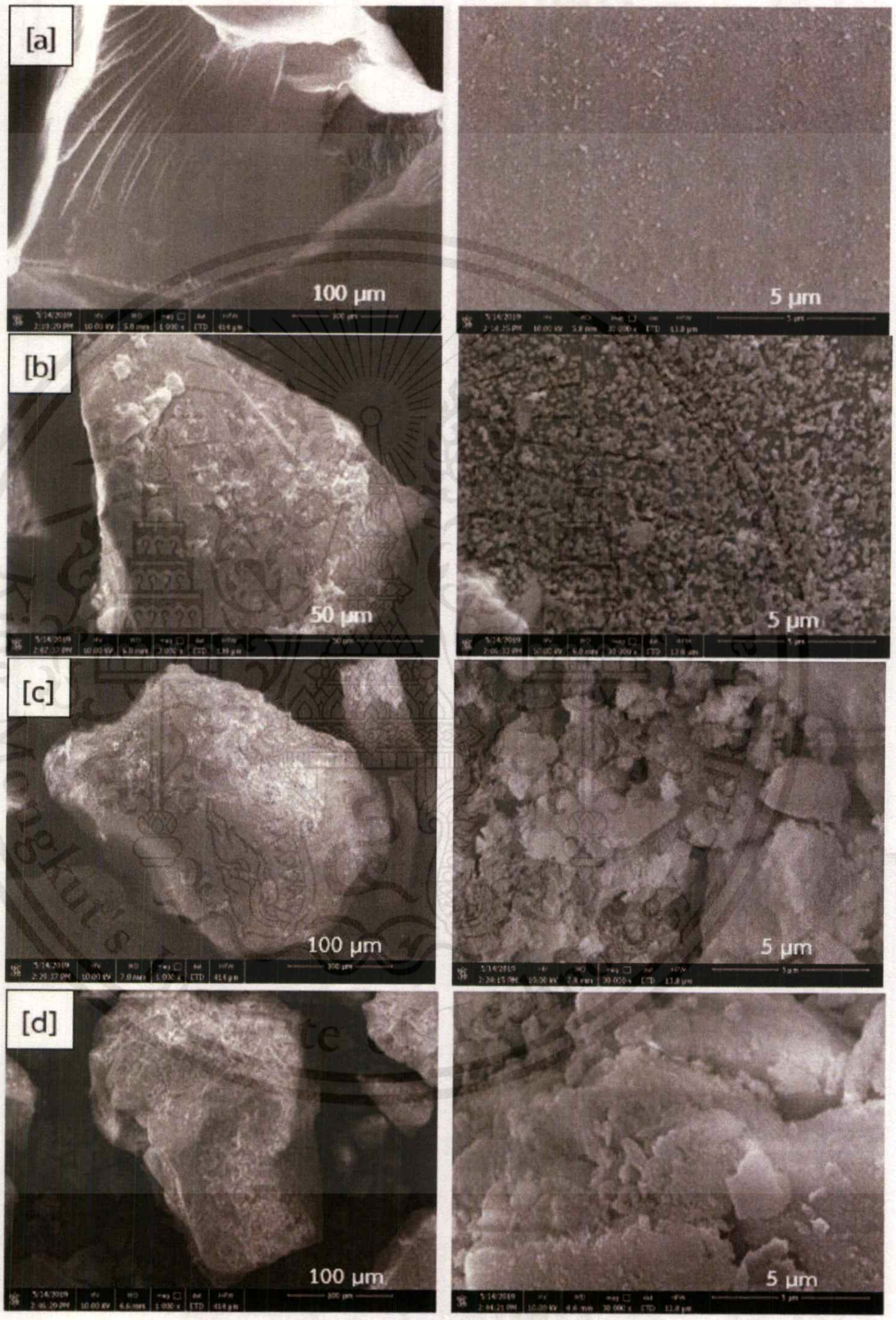
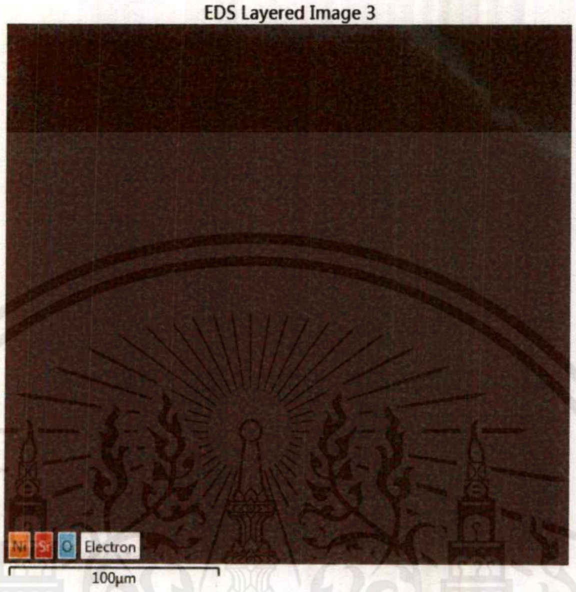


Figure B9 SEM images of (a) 2%Ni/SiO_2 [SEA], (b) 2%Cu/SiO_2 [IM], (c) 2%Ni-2%Cu/SiO_2 [SEA-IM] and (d) 2%Ni-5%Cu/SiO_2 [SEA-IM] catalysts.

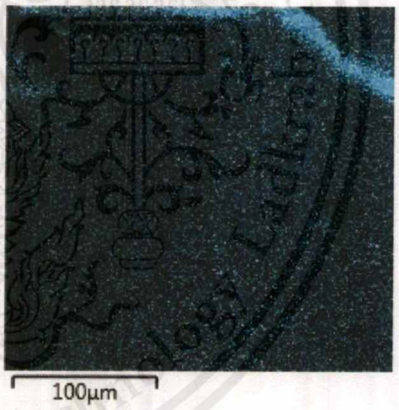
5. Energy dispersive X-ray spectroscopy (EDX)

EDS Layered Image 3



Si Kα1

O Kα1



Ni Kα1

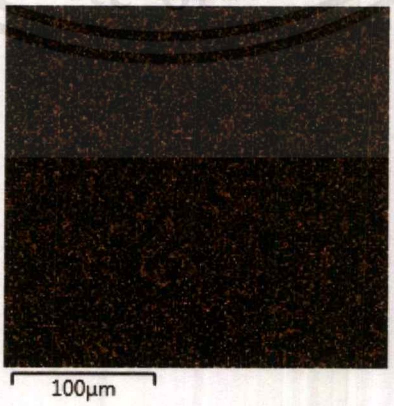
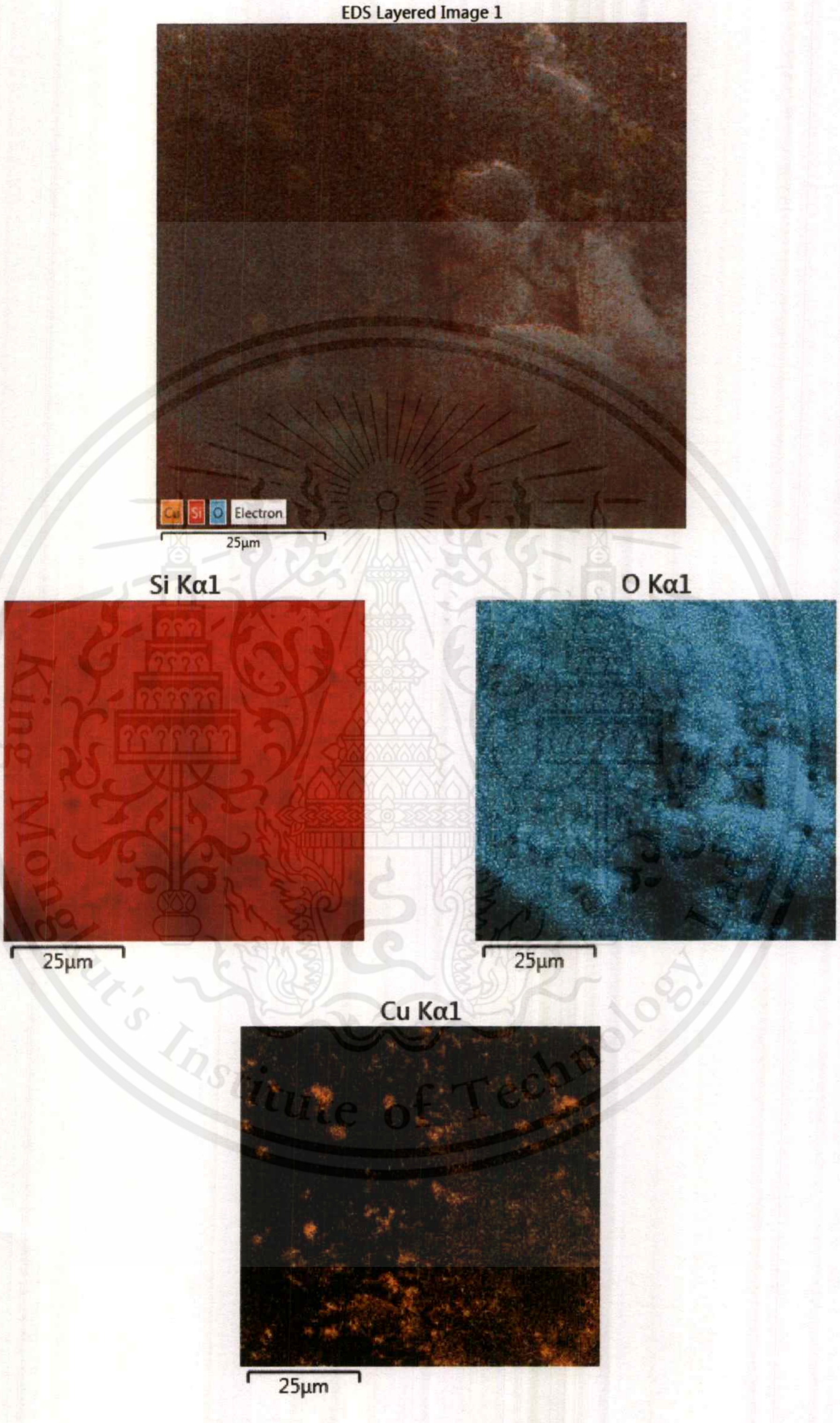


Figure B10 EDX images and map sum spectrum of 2%Ni/SiO_2 [SEA] catalyst.

Table B3 Sum spectrum of 2%Ni/SiO_2 [SEA] catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
O				52.11		63.34	
Si	K series	61.16	0.48464	45.06	0.07	32.68	SiO_2
Ni	K series	3.68	0.03675	2.84	0.05	0.98	Ni
Total				100.00		100.00	


EDS Layered Image 1
Cu
Si
O
Electron
25μm
Si Kα1
25μm
O Kα1
25μm
Cu Kα1
25μm

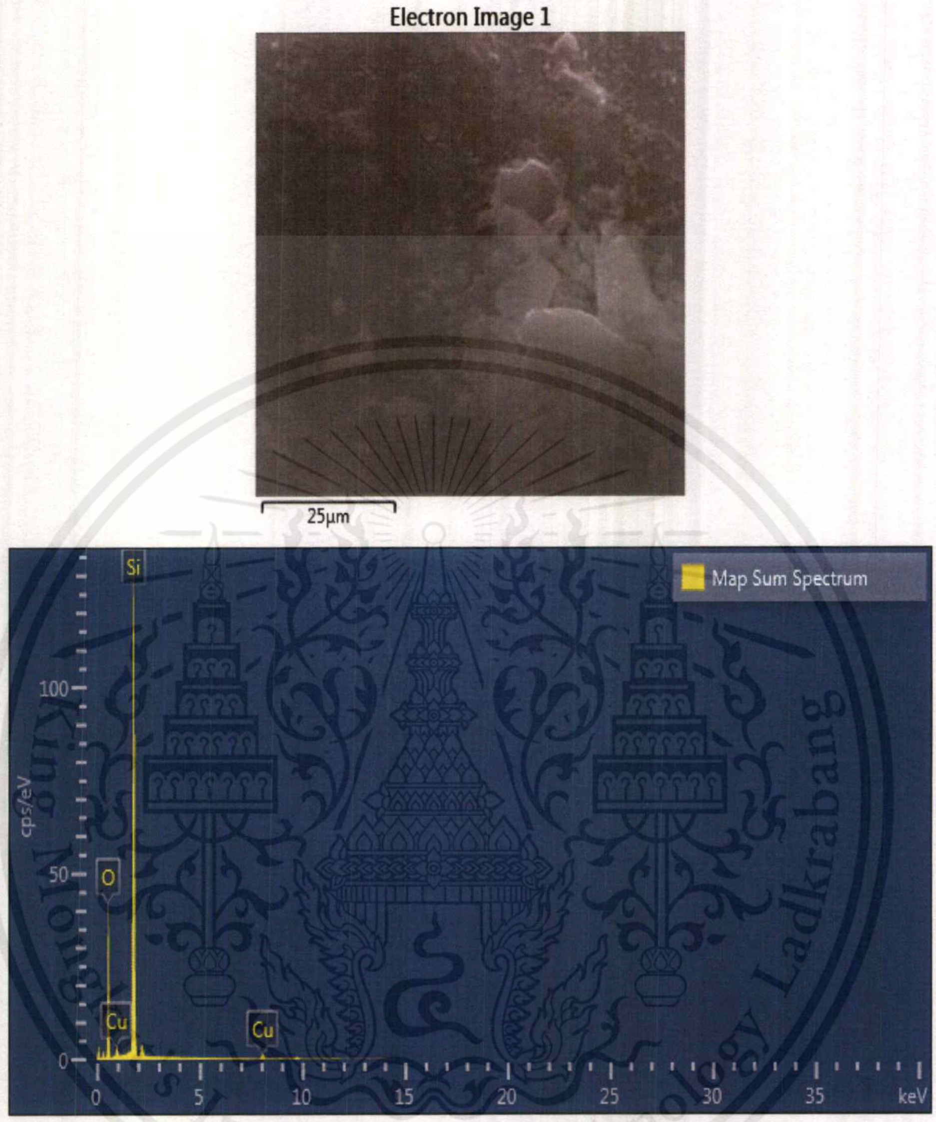
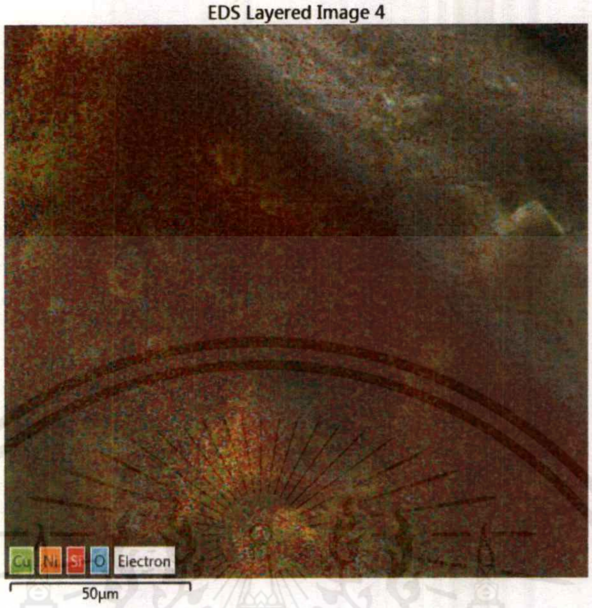


Figure B11 EDX images and map sum spectrum of 2%Cu/SiO_2 [IM] catalyst.

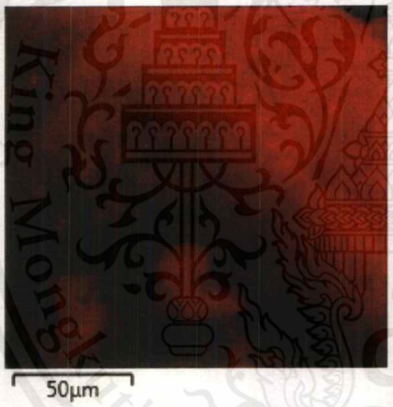
Table B4 Sum spectrum of 2%Cu/SiO_2 [IM] catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
O				52.18		66.39	
Si	K series	105.43	0.83540	45.23	0.04	32.78	SiO_2
Cu	K series	5.49	0.05493	2.59	0.03	0.83	Cu
Total				100.00		100.00	

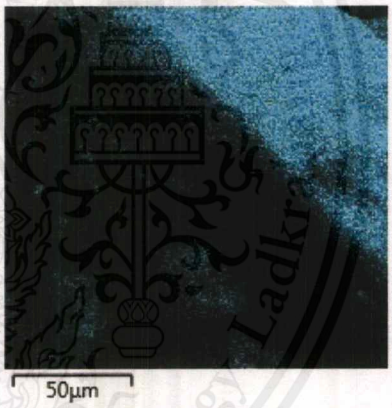
EDS Layered Image 4



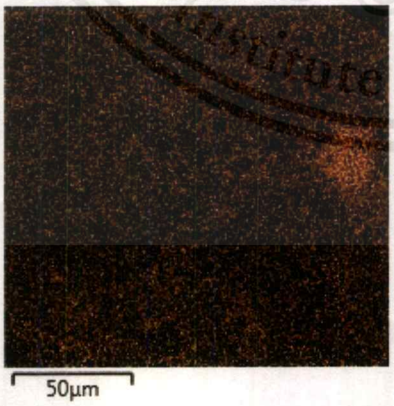
Si Kα1



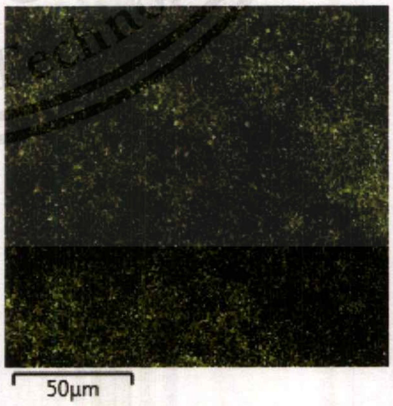
O Kα1



Ni Kα1



Cu Kα1



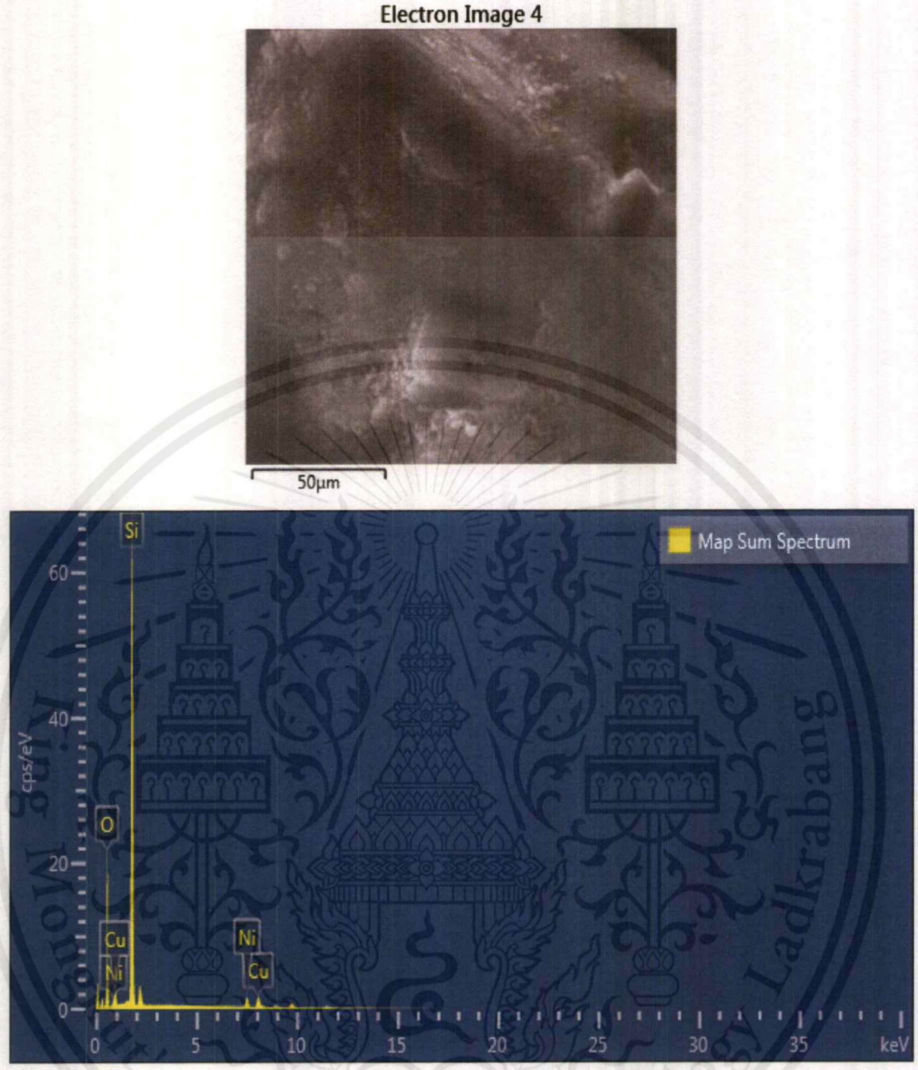
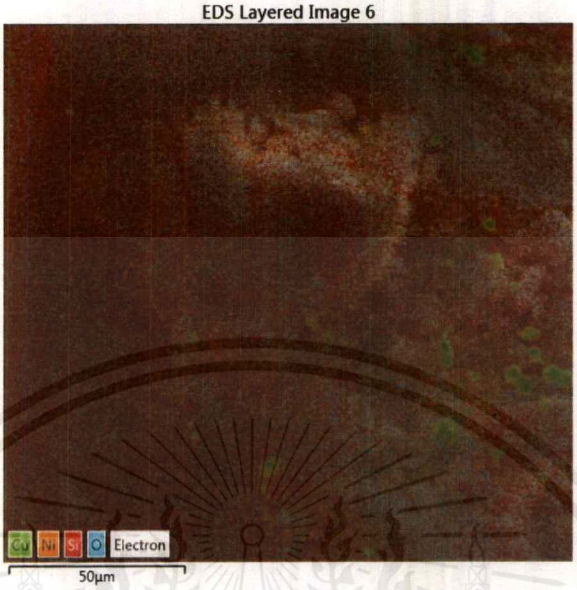


Figure B12 EDX images and map sum spectrum of 2%Ni-2%Cu/SiO_2 [SEA-IM].

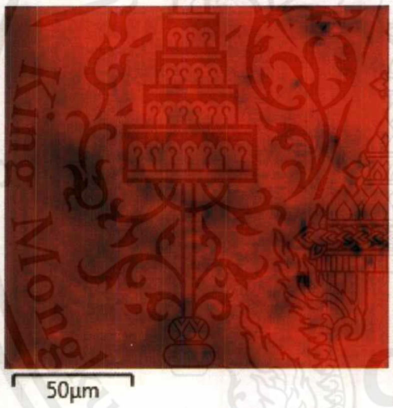
Table B5 Sum spectrum of 2%Ni-2%Cu/SiO_2 [SEA-IM] catalyst.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
O				49.47		65.61	
Si	K series	52.14	0.41317	41.32	0.08	31.22	SiO_2
Ni	K series	5.02	0.05015	3.77	0.05	1.36	Ni
Cu	K series	6.88	0.06884	5.43	0.07	1.81	Cu
Total				100.00		100.00	

EDS Layered Image 6

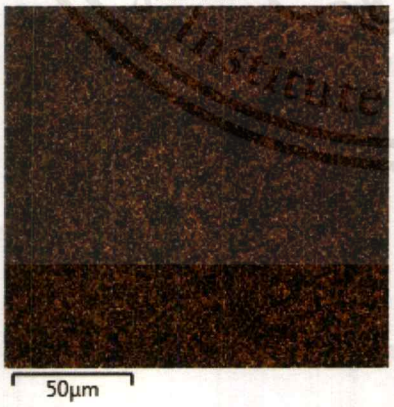


Si Kα1

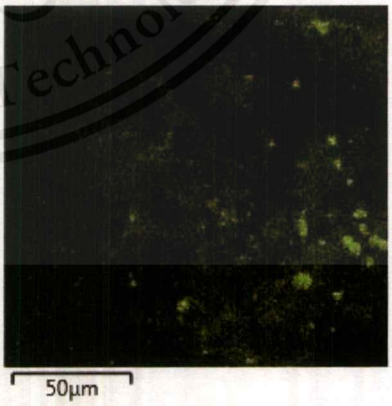


O Kα1

Ni Kα1



Cu Kα1



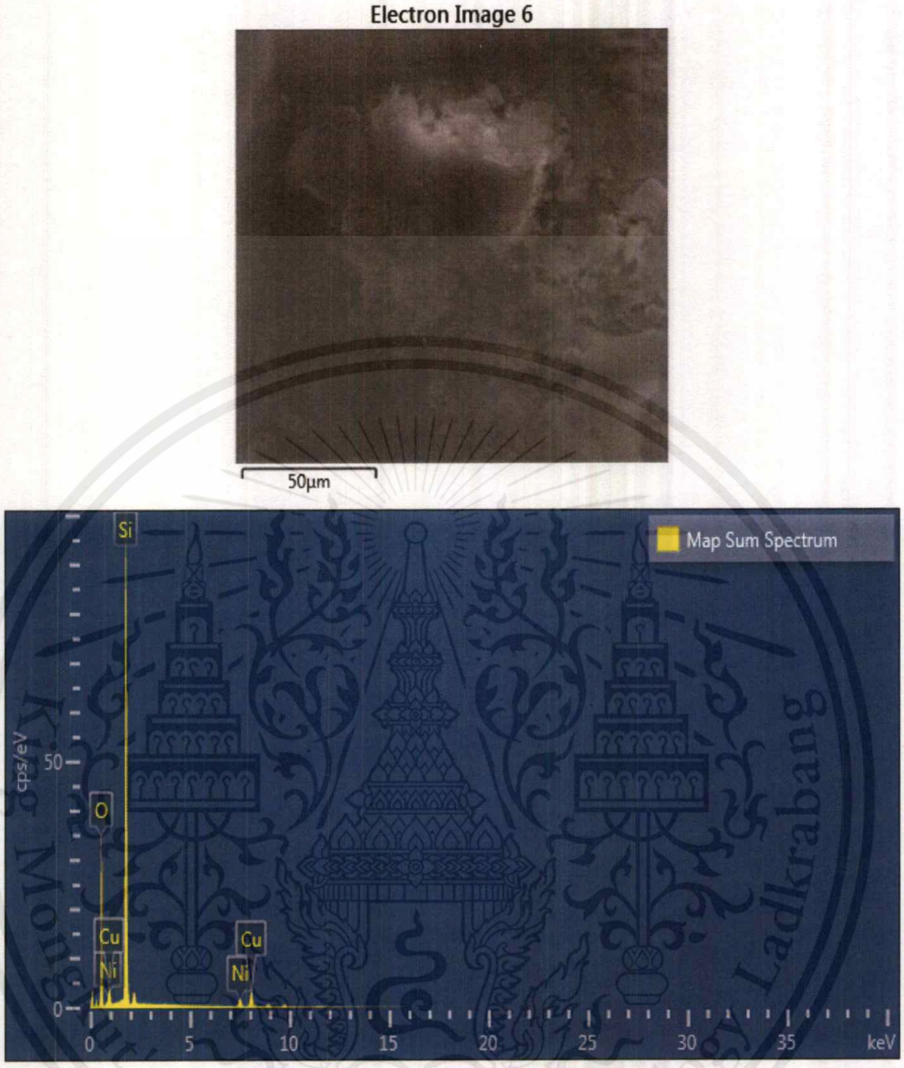


Figure B13 EDX images and map sum spectrum of 2%Ni-5%Cu/SiO_2 [SEA-IM].

Table B6 Sum spectrum of 2%Ni-5%Cu/SiO_2 [SEA-IM] catalyst

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
O				49.12		65.51	
Si	K series	77.20	0.61171	40.84	0.05	31.03	SiO_2
Ni	K series	6.26	0.06258	3.10	0.03	1.13	Ni
Cu	K series	13.34	0.13344	6.93	0.05	2.33	Cu
Total				100.00		100.00	

APPENDIX C

REACTION DATA

Table C1 The area of all product of hydrogenation of furfural[a]

Catalysts	Area					
		Product				
	Feed	Furfural	Furfuryl alcohol (FA)	Tetrahydrofurfuryl alcohol (THFA)	2-furaldehyde dimethyl acetal	Ethanone, 1-(2-furanyl)
2%Ni/SiO_2[SEA]	3073796.1	1869471.8	619991.3	81300.5	27580.4	68576.2
2%Cu/SiO_2[IM]	3268963.2	2794993.2	238677.7	0.0	274841.8	818.8
2%Ni-2%Cu/SiO_2[SEA-IM]	3193309.2	1386280.1	879932.7	111138.0	834682.7	46300.4
2%Ni-5%Cu/SiO_2[SEA-IM]	3147044.4	1279769.1	1331716.8	72664.4	523074.8	17024.6

[a] Reaction conditions: Catalyst 0.2 g, 200 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

Table C2 The area of all product of hydrogenation of furfural[b]

Catalysts	Area					
	Feed	Product				
		Furfural	Furfuryl alcohol (FA)	Tetrahydrofurfuryl alcohol (THFA)	2-furaldehyde dimethyl acetal	Ethanone, 1-(2-furanyl)
2%Ni/SiO_2[SEA]	1054925.6	0.0	232573.3	407358.4	20674.4	0.0
2%Cu/SiO_2[IM]	860142.4	286362.9	332094.6	0.0	17714.3	1930.6
2%Ni-2%Cu/SiO_2[SEA-IM]	1067195.3	156449.8	328731.6	110359.2	51832.5	14664.4
2%Ni-5%Cu/SiO_2[SEA-IM]	865141.0	53449.1	386609.5	146089.3	65711.9	9488.7

[b] Reaction conditions: Catalyst 0.2 g, 50 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

Calculation of furfural conversion, furfuryl alcohol selectivity and reaction yield

Calculation of conversion

Conversion can be calculated from the following equation:

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

For example;

FF Conversion (%) of 2%Ni-5%Cu/SiO_2 [SEA-IM]

$$\text{FF Conversion (\%)} = \frac{(865141.0/31502.6) - (53449.1/34394.8)}{(865141.0/31502.6)} \times 100 = 94.34\ \%$$

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 2%Ni-5%Cu/SiO_2 [SEA-IM]

$$\text{\% Yield of FA} = \frac{(386609.5/34394.8)}{(865141.0/31502.6)} \times 1.23 \times 100 = 50.34\ \%$$

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 2%Ni-5%Cu/SiO_2 [SEA-IM]

$$\text{\% Selectivity of FA} = \frac{386609.5}{(386609.5+146089.3+65711.9+9488.7)} \times 100 = 63.60\ \%$$

Table C3 Catalytic performance of catalysts for yield hydrogenation of furfural to furfuryl alcohol.[a]

Catalyst	Yield (%)			
	FA[b]	THFA[c]	Acetal[d]	Ethanone, 1-(2-furanyl)
2.0%Ni/SiO_2 [SEA]	27.72	1.98	1.25	2.49
2.0%Cu/SiO_2 [IM]	9.05	0.00	10.60	0.03
2.0%Ni-2.0%Cu/SiO_2[SEA-IM]	33.05	2.27	31.86	1.41
2.0%Ni-5.0%Cu/SiO_2[SEA-IM]	47.67	1.42	19.03	0.50

Table C4 Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol.[a]

Catalyst	Conversion (%)	Selectivity (%)			
		FA[b]	THFA[c]	Acetal[d]	Ethanone, 1-(2-furanyl)
2.0%Ni/SiO_2 [SEA]	32.04	77.75	10.20	3.46	8.60
2.0%Cu/SiO_2 {IM]	13.80	46.40	0.00	53.44	0.16
2.0%Ni-2.0%Cu/SiO_2[SEA-IM]	57.67	47.00	5.94	44.59	2.47
2.0%Ni-5.0%Cu/SiO_2[SEA-IM]	62.75	68.49	3.74	26.90	0.88

[a] Reaction conditions: Catalyst 0.2 g, 200 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

[b] FA: furfuryl alcohol

[c] THFA: tetrahydrofurfuryl alcohol

[d] Acetal: 2-furaldehyde dimethyl acetal

Table C5 Catalytic performance of catalysts for yield hydrogenation of furfural to furfuryl alcohol.[b]

Catalyst	Yield (%)			
	FA[b]	THFA[c]	Acetal[d]	Ethanone, 1-(2-furanyl)
2%Ni/SiO_2 [SEA]	30.30	28.91	2.74	0.00
2%Cu/SiO_2 [IM]	47.88	0.00	2.60	0.23
2%Ni-2%Cu/SiO_2[SEA-IM]	36.94	6.67	5.92	1.34
2%Ni-5%Cu/SiO_2[SEA-IM]	50.34	10.36	8.70	1.00

Table C6 Catalytic performance of catalysts for selective hydrogenation of furfural to furfuryl alcohol.[b]

Catalyst	Conversion (%)	Selectivity (%)			
		FA[b]	THFA[c]	Acetal[d]	Ethanone, 1-(2-furanyl)
2%Ni/SiO_2 [SEA]	100.00	35.21	61.66	3.13	0.00
2%Cu/SiO_2 [IM]	66.43	94.41	0.00	5.04	0.55
2%Ni-2%Cu/SiO_2[SEA-IM]	85.71	65.02	21.83	10.25	2.90
2%Ni-5%Cu/SiO_2[SEA-IM]	94.34	63.60	24.03	10.81	1.56

[b] Reaction conditions: Catalyst 0.2 g, 50 μL of furfural, 10 mL of methanol, Hydrogen pressure 20 bar, Temperature at 100 °C and Stirring speed of 900 rpm with reaction time 2 hours.

[b] FA: furfuryl alcohol

[c] THFA: tetrahydrofurfuryl alcohol

[d] Acetal: 2-furaldehyde dimethyl acetal