Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over Pt- and PtFe-incorporated mesoporous carbon

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ปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟิวรัลเป็นเฟอร์ฟิวริลแอลกอฮอล์บนตัวเร่งปฏิกิริยาแพลทินัมและแพลทินัมเหล็กในเมโซพอรัสคาร์บอน

น.ส.สุรีย์พร ศักดิ์นภาวุฒิ

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สุรีย์พร ศักดิ์นภาวุฒิ : ปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟิวรัลเป็นเฟอร์ฟิวริลแอลกอฮอล์บนตัวเร่งปฏิกิริยาแพลทินัมและแพลทินัมเหล็กในเมโซพอรัสคาร์บอน. (Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over Pt- and PtFe-incorporated mesoporous carbon) อ.ที่ปรึกษาหลัก : ศ. ดร.จูงใจ ปั้นประณต, อ.ที่ปรึกษาร่วม : ผศ. ดร.แหลมทอง ชื่นชม

งานวิจัยนี้มุ่งเน้นการศึกษาปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดในวัฏภาคของเหลวของเฟอร์ฟิวรัลเป็นเฟอร์ฟิวริลแอลกอฮอล์ดำเนินการที่อุณหภูมิ 50 องศาเซลเซียส ความดันไฮโดรเจน 20 บาร์ โดยใช้น้ำและเมทานอลเป็นตัวทำละลาย งานวิจัยได้แบ่งออกเป็น 2 ส่วน ส่วนแรกศึกษาลักษณะเฉพาะและสมบัติของตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับเมโซพอรัสคาร์บอน ที่เตรียมด้วยวิธีการจัดเรียงตัวเองโดยการใช้แม่พิมพ์ทางเคมีแบบซอฟท์ในขั้นตอนเดียวเปรียบเทียบกับแพลทินัมที่เตรียมด้วยวิธีเคลือบฝังบนตัวรองรับเมโซพอรัสคาร์บอน, ถ่านกัมมันต์ และเมโซ/มาโครพอรัสคาร์บอนที่ไม่เป็นระเบียบ พบว่า ตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับออเดอร์เมโซพอรัสคาร์บอน มีขนาดอนุภาคของแพลทินัม (~4 นาโนเมตร) ซึ่งใหญ่กว่าบนตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีเคลือบฝังทั้งหมดที่มีขนาดอนุภาคของแพลทินัมอยู่ระหว่าง 0.5 -2 นาโนเมตร รวมถึงแสดงค่าการเปลี่ยนของเฟอร์ฟิวรัลและการเลือกเกิดเป็นเฟอร์ฟิวริลแอลกอฮอล์สูงสุด ในงานวิจัยส่วนที่สองทำการศึกษาการเติมธาตุเฟอร์โรแมกเนติก (เหล็ก, โคบอลต์, นิกเกิล และ นีโอดิเมียม) ในตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับถ่านกัมมันต์ ในปฏิกิริยานี้ พบว่าการเติม 0.15 เปอร์เซ็นต์โดยน้ำหนักของเหล็กบนตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับถ่านกัมมันต์แสดงค่าการเปลี่ยนของเฟอร์ฟิวรัลได้อย่างสมบูรณ์และการเลือกเกิดเป็นเฟอร์ฟิวริลแอลกอฮอล์ 74 เปอร์เซ็นต์ หลังจากการทำปฏิกิริยาในน้ำเป็นเวลา 1 ชั่วโมง ซึ่งประสิทธิภาพที่ดีของตัวเร่งปฏิกิริยาสอดคล้องกับการกระจายตัวสูงของแพลทินัม, การแสดงตำแหน่งแพลทินัมโลว์โคออดิเนชั่น และความแข็งแรงของอันตรกิริยาระหว่างแพลทินัมและเหล็ก อย่างไรก็ตาม ปริมาณน้อยสุดของเหล็กที่เติมในตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับถ่านกัมมันต์ที่สามารถทำให้แยกตัวเร่งปฏิกิริยาด้วยแท่งแม่เหล็กได้คือ 0.5 เปอร์เซ็นต์โดยน้ำหนัก โดยตัวเร่งปฏิกิริยายังคงแสดงคุณสมบัติที่ดีทางแม่เหล็กหลังจากใช้งานไปแล้ว 3 รอบ

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Sureeporn Saknaphawuth : Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over Pt- and PtFe-incorporated mesoporous carbon. Advisor: Prof. JOONGJAI PANPRANOT, Ph.D. Co-advisor: Asst. Prof. Laemthong Cheunchom, Ph.D.

This research aims to investigate the liquid-phase selective hydrogenation of furfural to furfuryl alcohol in a batch reactor at 50°C, 20 bar H_2 using water and methanol as the solvent. This study has been divided into two sections. The characteristics and catalytic properties of OMC-supported Pt catalysts (Pt/OMC-one-pot) prepared by one-step modified soft-template self-assembly method were compared with the Pt impregnated on OMC, activated carbon (AC), and non-uniform meso/macroporous carbon (MC) in the first section. Larger Pt particle size (~4 nm) was obtained on the Pt/OMC-one-pot comparing to all the impregnated ones, in which the Pt particle sizes were in the range 0.5 – 2 nm. The Pt/OMC-one-pot exhibited the highest furfural conversion and FA selectivity under aqueous conditions. In the second section, ferromagnetic element (x = Fe, Co, Ni, and Nd) promoted Pt/AC catalysts were investigated in this rection. The 0.15FePt/AC exhibited complete conversion of furfural with FA selectivity 74% after only 1 h reaction time in water. The superior catalyst performances were correlated with the higher Pt dispersion, the presence of low coordination Pt sites and the strong Pt-Fe interaction However, to simply use a magnet for catalyst separation, 0.5 wt% Fe was the minimum Fe loading on the Pt/AC. The 0.5FePt/AC still exhibited good magnetic properties after the 3rd consecutive runs.

Field of Study: Chemical Engineering Student's Signature ....
Academic Year: 2021 Advisor's Signature ....
Co-advisor's Signature ....

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Because of the limited amount of fossil resources and environmental problems concerned with their usage, the alternative energy resources have been extensively explored. Biomass as a promising renewable resource has attracted more and more attention to replace or supplement the fossil fuels for sustainable development. Furfural is the most important biomass-derived chemical that use in the chemical industry [1-4], it can be converted into many downstream and derivative products [4]. Hydrogenation of furfural using heterogeneous catalyst has been widely studies, furfuryl alcohol (FA) is the most common hydrogenation product of furfural, approximately 62% of furfural currently produced is transformed into FA [2]. FA is widely used in the fine chemical industry of drug intermediates, lubricants, adhesive, and dispersing agents and in the polymer industry of furan resin, furfural resin, and phenolic resin [5-7].

Furfural consists of two powerful and functional groups, an aldehyde (C=O) and a conjugated system (C=C-C=C) [1]. To produce FA, the aldehyde group (C=O) of furfural can be hydrogenated and then transformed to FA. The catalytic hydrogenation of FFA to FA is usually performed in the gas or liquid phase [8-11]. Compared with gas-phase hydrogenation process, hydrogenation of furfural in the liquid phase has the advantages of high selectivity and low energy consumption [5, 12]. In the present industrial processes of furfural production, copper chromite (Cu–Cr) are used as catalysts for both the liquid-phase and gas-phase hydrogenations [13-15], operating at high temperature (between 130 and 200°C) and high pressure (up to 30 bar) [16]. Although copper chromite exhibits good activity and selectivity toward FA, Cr is very toxic and carcinogenic and can cause serious pollution of environment [5, 12, 16]. Thus, the development of Cr-free catalysts has been investigated for the FA production from furfural hydrogenation. A variety of Cr-free catalysts have been studied, including Pt [16-21], Pd [22-26], Ru [24], Co [27], Cu [28-31] and Ni [32, 33]. Among these catalysts, Platinum (Pt) is the precious catalysts which have good catalytic performance for the selective hydrogenation of furfural to FA [16, 19, 20]. Moreover, Pt-based catalysts have also been employed in the furfural hydrogenation reaction under mild conditions [16].

Order mesoporous carbon (OMC) is interested to use in many areas, such as catalyst support, electrode material and adsorbents for gas separation because of high surface areas, large pore volumes, tunable pore sizes, and good gas penetrability [34]. In order to prepare mesoporous carbon, either activation processes [34-36] or hard templating nanocasting [37] are mainly used but they inherit severe drawbacks in industrial applications due to the use of toxic activating agents (for example KOH) in the activation processes or HF (to remove the hard template) in the nanocasting. To avoid the toxic chemicals employed, the soft - templates are very attractive and the strategy of this process is the direct use of the self-assembly of the surfactant/amphiphile block co-polymers as templates with low-cost and simply decomposable soft templates to form organic-organic composites, and mesoporous carbons are obtained after subsequent carbonization (pyrolysis) [38].

In liquid phase reaction, carbon powders are extremely difficult to separate from solution and typically require complex and expensive steps such as filtration or centrifugation. The magnetic properties of catalysts make catalyst separation easy by using a simple external magnet. Additional of a second metal have including Co, Ni, Fe has also resulted in significant improvement of Pt-based catalysts for FA production. Although the improvement of Pt catalysts promoted by ferromagnetic element such as Fe and Ni as promoter for Pt catalysts in the hydrogenation of furfural to FA has been demonstrated, the comparison of the catalytic performances among them as well as their magnetic properties have been reported to a less extent, especially under different solvents.

In this work, the liquid phase hydrogenation of furfural has been investigated using 0.5%wt Pt supported on ordered mesoporous carbon (OMC) which is prepared via the soft-templating method. The Pt/OMC one-pot synthesis catalyst was then compared with the catalysts which were prepared by wet impregnation method using different carbon material types. Furthermore, the effect of various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts will be also studied in this reaction.

1.2 Objective

1.2.1 To investigate the characteristics and catalytic properties of Pt/OMC catalyst prepared by one-step of modified soft-template self-assembly method in comparison to impregnation method in the selective hydrogenation of furfural to furfuryl alcohol.

1.2.2 To study the effect of various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts for the liquid phase hydrogenation of furfural to furfuryl alcohol.

1.3 Research scope

1.3.1 Preparation of Pt/Carbon catalysts by one-step of modified soft-template self-assembly and impregnation method with Pt content 0.5 wt% support, the different carbon materials including activated carbon (AC), non-uniform meso/macroporous (MC), and ordered mesoporous carbon (OMC), which were prepared by impregnation method, were used to compare the catalytic performance.

1.3.2 Preparation of various ferromagnetic elements promoted Pt/activated carbon catalysts, bimetallic catalysts, FePt/AC (0.5 wt%Pt and 0.1-10 wt%Fe), and 0.15MPt/AC (0.5 wt%Pt and 0.15wt%M: Ni and Co) by co-impregnation method.

1.3.3 The catalysts which were prepared by impregnation method were calcined at 36350°C under N_2 flow for 4 h and reduced at 400°C for 2h. under H_2 flow (25 cm^3/min).

1.3.4 The catalysts which were prepared by one-step of modified soft-template self-assembly method were calcined at 800°C under N_2 flow for 3 h.

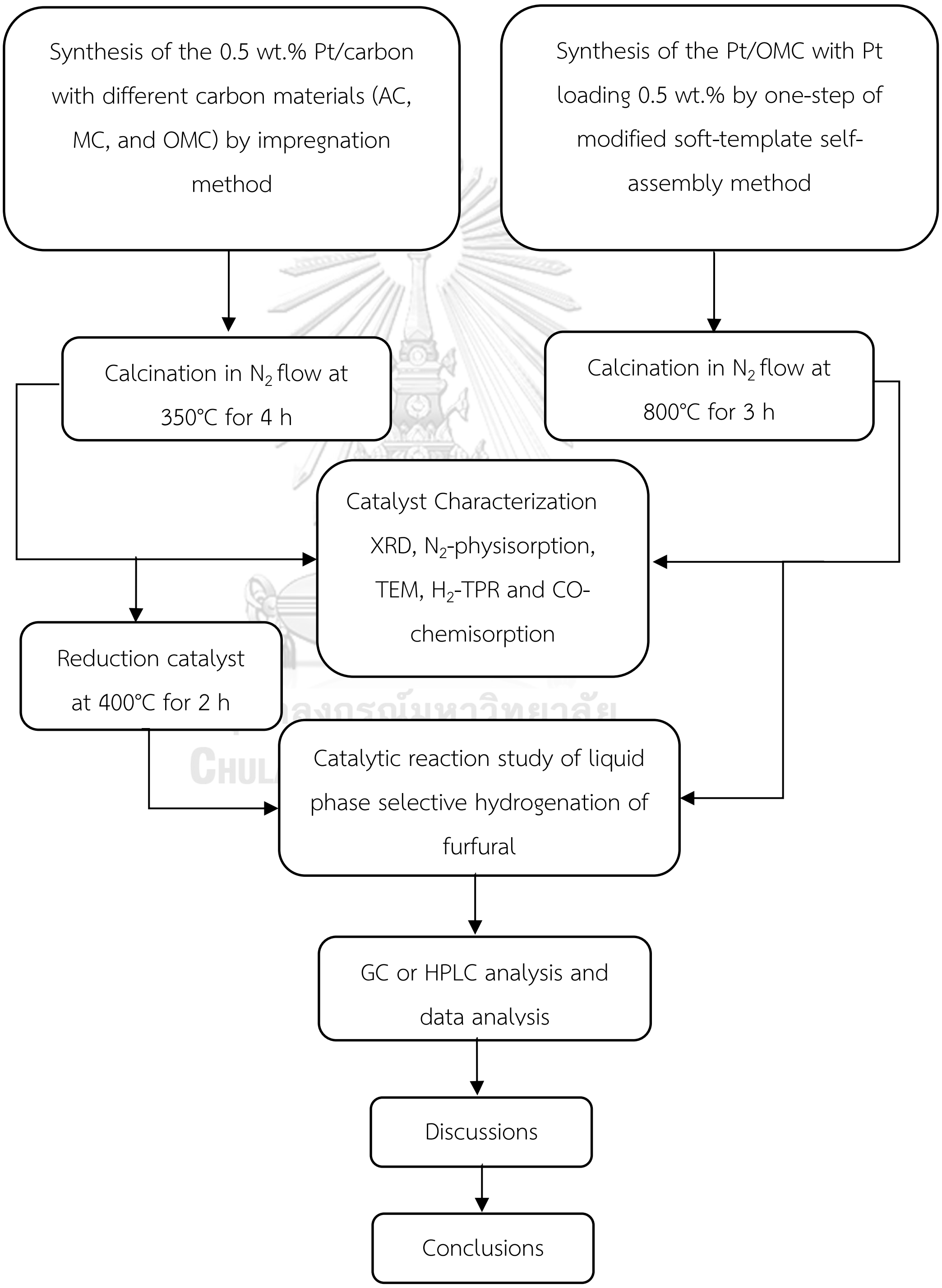
1.3.5 The bimetallic catalysts which were prepared by co-impregnation method were calcined at 500°C under N_2 flow for 2 h and reduced at 500°C for 2h. under H_2 flow (25 cm^3/min).

1.3.5 The catalysts were tested in the hydrogenation of furfural in a batch reactor at constant temperature 50°C and pressure 20 bars of hydrogen for 2 h in methanol or 1 h in water as a solvent.

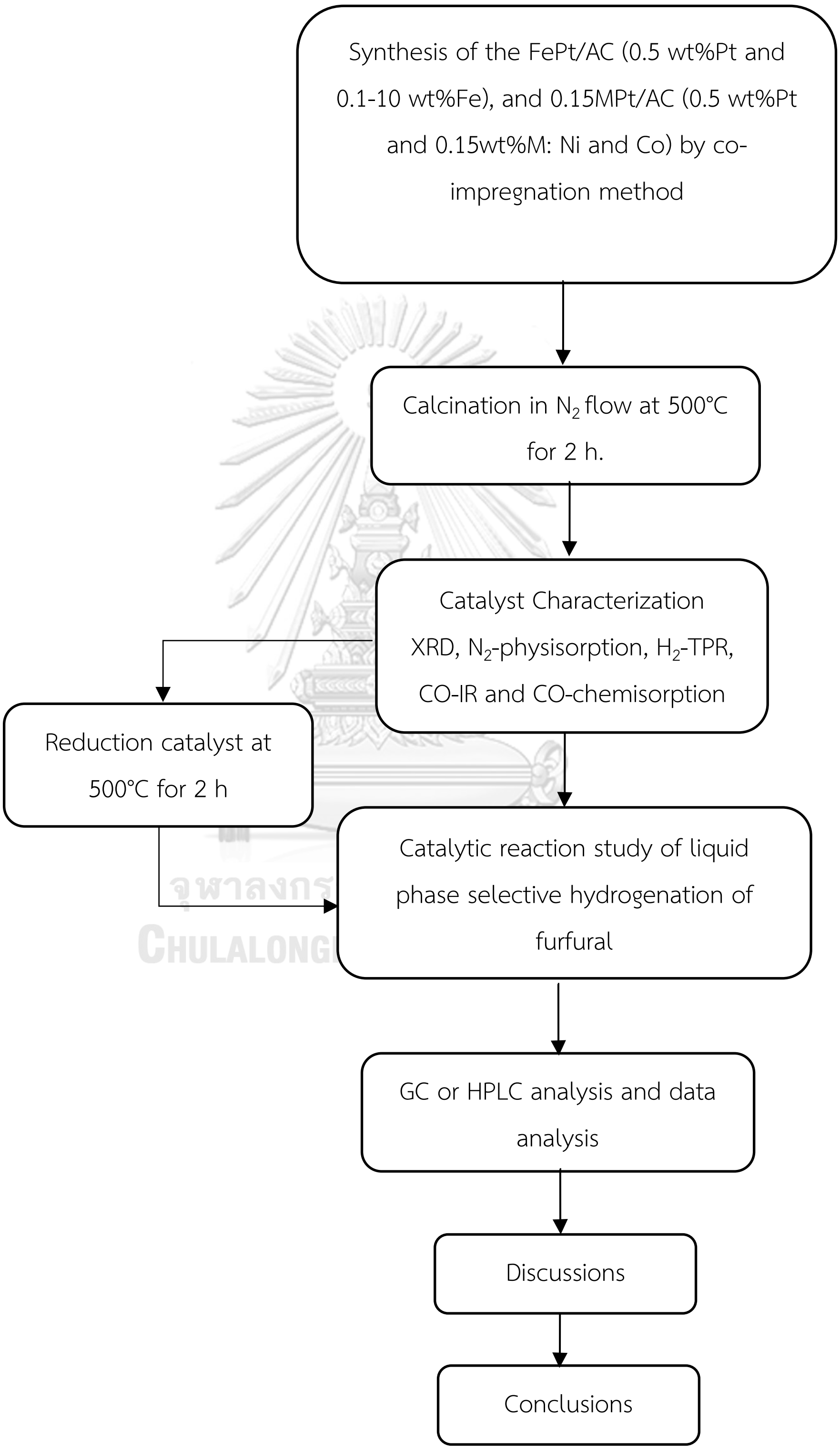
1.3.6 Characterization of the prepared catalysts by various method including X-ray diffraction (XRD), CO pulse chemisorption, Infrared spectroscopy of adsorbed CO (CO-IR), H_2-temperature programmed reduction (H_2-TRR), and Transmission electron spectroscopy (TEM).

1.4 Research methodology

Part I investigation the characteristics and catalytic properties of Pt/OMC catalyst prepared by one-step of modified soft-template self-assembly method in comparison to impregnation method in the selective hydrogenation of furfural to furfuryl alcohol



Part II study the effect various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts for the liquid phase hydrogenation of furfural to furfuryl alcohol.



1.5 Research Plan

Table 1. 1 The research plan

Research Plan	2017 (Semester)		2018 (Semester)		2019 (Semester)		2020 (Semester)		2021 (Semester)	
	1	2	3	4	5	6	7	8	9	10
1.Literature Review	■	■	■	■	■	■	■	■	■	■
2.Preparation of the catalysts part I			■	■						
- Characterization of catalysts				■	■					
- Reaction test for all catalysts				■	■	■				
3.Preparation of the catalysts part II						■	■			
- Characterization of catalysts							■	■		
- Reaction test for all catalysts							■	■	■	
4.Result and Discussion				■	■	■	■	■	■	■

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogenation Reactions

Hydrogenation is chemical reaction between molecular hydrogen (H_2) and other atoms for converting one functional group into another. The process is commonly used to reduce or saturate organic compounds. Hydrogenation generally constitutes the addition of pairs of hydrogen atoms to a molecule [39]. The application of hydrogenation reaction is useful in pharmaceuticals, agrochemicals, food industry, and petrochemical industry.

Hydrogenation reactions are normally performed using both homogeneous, and heterogenous catalysts. There is no limitation on the phase to be considered but most of the processes using homogeneous catalysts operates in a liquid phase. For heterogenous catalysts, the reaction occurs either in the liquid or gas phase because the catalyst is usually in a solid form. Compared with the homogeneous catalysts, the heterogeneous catalysts have some advantage for the separation processes. The homogeneous catalysts are in the same phase as the reactants, thus the separation of these catalysts from products is difficult and complex systems such as ion-exchange, liquid-liquid extraction and distillation, whereas the heterogeneous catalysts are in different phases from the reactants, so the separation processes are cheap and simple such as filtration, furthermore, the homogeneous catalysts show good thermal stability [40].

2.2 Properties of Platinum

The chemical element platinum, symbol Pt, is classed as a transition metal. It is an atomic number of 78 and a member of group 10 of the periodic table of the elements. Platinum is a lustrous silvery-white, malleable, ductile, precious, highly unreactive metal. There is six naturally occurring isotopes: the most abundant are platinum-194, which accounts for 33%, platinum-195 (34%) and platinum-196 (25%). The others are platinum-198 (7%), platinum-192 (1%) and platinum-190 (0.01%) [41]. Platinum is widely used in many industries such as catalytic converters, automotive, electronic, chemical, jewelry, dental, and glass industries [42].

Platinum metal catalysts are widely used in both supported and nonsupported form in hydrogenation reaction. The use of supported catalyst is recommended to obtain maximum efficiency of the metal because support catalyst exhibits a higher activity than nonsuppoted. Furthermore, supported catalysts usually present a greater resistance to poisoning [43].

Table 2. 1 Physical properties of Platinum [44].

Physical properties	
Atomic number	78
Atomic weight	195.084
Element category	Transition metal
Electron configuration	$[Xe]4f^{14}5d^{9}6s^{1}$
Melting point	2041.4 K (1768.3°C, 3214.9°F)
Boiling point	4098 K (3825°C, 6917°F)
Density	21.45 g/cm^3
Structure	Face-centered cubic (fcc)
Color	Silvery-white

2.3 Porous carbon as a catalyst support

Porous carbon materials are widely used in many applications such as adsorption, gas storage, separation, catalysis and electrochemistry due to its high specific surface and large pore volume in combination with good chemical and mechanical stability. According to the International Union of Pure and Applied Chemistry (IUPAC), the porous materials can be classified into 3 types; 1. microporous with diameter below 2 nm, 2. mesoporous with diameter in range of 2-50 nm, and 3. macroporous with diameter more than 50 nm [45]. Activated carbon is the most commonly applied material because of its low cost and the possibility of large-scale processing. However, characteristic of activated carbon is not only a locally in homogeneous structure, but also a wide distribution of pore size. Moreover, activated carbon have the abundant presence of micropores (size < 2 nm) effect to mass transfer limitation and pore accessibility in application such as adsorption, chromatography and Li-batteries. Thus, material possessing controllable pore dimensions in the size range of mesopores are desired to improve diffusion of larger molecules into the internal surface [38]. The high surface area of porous carbon materials is synthesized various methods. The use of carbonization of various precursors by using different materials as templates is concerned with the resultant carbons, morphology and pore structure. Firstly, the templates are proposed to control the morphology of carbon materials and then used to prepare nanoporous carbons with controlled size, volume and alignment of the pores. The carbonization using templates is divided in 2 groups related to morphology and pore structure control as in **Table 2.2** [46].

Table 2. 2 Template-assisted carbonization [46].

	Template	Resultant carbon
Morphology control	Inorganic layered compounds (clays)	Lamellar morphology
	Anodic aluminum oxide (AAO) films	Tubular morphology
	Organic foams (polyurethane foams)	Foamy morphology
Pore structure control	Hard - template	
	- Zeolites	Microporous, ordered
	- Mesoporous silicas	Mesoporous, ordered
	- MgO	Mesoporous
	Soft - template	
	- Soft - template Block copolymer surfactants	Mesoporous, ordered
	- Metal-organic frameworks (MOFs)	Micro- and mesoporous

In order to prepare mesoporous carbon, both hard and soft - templates is interesting but hard - templates, inorganic template, inherits severe drawbacks in industrial applications due to the necessity of removing it with hazardous chemicals such as HF or NaOH. Thus, to avoid the chemicals employed for the removal of hard - templates, soft - templates are attractive [38].

2.4 Soft template synthesis

Soft-template synthesis is a simple and useful alternative to fabricate a mesoporous material. Mesoporous carbons with ordered mesoporosity and narrow pore size distribution were successfully prepared by using some block copolymer surfactants as organic templates, such as poly(ethylene oxide)- block-poly(-propylene oxide)-block-poly(ethylene oxide) (PEO106-PPO70-PEO106) (Pluronic F127), PEO20-PPO70-PEO20 (Pluronic P123), polystylene-block-poly(4-vinylpridine) (PSeP4VP), etc. The strategy of this process was the direct use of the self-assembly of the surfactant/amphiphile block co-polymers as templates. Typical synthesis procedures involve with 3 components; 1. the mixing of a solvent (such as ethanol, water, THF, or mixtures of them), 2. carbon precursor (e.g. a resin of low molecular weight containing OH groups), and 3. template (e.g. tri-block-copolymers of the type PEO-b-PPO-b-PEO). An ordered mesophase is produced from this mixture. Then, the mesophase is stabilized via thermal or catalytic cross-linking and finally, the template is removed, e.g. by thermal treatment [51].

Bernsmeier et al. [47] studied the binder-free Pd/OMC films as catalyst which was synthesized by soft-template technique with Pluronic F127 as template or structure-directing agent, and resorcinol as carbon precursor. This catalyst contained small Pd particles well distributed in a mesoporous carbon matrix with high surface area, chemical, mechanical, and thermal stability, and electrical conductivity. The binder-free Pd/OMC films was highly active in both the gas-phase hydrogenation of butadiene and the electrocatalytic hydrogen evolution reaction.

2.5 Magnetic mesoporous carbon

Mesoporous carbon is appropriate for the several applications. However, in liquid phase reaction, carbon powders are extremely difficult to separate from solution. Normally, a filtration or centrifugation procedure, which is very complex, is used for separation. At present, magnetic separation as a promising strategy has been paid more and more attention because it can be easily separated under an applied magnetic field. This soft-template strategy is no multi-step procedure and allows for the easy in-situ incorporation of active metal catalyst species or other hetero-atoms [34-36]. The presence of Fe particles into the soft-template mesoporous carbon catalyst by the simple addition of Fe^{3+} and in-situ reduction of Fe^{3+} into magnetic Fe species render the catalyst an easy magnetic-separable property [48].

Tian et al. [49] presented a simple and novel route to synthesize magnetic Fe-containing ordered mesoporous carbons (Fe/OMCs) by a soft-template method. Phenolic resin was used as a carbon precursor, triblock copolymer F127 as a template agent, TEOS as a silica precursor and hydrated iron nitrate as an iron source. The result showed the iron nanoparticles were uniformly distributed in the OMCs. The specific surface area and the total pore volumes increased with the increase of carbonization temperature from 600 to 850 ^{o}C and with the increase of TEOS loading.

Putro et al. [50] studied the hydrogenation of furfural to FA over Ni-Fe alloy catalysts which prepared by environmentally friendly method. The results exhibited high selectivity in the hydrogenation of furfural to give 95% yield of FA under 1 MPa of H2 at 423 K within 3 h. The reusability test was conducted under the same reaction condition. The catalyst was recycled up to 4 times with no significant loss of catalytic activity indicated that a high stability of the catalysts on furfural hydrogenation.

2.6 Hydrogenation of furfural to furfuryl alcohol

Furfural is an important organic chemical with the formula C_4H_3OCHO. It is produced from agriculture products containing pentose in the structure such as sugar cane bagasse, corncobs, and rice straw. Furfural is also the precursor for may furan-based chemical and solvents, the conversion of furfural to value-added chemical and biofuels is exhibited in Figure 1. Among these letters, approximately 62% of furfural is converted to furfuryl alcohol (FA) [2]. FA is a chemical intermediate wildly used in polymer industry of furan resin and in fine chemical industry of lubricants, drug intermediates, adhesives as Figure 2 [5-7]. The hydrogenation of furfural to FA is performed either in the gas phase or in the liquid phase. Compared with gas-phase hydrogenation process, hydrogenation of furfural in the liquid phase has the advantages of high selectivity and low energy consumption [12, 19]. Furfural consists of two functional groups, which are C=C and C=O. To produce FA, furfural is hydrogenated at C=O and transform to FA. However, the solvent usually has an impact on the catalytic activity in a liquid-phase reaction [19] and the side reaction, which is the reaction between alcohol and furfural, product may be observed when alcohols were used as solvent. This reaction is the acetalization of furfural. For example, when methanol is used as a solvent, 2-furaldehyde dimethyl acetal is observed and called solvent product (SP) as Figure 3.

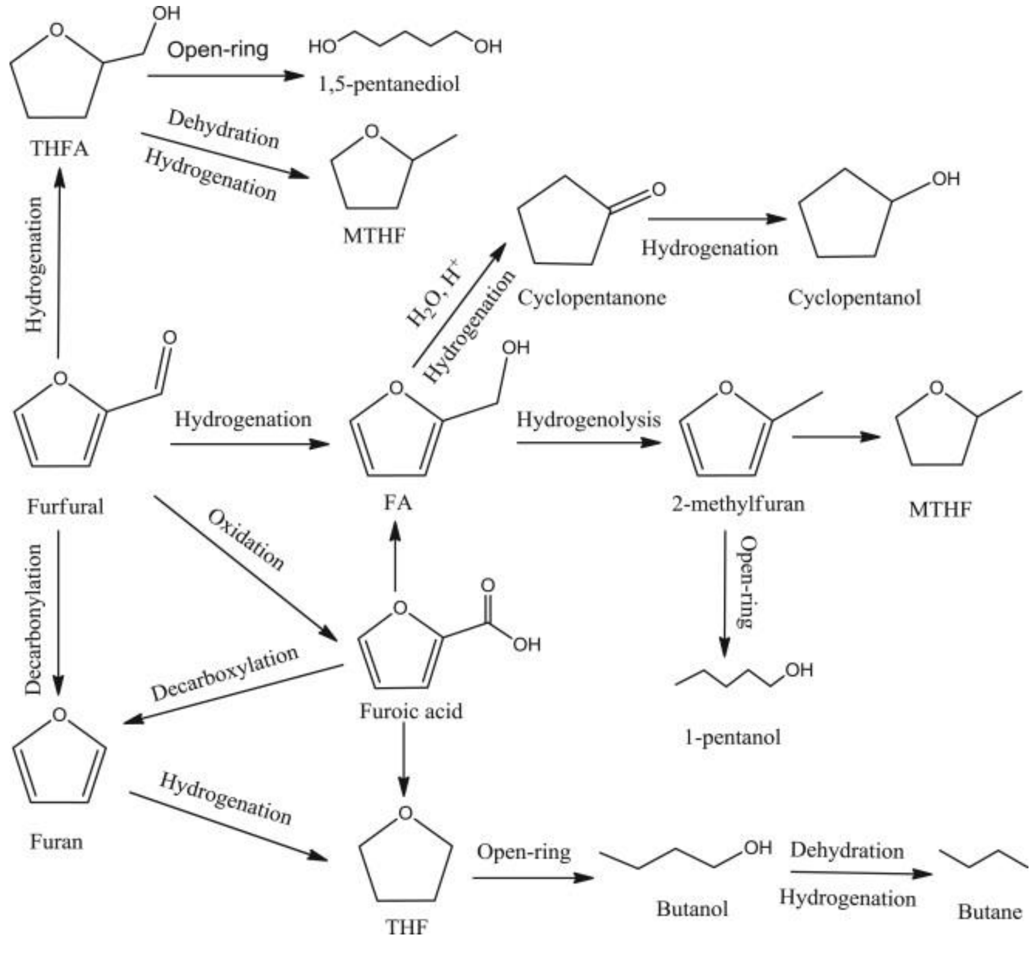


Figure 2. 1 Conversion of furfural to various value-added chemicals and biofuels [1].

Resins

Drug intermediates

Lubricant oil

Figure 2. 2 The applications of furfural alcohol.

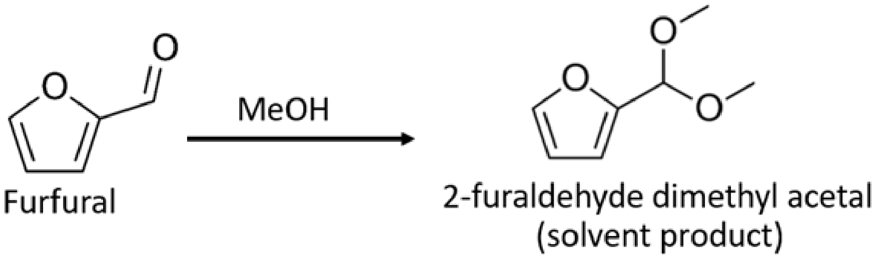


Figure 2. 3 The side reaction product from using methanol as a solvent [51].

Table 2. 3 Summary of the research of hydrogenation of furfural on various catalysts under different reaction condition.

Researcher	Studies	Catalyst and preparation method	Reaction condition	Results
Lee et al. [26]	Studied Pd/C catalysts with various carbons to investigate the supporting effects of carbon in Pd-catalyzed furfural hydrogenation	- Pd/CMK-3, Pd/CMK-5, Pd/CMK-8, and Pd/MSU-F-C. - Prepared by the chemical reduction method - Carbon supports synthesized by nanocasting method.	- No reduction was required - Operated at 180 °C,5 h, and H_2 pressure 2 MPa. - Used 2-propanol and water as solvent.	-Pd/CMK-5 provided the highest conversion of furfural in both 2-propanol (100%) and water (86.4%) solvents, with selectivities of 20.3 (FA), 31.5 (THFA), 13.4 (MF), and 16.3% (CPL) for 2-propanol as solvent.
Salnikova et al. [52]	studied the catalytic tests of palladium catalysts on different supports types ; aluminium oxide (Al_2O_3), hypercrosslinked polystyrene (HPS), and magnetite/hypercrosslinked polystyrene	- 3% Pd/Al_2O_3, 3% Pd/HPS, and 3%Pd/Fe_3O_4/HPS - Prepared by impregnation method	- Operated at 120 °C, 2 h, and H_2 pressure 6 MPa. - Used propanol-2 as solvent.	-3%Pd/Fe_3O_4/HPS was the most effective catalyst which had the > 95%conversion of furfural and > 94 %selectivity for furfuryl alcohol and easy separation from the reaction mixture

	(Fe_3O_4/HPS) in of furfural hydrogenation.			by magnet.
Xu et al. [53]	Studied the catalyst activity of mesoporous N-doped carbon encapsulated Co catalysts (Co-N-C) in hydrogenation of furfural to FA.	- Co-N-C-600, Co-N-C-700, Co-N-C-800, and Co-N-C-900. - Synthesized through a facile carbonization.	- Operated at 150 °C, 6 h, and N_2 pressure 0.5 MPa. - Used 1,4-dioxane as solvent.	- Co-N-C-700 was highly efficient for achieving 100% furfural conversion and>99% FA selectivity.
Taylor et al. [16]	Investigated the selective hydrogenation of furfural to FA mild over Pt nanoparticles supported on SiO_2, ZnO, γ-Al_2O_3, CeO_2 and MgO and different types of solvents	- Pt/ SiO_2, Pt/ZnO, Pt/γ-Al_2O_3, and Pt/CeO_2. - prepared by adapting the method of Jones et al.	- Reduced at 200 °C in flowing 10% H_2/N_2 for 1 h. - Operated at 50 °C, 7 h, and H_2 pressure 0.1 MPa. - Used methanol, ethanol, n-butanol, totuene and hexane as solvent.	- Pt/γ-Al_2O_3 catalyst exhibited the highest catalytic performances in methanol with 80% conversion of furfural and 99% selectivity of FA. - Methanol and n-butanol promoted FA yield, while Hexene (non-polar) conferred poor furfural conversion.
Bhogeswararao et al. [54]	Studied the effect of γ–Al_2O_3 supported Pt and Pd catalysts in the	- 5%Pt/ γ–Al_2O_3 and 5%Pd/ γ–Al_2O_3 - Prepared by wet	- Reduced at in a flow of H_2 for 2.5 h at 250	- At 25 °C, the Pt/γ–Al_2O_3 were selective for hydrogenation of

	selective liquid phase hydrogenation of furfural to furfuryl alcohol	impregnation method.	and 350°C for Pd/Al_2O_3 and Pt/Al_2O_3, respectively. - Operated at 25, 180, 210, and 240°C for 5 h and H_2 pressure 2 MPa. - Used iso-propanol as solvent.	C=O group, producing furfuryl alcohol FA but the Pd/γ–Al_2O_3 catalysts hydrogenated both ring and C=O groups, producting FA and (THFL). - At ≥ 180 °C, the Pd/γ–Al_2O_3 enabled decarbonylation of furfural giving furan in 82% yield.
Zhang et al. [48]	Investigated the effect of bimetallic overlayer catalysts (Ni@Pt/SiO_2 and Cu@Pt/SiO_2) and compared with monometallic catalysts (Ni/SiO_2, Cu/SiO_2, Pt/SiO_2) for furfural hydrogenation.	- Ni/SiO_2, Cu/SiO_2, Pt/SiO_2, Ni-Pt/SiO_2, and Cu-Pt/SiO_2 were prepared by incipient wetness impregnation. - Ni@Pt/SiO_2 and Cu@Pt/SiO_2 were synthesized using directed deposition technique.	- Reduced at 400°C for 2h. - Operated at 250 °C, 1.5 h, and H2 pressure 0.69 MPa. - Used 2-propanol as solvent.	- Ni@Pt/SiO_2 and Cu@Pt/SiO_2 catalysts exhibited higher reactivity in furfural conversion compared to their parent metals. - Cu@Pt/SiO_2 overlayer catalyst showed high FA selectivity.
Musci et al. [55]	Studied the catalytic aqueous phase hydrogenation	- Ru/C was prepared by impregnation method.	-Reduced at 300°C for 2h - Operated at	- Ru/C showed low a low selectivity to FA with only 47%

	of furfural, employing Ru-based catalysts supported on activated carbon and the effect of the addition of Sn as a promoter of conversion and selectivity.	- $RuSn_{0.4}/C$ and $RuSn_{0.8}/C$ were synthesized using a methodology derived from SOMC/M techniques.	90 °C, 5 h, and H_2 pressure 1.25 MPa. - Used water as solvent.	- $RuSn_{0.4}/C$ (Sn/Ru ratio = 0.4) catalyst showed the highest catalytic performance at 91% conversion of furfural and 90% selectivity of FA.
Merlo et al. [17]	Studied the effect of tin content on the activity, selectivity and stability of Pt/SiO_2 catalysts modified with $SnBu_4$ in the liquid-phase hydrogenation of furfural to furfuryl alcohol.	-Pt/SiO_2 was prepared by ion exchange. - $PtSn/SiO_2$ catalysts, with various Sn/Pt atomic ratio were prepared by controlled surface reactions techniques.	- Operated at 100 °C, 8 h, and H2 pressure 1 MPa. - Used 2-propanol as solvent.	- Sn/Pt with atomic ratio (0.3) provided the highest reaction rate (2.3 $mmolgPt^{-1}s^{-1}$) and FA selectivity of 96.18 %.

Lee et al. [26] studied Pd/C catalysts with various carbons to investigate the supporting effects of carbon in Pd-catalyzed furfural hydrogenation. Various order mesoporous carbons (OMCs) with different pore sizes and structures, including CMK-3, CMK-5, CMK-8, MSU-F-C (MSU; Michigan State University), multiwalled carbon nanotube (CNTs) and a commercial carbon (Vulcan XC) were used as the supports. OMCs are synthesized by the nanocasting method and Pd/C catalysts with various carbon supports were prepared through the chemical reduction method by using sodium borohydride as a reducing agent. The liquid-phase hydrogenation of furfural were operated at 180 °C,5 h, and H_2 pressure 2 MPa. The results indicated that CMK-5 with the largest surface area and hexagonal hollow tubular framework was showed to be the most efficient carbon support for Pd/C catalysts,with the highest conversion of furfural in both 2-propanol (100%) and water (86.4%) solvents.The major products of the Pd/CMK-5 catalyst were FA, THFA (tetrahydrofurfuryl alcohol), MF (2-methylfuran), and CPL (cyclohexanol) , with selectivities of 20.3, 31.5, 13.4, and 16.3%, respectively. Furfural conversion increased in the order: Pd/CMK-5 > Pd/CMK-3 > Pd/CMK-8 > Pd/MSU-F-C > Pd/Vulcan > Pd/CNT. In addition, the type of solvent was affect to the product selectivity in furfural hydrogenation over various Pd/C catalysts.

Salnikova et al. [52] studied the catalytic tests of palladium catalysts in a complex multistage process of furfural hydrogenation. The palladium catalysts were prepared on different supports types ; aluminium oxide (Al_2O_3), hypercrosslinked polystyrene (HPS), and magnetite/hypercrosslinked polystyrene (Fe_3O_4/HPS). Reactions were performed at a temperature of 120 °C and a hydrogen pressure of 6 MPa and Propanol-2 as the solvent for 2 h. The 3wt% of palladium catalysts were prepared by impregnation method. Studies have shown that the nature of the support had a significant effect on the conversion of furfural and the selectivity for furfuryl alcohol. 3%Pd/Fe_3O_4/HPS was the most effective catalyst, in the presence of which the conversion of furfural was> 95% with selectivity for furfuryl alcohol> 94 %. Moreover, catalysts based on HPS are more stable in comparison Al_2O_3 support after ten catalytic cycles , especially Fe_3O_4/HPS support which had the advantage of this catalyst in easy separation from the reaction mixture by magnet.

Xu et al. [53] investigated the catalyst activity of mesoporous N-doped carbon encapsulated Co catalysts (Co-N-C) in hydrogenation of furfural to FA. The catalysts were prepared via pyrolysis of the mixture of $Co(phen)_2(OAc)_2$ complex as the precursor and nano-MgO as template for high-temperature annealing in nitrogen atmosphere. The pyrolysis temperatures were adjusted to 600, 700, 800, and 900 °C. The catalytic performances of various catalysts have been tested at 150 °C for 6 h, 0.5 MPa N_2 and 1,4-dioxane as solvent. The optimized Co-N-C-700 was highly efficient for achieving 100% furfural conversion and>99% FA selectivity. Additionally, it could be reused for 5 times without obvious loss in catalytic efficiency.

Taylor et al. [16] investigated the selective hydrogenation of furfural to FA mild over Pt nanoparticles supported on SiO_2, ZnO, γ-Al_2O_3, CeO_2 and MgO and different types of solvents including methanol, ethanol, n-butanol, totuene and hexane. The reactions were operated at 50 ℃, 7 h, and H_2 pressure 0.1 MPa and catalysts were reduced at at 200 °C in flowing 10% H2/N2 for 1 h. The results showed that Pt/γ-Al_2O_3 catalyst exhibited the highest catalytic performances in methanol with 80% conversion of furfural and 99% selectivity of FA. The presence of 2-furaldehyde diethyl acetal and 2-furaldehyde dimethyl acetal was the side product between furfural and alchol solvents , ethanol and methanol, respectively. On the other hand, non-polar (hexene and toluene) solvents conferred poor furfural conversion. In addition, the result showed that methanol was the most suitable solvent for furfural hydrogenation. All catalysts were found a good stability in the repeated use.

Bhogeswararao et al. [54] studied the effect of γ–Al2O3 supported Pt and Pd catalysts in the selective liquid phase hydrogenation of furfural to furfuryl alcohol. The 5 wt%catalysts were prepared by impregnation method. The reactions were operated at various tempaertures, which was 25,180,210, and 240°C, 5 h, H2 pressure 2 MPa and iso-propanol as solvent. The results indicated that at operation tempetures of 25°C, the Pt/γ–Al2O3 were selective for hydrogenation of C=O group,producing furfuryl alcohol FA, while the Pd/γ–Al2O3 catalysts hydrogenated both ring and C=O groups, producting FA and tetrahydrofurfuryl alcohol (THFL). At temperatures more than 180°C, the Pt/γ–Al2O3 facilitated hydrogenolysis of C=O and C-O groups enabling 2-methyl furan (2-MF) and furan ring-opened products. At these reaction conditions, the Pd/γ–Al2O3 enabled decarbonylation of furfural giving furan in 82% yield.

Zhang et al. [59] studied the effect of bimetallic overlayer catalysts (Ni@Pt/SiO_2 and Cu@Pt/SiO_2) and compared with monometallic catalysts (Ni/SiO_2,

Cu/SiO_2, Pt/SiO_2) for furfural hydrogenation. Silica-supported bimetallic Ni@Pt and Cu@Pt overlayer catalysts were synthesized using the directed deposition technique, whereas monometallic parent catalysts (pure Ni, pure Cu, and pure Pt) and non-structured bimetallic alloy catalysts (Ni-Pt and Cu-Pt) were synthesized using incipient wetness impregnation of silica gel. The furfural hydrogenation was performed at 250 °C, for 1.5 h, H_2 pressure 0.69 MPa and 2-propanol as solvent. Both overlayer catalysts exhibited higher reactivity in furfural conversion compared to their parent metals. Cu@Pt and pure Cu showed selectivity higher than pure Pt. Moreover, Cu@Pt overlayer catalyst indicated not only high furfuryl alcohol selectivity but also reactivity.

Musci et al. [55] studied the catalytic aqueous phase hydrogenation of furfural, employing Ru-based catalysts supported on activated carbon and the effect of the addition of Sn as a promoter of conversion and selectivity. Ru/C, with Ru loading 3wt%, was prepared by impregnation method, while RuSn bimetallic catalysts with Sn/Ru molar ratio between 0.1 and 0.8 were synthesized using a methodology derived from SOMC/M techniques. The monometallic Ru/C catalyst presented a low selectivity to FA (47% at 85% conversion). The bimetallic $RuSn_{0.4}/C$ catalyst demonstrated the promising potential of this system in this reaction because provided the highest catalytic performance with 91 % conversion of furfural and 90 % selectivity of FA.

Merlo et al. [17] studied the effect of tin content on the activity, selectivity and stability of Pt/SiO_2 catalysts modified with $SnBu_4$ in the liquid-phase hydrogenation of furfural to furfuryl The monometallic catalyst was prepared by ion exchange, using SiO_2 as support and Bimetallic PtSn catalysts, with various Sn/Pt atomic ratio were prepared by controlled surface reactions, using techniques derived from the Surface Organometallic Chemistry on Metals (SOMC/M). The results showed that PtSn systems were more active than the monometallic catalyst and the lowest Sn/Pt atomic ratio (0.3) provided the highest reaction rate and FA selectivity of 96.18 %. In addition, the catalyst PtSn0.3 gave a high level of conversion after three reaction cycles.

Table 2. 4 Summary of the research of liquid phase hydrogenation of furfural to FA by using Pt based catalysts with various type of carbon supports.

Researcher	Studies	Catalyst and preparation method	Reaction condition	Results
Lui et al. [56]	Investigated the effect of transition metal loading on Pt/MWNT catalysts for furfural hydrogenation.	Pt/MWNT, Pt-Cr/MWNT, Pt-Fe/ MWNT, Pt-Co/ MWNT, and Pt-Ni/ MWNT and prepared by co-impregnation method.	- Reduced at 400 °C for 4 h by H_2 flow. - Operated at 100 °C, 30 MPa H_2 for 5 h. - Used ethanol as solvent.	- Pt-Fe/MWNT showed high conversion (95.2%) and selectivity (91.8%), while Pt/ MWNT is only 64.5% of conversion and 37% of selectivity.
Fuente-Hernández et al. [57]	Studied a biochar-supported platinum catalyst in a batch reactor for the liquid phase hydrogenation of furfural.	3% Pt/BC, and 5% Pt/BC and prepared by wet impregnation method.	- Reduced at 250 °C for 1 h by H_2 flow. - Operated at 170-320 °C, 3.4-10.3 MPa H_2 for 1-6 h. - Used toluene, isopropanol, isobutanol, and hexane as solvent.	- 3% Pt/BC with reaction conditions of 210 °C for 2 h, 10.3 MPa, and toluene as the solvent exhibited furfural conversion (60.8%) at high selectivity (79.2%) to FA
Chen et al. [19]	Reported the selective hydrogenation of furfural to furfuryl alcohol over Pt nanoparticles supported on graphitic carbon nitride (g-C_3N_4) nanosheets catalysts.	0.5 %Pt@TECN and 5%@TECN and prepared by Ultrasound-assisted reduction method.	- No reduction was required. - Performed at 100 °C, 1 MPa H_2 for 1 and 5 h. - Used water, ethanol, toluene, isopropanol, and octane as solvent.	- 5%Pt@TECN with 5 h of reaction time presented about 99% of conversion and selectivity in water. - Furfural conversion of ethanol, toluene and isopropanol ranged from 51.2 to 91.5% and 70.5 to 96.7% of FA selectivity.
Wang et al. [21]	Studied the hydrogenation of furfural under mild condition using Multiwalled Carbon Nanotube (MWNT)-	5% Pt/MWNT and prepared by Wet impregnation.	- Reduced at 250 °C for 1 h by H_2 flow. - Carried out at 150 °C under 2 MPa H_2 for 5 h.	- Pt/MWNT-4 catalyst exhibited a very good activity, 94.4% of furfural conversion and 79% of FA selectivity

	Supported Pt Catalysts		- Used 1wt% tetradecane in propanol as solvent.	
Dohade et al. [58]	Reported the hydrogenation of furfural over Pt/C	3% Pt/C, 3% Pt3%Co/C and prepared by Wet impregnation.	- Reduced at 400 °C for 2 h by H_2 flow. -180 °C, 1 Mpa H_2 for 8 h - Used isopropanol as solvent.	- 3%Pt/C catalysts showed the 100% conversion of furfural and 71% selectivity of FA. - 3%Pt3%Co/C catalyst with 100% conversion of furfural, enhanced selectivity of 2-methylfuran (2-MF) instead of FA.
Liu et al. [20]	Reported the design of Pt catalysts supported on biomass-derived porous heteroatom doped carbon materials for selective hydrogenation of furfural in water	Pt/NC-BS-500 and prepared by an ultrasound-assisted reduction method	- No reduction was required. - Performed at 100 °C, 1 MPa H_2 for 1 and 4 h. - Used water as solvent	- The Pt/NC-BS-500 catalyst was highly efficient for furfural hydrogenation, with a furfural conversion of >99% and FA selectivity of >99%. - No obvious decrease in the furfural after four reactions.

Lui et al. [56] investigated the effect of transition metal (Cr, Mn, Fe, Co, Ni) loading on Pt/MWNT catalysts in ethanol as solvent for furfural hydrogenation. The catalysts were prepared by co-impregnation method, which loaded Pt of 0.5wt%, and reduced at 400 °C for 4 h by H_2 flow; in addition, the catalysts were operated at 100 °C, 30 MPa H_2 for 5 h. The results showed that bimetallic Pt-based catalysts exhibited higher catalytic activity compared to monometallic catalysts. The conversion varies in order: Pt–Ni/MWNT (95.9%) > Pt–Fe/MWNT (95.2%) > Pt–Co/MWNT (86.7%) > Pt–Mn/MWNT (85.9%) > Pt–Cr/MWNT (85.4%) > Pt/MWNT (64.5%). Pt–Fe/MWNT possessed the highest selectivity (91.8%) towards FA, whereas Pt/MWNT was only 37%. Moreover, Pt-Fe/AC was also compared in this reaction, the conversion and selectivity were 52.9 % and 28.6 %, respectively. The main byproduct in this process was 2-furaldehyde diethyl acetal (FDA) which would be easily produced in ethanol solvent as called solvent product.

Fuente-Hernández et al. [57] studied a biochar-supported platinum catalyst in a batch reactor for the liquid phase hydrogenation of furfural. Biochar (BC) produced from torrefaction (slow pyrolysis) and Pt was loaded by impregnation. Reactions were performed between 170 °C and 320 °C, using 3wt% and 5wt% of Pt supported on a maple-based biochar under hydrogen pressure varying from 3.4 MPa to 10.3 MPa for reaction times between 1 h and 6 h in various solvents, which were toluene, isopropanol, isobutanol, and hexane. Catalysts were activated in situ in flowing H_2 with flow rate 50 mL/min at 250 °C, for 1 h. The results indicated that variation of temperature had an impact, both on conversion and selectivity to FA. FA selectivity was deceased when longer reaction time; further, solvent polarity tends to increase the hydrogenation rates. Furfural conversion at high selectivity to FA was found for 3wt% Pt/BC with reaction condition of 210 °C for 2 h and 10.3 MPa H_2, with toluene as the solvent.

Chen et al. [19] reported that the Pt nanoparticles supported on graphitic carbon nitride (g-C_3N_4) nanosheets showed superior activity in the hydrogenation of furfural toward FA in water and without obvious loss of activity and selectivity when reused for four times. 0.5wt% and 5wt% of Pt nanoparticles was deposited on g-C_3N_4 which were donated as TECN by an ultrasound-assisted reduction method. Reaction conditions were performed at 100 °C, 1 MPa H_2 for 1 and 5 h. with various solvents including water, ethanol, toluene, isopropanol, and octane. Among these solvents examined, the best activity for furfural hydrogenation, giving >99% yield after 5 h in water was showed, whereas the reaction in ethanol, toluene and isopropanol obtained relative temperate furfural conversion of 51.2–91.5% after 5 h, with the desired FA selectivity of 70.5–96.7%. 2-furaldehyde diethyl acetal and 2-isopropoxymethylfuran which is the acetalization of furfural was also observed when ethanol and isopropanol was used as solvent, selectivity.

Wang et al. [21] studied the effect of MWNT pretreatment, H_2 pressure, and reaction temperature on hydrogenation of furfural under mild condition using

Multiwalled Carbon Nanotube (MWNT)-Supported Pt Catalysts, the catalysts were treated for 1, 2, and 4 h, and labeled as MWNT-1, MWNT-2, and MWNT-4, accordingly. A typical reaction was carried out at 150 °C under 2 MPa H_2 for 5 h with 1wt% tetradecane in propanol as solvent. The Pt/MWNT-4 catalyst exhibited a very good activity, 94.4% of furfural conversion and 79% of FA selectivity. Low pressure and low temperature shifted the selectivity toward furfural alcohol.

Dohade et al. [58] reported that the conversion of furfural and selectivity of FA of hydrogenation of furfural over 3%Pt/C which prepared by wet impregnation method was 100% and 71%, respectively. The reactions were performed at 180 °C, 1 MPa H_2 for 8 h and isopropyl alcohol as solvent. The catalysts were reduced at 400 °C for 2 h in H_2 flow (10 mL/min). The bimetallic catalysts were studied by using Co, in the presence of 3%Pt3%Co/C catalyst with 100% conversion of furfural, enhanced yield of 2-methylfuran (2-MF) to 56% (2-MF selectivity 56%) instead of FA was observed, FA selectivity was showed only 30% FA selectivity.

Liu et al. [20] reported the design of Pt catalysts supported on biomass-derived porous heteroatom doped carbon materials for selective hydrogenation of furfural in water. The porous heteroatom doped carbon supported Pt materials with a metal loading of 5.0 wt% were prepared using an ultrasound-assisted reduction method. The results indicated that highly active Pt/NC-BS catalysts were explored for selective transformation of furfural into FA in water. The prepared catalyst had a high BET surface area, large porosity and abundant surface functional groups. The Pt/NC-BS-500 catalyst was highly efficient for furfural hydrogenation, with a furfural conversion of >99% and FA selectivity of >99% at 100 °C using 1 MPa H_2 for 4 h of reaction time. Moreover, conversion was observed the selectivity for FA was maintained at>98% during the recycling experiments, no obvious decrease in the furfural after four reactions, indicating that the Pt/NC-BS-500 catalyst was highly stable during furfural hydrogenation
in water.

CHAPTER III

MATERIALS AND METHODS

This chapter describes the experimental detail of this research including materials, catalyst preparation, catalyst characterization, catalytic activity for the selective hydrogenation of furfural to furfuryl alcohol.

3.1 Catalyst preparation

3.1.1 Preparation of Pt/OMC catalyst by one-pot method

The 5 wt%Pt/OMC one pot carbon material catalyst was synthesized via one-step of modified soft-template self-assembly method. Briefly, 1.1 g of resorcinol and 0.3 g of F127 was mixed in 4.5 mL of 99.99% ethanol and 4.5 mL of 3 M HCl. 1.3 g of formaldehyde was added in the clear solution and thoroughly mixed. Six minutes after added formaldehyde solution, separation of the sediment from the mixture was done by centrifugation at 4000 rpm for 3 min. The bottom-layer was then dissolved in a solution of 3.5 mg Platinum (II) acetylacetonate in 5 mL of THF and vortexed until a homogenously solution was obtained. The mixture was poured onto petri-dishes and kept at room temperature for 24 h. Then, the as-received solid film was heated at 100°C for 48 h. As-prepared material named Pt-MC. The catalyst was calcined at 800°C for 3 h under N_2 atmosphere with heating rate of 1°C /min. The calcined catalyst is here called Pt/OMC one pot.

Table 3. 1 Chemicals used for catalyst preparation by one-pot method.

Chemicals	Formula	Suppliers
Resorcinol (1,3-Dihydroxybenzene, > 99%)	$C_6H_6O_2$	Tokyo Chemical Industry
Triblock copolymer Pluronic F127	-	Sigma-Aldrich
Ethanol (97%)	C_2H_6O	Sigma-Aldrich
hydrochloric acid (37%)	HCl	RCI Labscan
Tetrahydrofuran	C_4H_8O	RCI Labscan
Formaldehyde (37- 40 % w/v)	HCHO	Loba Chemie

3.1.2 Preparation of Pt/Carbon by impregnation Method

The three carbon supported platinum catalysts were prepared by wet impregnation method as the desired amounts of 0.5 wt% of platinum. Platinum (II) acetylacetonate was dissolved in xylene and then the aqueous solution was slowly dropped onto each different carbon types, including activated carbon (AC), non-uniform meso/macroporous carbon (MC), and prepared ordered mesoporous carbon (OMC), OMC support were synthesized by using one-pot method. The impregnated catalysts were dried overnight at 110 °C in the oven. Finally, the catalysts were calcined in N_2 at 350°C for 4 h. Further, the catalysts were assigned name Pt/AC, Pt/MC, and Pt/OMC respectively.

3.1.3 Preparation of various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts by co-impregnation Method

The Pt/AC (0.5 wt%) , FePt/AC (0.5 wt%Pt and 0.1-10 wt%Fe), and 0.15MPt/AC (0.5 wt%Pt and 0.15wt%M: Ni and Co) were prepared by co-impregnation method using commercial activated carbon, tetraammineplatinum (II) chloride hydrate, ferric nitrate, cobalt (II) nitrate, and nickel (II) nitrate hexahydrate, as C, Pt, Fe, Co, and Ni precursors, respectively.The Pt and the second metal precursors were dissolved in deionized water and then the aqueous solution was slowly dropped onto the activated carbon. The impregnated catalysts were dried overnight at 110 °C in an oven. Finally, the catalysts were calcined in N_2 at 500 °C for 2 h. The catalysts were denoted as Pt/AC and xMPt/AC when x was wt% and M was the second metal. The 0.15NdPt/AC (0.5 wt%Pt and 0.15wt%Nd) was prepared by physical mixing. Firstly, the Pt/AC catalyst from impregnation was mixed with neodymium powder in toluene at room temperature and stirred for 40 min for uniform mixing. The solvent was removed from the mixture by centrifugation and washed by DI water. Then, the solid catalyst was dried at 110 °C overnight and calcined at 500 °C for 2 h in N_2 flow. The catalysts were denoted as 0.15NdPt/AC.

Table 3. 2 Chemicals used for catalyst preparation by impregnation method.

Chemicals	Formula	Suppliers
Platinum (II) acetylacetonate (99.99%)	$Pt(C_5H_7O_2)_2$	Sigma-Aldrich
Xylene (99.8%)	C_8H_{10}	Merck
Tetraammineplatinum (II) chloride hydrate (99.99%)	$(Pt\ (NH_3)_4Cl_2{\cdot}xH_2O)$	Sigma-Aldrich
Ferric nitrate nonahydrate (≥ 97.0%)	$(FeN_3O_9.9H_2O)$	Fluka
cobalt (II) nitrate hexahydrate (≥ 98%)	$Co(NO_3)_2{\cdot}6H_2O$	Carlo Erba
nickel (II) nitrate hexahydrate (≥ 98%)	$Ni(NO_3)_2{\cdot}6H_2O$	ACS
neodymium powder (< 400 mm, ≥ 99.0%)	Nd	Sigma-Aldrich
Mesoporous carbon (>99.95%)	C	Sigma-Aldrich
Activated carbon (C = 90.81 wt%, O = 9.02 wt% and P = 0.18 wt%)	C	Sigma-Aldrich

3.2 Catalyst Characterization

3.3.1 X-ray diffraction (XRD)

The XRD patterns were collected using a Bruker D8 Advance with a Ni filter and Cu Kα radiation. in scanning range from 20° to 80° 2θ (scan rate = 0.5 sec/step).

The crystallite size (dXRD) was calculated using the Scherrer's equation and α-alumina as the external standard.

3.2.2 N_2-physisorption

The BET (Brunauer–Emmett–Teller) surface area, average pore size diameter, and pore size distribution were determined by physisorption of N2 using a Micrometrics ASAP 2020 instrument.

3.2.3 Hydrogen Temperature-programmed reduction (H_2-TPR)

The H_2-TPR experiments were performed to determine reducibility and the interaction of metal and support on a MicromeriticsChemisorb 2750 with ChemiSoftTPx software. The unreduced catalyst was placed in a quartz U-tube reactor and pretreated with a N_2 flow (25 cm^3/min, 1h, 250°C). Then, a gas mixture of 10%H_2/Ar was passed through the quartz reactor to the catalyst sample with a temperature ramp from room temperature to 850°C witht heating rate 10 °C/min.

3.2.4 CO pulse chemisorption

The amounts of CO chemisorbed on the catalyst, active sites, and percentages of platinum dispersion were measured from CO-pulse chemisorption technique on a MicromeriticsChemisorb 2750 with ChemiSoftTPx software. About 0.07 g of catalyst, He gas flow 25 cm^3/min to removed air and then the catalyst was reduced under H_2 flow (25 cm^3/min) at 400 °C for 2 h with a heating rate of 10 °C/min. And cooled down to the room temperature, then He gas was inserted into the sample cell (25 cm^3/min) for removed air. Next, injected 10 µL of carbon monoxide into the catalysts and replaced until the desorption peak were unchanged

3.2.5 Transmission electron spectroscopy (TEM)

Transmission electron spectroscopy (TEM) was used to determine about morphology and crystallite sizes of catalysts by using a JEOL-JEM 2010 transmission electron microscope using energy-dispersive X-ray detector operated at 200 kV.

3.2.6 Infrared spectroscopy of adsorbed CO (CO-IR)

The CO absorbed species on the catalysts were measured using FTIR-620 spectrometer (JASCO) with a MCT detector at a wavenumber resolution of 2 cm^{-1}. Prior to reduce the catalysts, He gas was introduced into the sample cell in order to remove the remaining air. The sample was reduced at 500°C with H_2 flow for 2 h and then cooled down to the room temperature with He gas. After that, carbon monoxide was introduced into the sample cell for 15 min and then was purged with He to eliminate the CO gas phase and physiosorbed CO. The IR spectrum of CO adsorbed onto the catalyst was recorded in the 1800-2300 cm^{-1}.

3.3 Catalytic test in the selective hydrogenation of furfural

The catalyst activity was tested in liquid phase selective hydrogenation of furfural to furfuryl alcohol. Reactions were performed in a 100 mL stainless steel autoclave reactor (JASCO, Tokyo, Japan). Prior to the catalyst test, the catalysts which prepared by impregnation method were reduced under H_2 flow (25 cm^3 /min) at 400 °C for 2 h. For the furfural hydrogenation, approximately 50 mg of catalyst, 50 μL of furfural and 10 mL of solvent were added into reactor. Then reactor was purged with hydrogen three times for remove the air. After that the reactor was executed at 50°C, 2 MPa of H_2 under stirring at 900 rpm. Hydrogenation process of furfural was under the conditions of certain temperature in desired time. After completion of the reaction, the reactor was cooled to below room temperature with an ice-water and depressurized carefully. For methanol solvent, the liquid products were analyzed by a gas chromatograph Shimadzu GC-2014 equipped with a flam ionization detector (FID), the capillary column with 30 M length and 0.32 mm inside diameter were used. Then 0.2 μL was injected into the column and helium was used as a carrier gas. Whereas water solvent, the liquid products were analyzed a high-performance liquid chromatography (HPLC). Two HPLC equipments were used in this experiment by separating 2 parts. For Part I, Agilent, HPLC 1100 G1361A equipped with column ZORBAX SB-C18 (80Å, 5 μm, 4.6 mm inner diameter x 250 mm length; Agilent). The injection volume was 20 μL and the absorbance detector wavelength was set at 230.4 nm. The mobile phase flow rate was 0.4 mL min^{-1} using a composed of 80% water and 20% acetonitrile (HPLC grade). While Part II, the liquid products were analyzed by Shimadzu 20A with UV detector of high-performance liquid chromatography (HPLC) with Aminex HPX-87H (300 × 7.8 mm) column at column temperature of 35°C using a composed of 86% 0.01N H_3PO_4 and 14% of acetonitrile (HPLC grade) with a flow rate of 0.4 ml min^{-1}. The UV detector wavelength was set at 215 nm. Chemicals used in the liquid-phase reaction, the operating conditions of gas chromatograph (GC), the operating conditions of high-performance liquid chromatography (HPLC) and schematic of the liquid-phase hydrogenation of furfural to furfuryl alcohol were shown in **Table 3.3, Table 3.4**, **Table 3.5** and **Table 3.6**, and **Figure 3.1**, respectively.

Table 3. 3 Chemicals used in the liquid-phase reaction.

Chemicals	**Formula**	**Suppliers**
Furfural (99%)	$C_5H_4O_2$	Sigma-aldrich
Furfuryl alcohol (98%)	$C_5H_6O_2$	Sigma-aldrich
Methanol	CH_3OH	Sigma-aldrich
Acetonitrile (≥ 99.8%)	CH_3CN	Merck
Sulfuric acid (95-97%)	H_2SO_4	Merck
Orthophosphoric acid (85%)	H_3PO_4	Carlo Erba

Table 3. 4 Gas-Chromatography operating conditions.

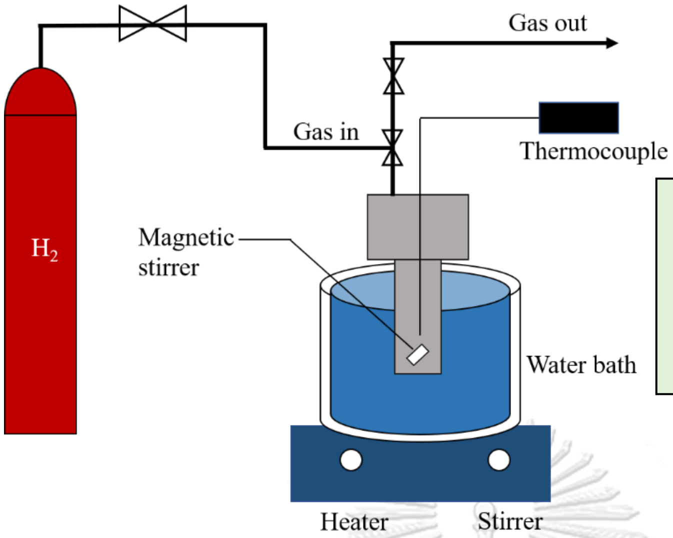
Gas chromatography (Shimadzu GC-2014)	**Conditions**
Detector	FID
Packed column	Rtx®5
Carrier gas	Helium (99.99 vol%)
Make-up gas	Air (99.9 vol%)
Column temperature	110 °C
Injector temperature	260 °C
Detector temperature	270 °C
Time analysis	41.80 min

Table 3. 5 The operating conditions of Agilent HPLC 1100 G1361A for the analysis of furfural and furfuryl alcohol.

High-performance liquid chromatography (Agilent 1100 G1361A)	**Conditions**
Detector	Ultra violet/Visible (UV)
Column	ZORBAX SB-C18 (80Å, 5 μm, 4.6 mm inner diameter x 250 mm length)
Mobile phase	20% Acetonitrile
Wavelength	230.4 nm
Time analysis	15 min

Table 3. 6 The operating conditions of Shimadzu 20A HPLC for the analysis of furfural and furfuryl alcohol.

high-performance liquid chromatography (Shimadzu 20A)	**Conditions**
Detector	Ultra violet/Visible (UV)
Column	Aminex HPX-87H (300 × 7.8 mm)
Mobile phase	86% 0.01N H_3PO_4 and 14% Acetonitrile
Column temperature	35 °C
Wavelength	215 nm
Time analysis	60 min



Reaction conditions:

50 μL of furfural in 10 mL of solvent at 50°C, 2 MPa of H_2 under stirring at 900 rpm

Figure 3. 1 Schematic of the liquid-phase hydrogenation of furfural.

CHAPTER IV

RESULTS AND DISCUSSION

This topic includes 2 research articles:

4.1 Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method

4.2 Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon

All research articles are partial fulfillment of dissertation for graduation.

4.1 Article I

Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method

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Article I: Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method

Abstract

Ordered mesoporous carbon (OMC) has attracted a great deal of attention as catalyst support due to their tunable morphological and textural properties. In this study, the characteristics and catalytic properties of OMC-supported Pt catalysts prepared by one-step modified soft-template self-assembly method (Pt/OMC-one-pot) were compared to the Pt impregnated on OMC, activated carbon (AC), and non-uniform meso/macroporous carbon (MC) in the selective hydrogenation of furfural to furfuryl alcohol (FA) under mild conditions (50°C, 2 MPa H_2). Larger Pt particle size (∼4 nm) was obtained on the Pt/OMC-one-pot comparing to all the impregnated ones, in which the Pt particle sizes were in the range 0.5 – 2 nm. Reduction step was not necessary on the Pt/OMC-one-pot and among the catalysts studied, the Pt/OMC-one-pot exhibited the highest furfural conversion and FA selectivity under aqueous conditions. The use of methanol as the solvent resulted in the formation of solvent product (2-furaldehyde dimethyl acetal) instead. The amount of Pt being deposited, location of Pt particles, and metal-support interaction strongly affected recyclability of the catalysts because some larger size Pt particles with weak metal-support interaction could be leached out during the liquid-phase reaction, rendering similar catalytic performances of the various porous carbon supported catalysts after the 3rd cycle of run.

Keywords: furfural; furfuryl alcohol; hydrogenation; soft-templating method; platinum catalyst

4.1.1 Introduction

Increasing global energy consumption is leading to a shortage of fossil fuels in the coming decades and also environmental problems, thus renewable energy sources such as solar, wind, hydropower, geothermal and biomass are interesting energy sources to replace fossil fuels for sustainable development. Furfural is one of the important biomass-derived chemicals that is being used in chemical industry for the production of many downstream products and derivatives [4]. The selective hydrogenation of furfural to furfuryl alcohol (FA) is an interesting reaction because FA is widely used in fine chemicals industry for producing drug intermediates, adhesive, lubricants, and dispersing agents and in the polymer industry of furan resin, furfural resin, and phenolic resin [5-7, 59].

Furfural consists of two functional groups, an aldehyde (C=O) and a conjugated system (C=C-C=C) [1]. The aldehyde group (C=O) of furfural can be hydrogenated and transformed to FA [59]. The catalytic hydrogenation of furfural to FA is usually performed in the gas or liquid phase [8-11]. In the industrial processes, copper chromite (Cu–Cr) is used as the catalyst for both liquid-phase and gas-phase hydrogenation [60], operating at high pressure (up to 30 bar), and high temperature (between 130 and 200 °C) [16]. These catalysts are active, selective, and quite stable; nonetheless, Cr is very toxic and carcinogenic and can cause serious pollution to the environment when being disposed [6, 12, 16, 59]. Consequently, Cr-free catalysts have been investigated for the FA production from furfural hydrogenation [59, 60] such as Pt [16-19, 21, 48], Pd [22-24, 26], Ru [24], Co [27], Cu [28-30] and Ni [31, 32]. Among these catalysts, Pt is the precious metal that exhibits high catalytic activity and high selectivity to FA under relatively mild conditions [19, 20].

Ordered mesoporous carbon (OMC) has been employed in various applications such as catalyst support, electrode material, and adsorbent for gas separation due to high surface area, large pore volume, tunable pore size, and good gas penetrability [32]. Mesoporous carbons are mainly prepared by activation processes [34-36] or hard templating nanocasting [37]. These methods, however, are not green since toxic activating agents such as KOH and HF are used. Soft-templating strategy is a promising and sustainable route for preparation of mesoporous carbons [38]. The soft-templating synthesis is based on the self-assembly of supramolecular arrangements of carbon precursor molecules with low-cost and easily decomposable soft templates to form organic-organic composites, and mesoporous carbons are obtained after subsequent carbonization (pyrolysis). Unlike the conventional activation processes, where the control of pore size and pore morphology is very difficult, pore morphology and size of mesopores by soft-templating can easily be controlled by varying carbon precursors and micelles of amphiphilic block-copolymers [38]. The soft-template strategy requires no multi-step procedure and allows easy incorporation of active metal species or other hetero-atoms [47, 61].

In this work, one-step synthesis of 0.5 wt% Pt incorporated OMC was achieved via the modified soft-templating method and tested in the liquid phase hydrogenation of furfural to FA under mild conditions. The catalysts were characterized by various techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), Infrared spectroscopy of adsorbed CO (CO-IR), and compared to those prepared by wet impregnation on OMC and the other Pt catalysts supported commercial activated carbon and commercial mesoporous carbon.

4.1.2 Experimental

4.1.2.1 Raw Materials and Chemicals

The chemicals used were as follows: triblock copolymer Pluronic F127, poly (ethylene oxide) – block – poly (propylene oxide) – block -poly (ethylene oxide) ($PEO_{106}PPO_{70}$ - PEO_{106}, Mw = 12,600 Da, F127), Platinum (II) acetylacetonate (97% purity), commercial activated carbon (C = 90.81 wt%, O = 9.02 wt% and P = 0.18 wt%), commercial mesoporous carbon (<500 nm particle size,>99.95% purity) were purchased from Sigma-Aldrich. Resorcinol (1,3-Dihydroxybenzene, > 99.0% purity) was purchased from Tokyo Chemical Industry. Ethanol (99% purity), HCl (37% purity), of tetrahydrofuran (C_4H_8O, THF, 99.8%, purity) were purchased from RCI Labscan and formaldehyde (37- 40 % w/v) were purchased from Loba Chemie.

4.1.2.2 Catalyst preparation

4.1.2.2.1 One-pot synthesis of Pt/OMC

Pt/OMC-one-pot carbon material catalyst was synthesized via the modified soft-template self-assembly method. Briefly, 1.1 g of resorcinol and 0.3 g of F127 was mixed in 4.5 mL of 99.99% ethanol and 4.5 mL of 3 M HCl. 1.3 g of formaldehyde was added in the clear solution and thoroughly mixed. Six minutes after added formaldehyde solution, separation of the sediment from the mixture was done by centrifugation at 4000 rpm for 3 min. The bottom-layer was then dissolved in a solution of 3.5 mg Pt acetylacetonate in 5 mL of THF and vortexed until a homogenously solution was obtained. The mixture was poured onto petri-dishes and kept at room temperature for 24 h. Then, the as-received solid film was heated at 100 ˚C for 48 h. The catalyst was calcined at 800 ˚C for 3 h under N_2 atmosphere with heating rate of 1 ˚C/min. The calcined catalyst is here called Pt/OMC-one-pot.

4.1.2.2.2 Preparation of carbon supported Pt catalysts by impregnation method

The other three carbon supported platinum catalysts were prepared by wet impregnation method with the desired amounts of 0.5 wt% of Pt. Platinum acetylacetonate was dissolved in xylene (MERCK; 99.8vol%) and then the aqueous solution was slowly dropped onto each different carbon types (commercial activated carbon, commercial mesoporous carbon, and prepared ordered mesoporous carbon). The impregnated catalysts were dried overnight at 110 °C in an oven. Finally, the catalysts were calcined in N_2 at 350°C for 4 h. The catalysts were assigned name Pt/AC, Pt/MC, and Pt/OMC respectively.

4.1.2.3 Catalyst Characterization

The H_2-TPR measurements were carried to determine reducibility and reduction temperature of platinum catalysts. A quartz U-tube reactor was used, and all the catalyst samples were pretreated with a N_2 flow (25 mL/min, 1 h, 150°C). The

TPR profiles were obtained by passing carrier gas (10% H_2 in nitrogen) through the catalyst samples (25 mL/min, ramping from room temperature to 800°C at 10°C/min). The BET (Brunauer–Emmett–Teller) surface area, average pore size diameter, and pore size distribution were determined by physisorption of N_2 using a Micrometrics ASAP 2020 instrument. The XRD patterns were collected using a Bruker D8 Advance with a Ni filter and Cu K_α radiation. The crystallite size (d_{XRD}) was calculated using the Scherrer's equation and α-alumina as the external standard. The relative percentages of platinum dispersion were determined by CO pulse chemisorption technique using a Micromeritics ChemiSorb 2750 (pulse chemisorption system). The catalysts were reduced under H_2 flow (25 cm^3 /min) at 400 °C for 2 h before the measurements. Transmission electron spectroscopy (TEM) was used to determine about morphology and crystallite sizes of catalysts by using a JEOL-JEM 2010 transmission electron microscope using energy-dispersive X-ray detector operated at 200 kV. Inductively coupled plasma mass spectrometer (ICP) was used to determine the actual amount of platinum loading.

4.1.2.4 Reaction test

The catalyst activity was tested in liquid phase selective hydrogenation of furfural to furfuryl alcohol. Reactions were performed in a 100 mL stainless steel autoclave reactor (JASCO, Tokyo, Japan). Prior to the catalyst test, the catalysts were reduced under H_2 flow (25 cm^3 /min) at 400 °C for 2 h. For the furfural hydrogenation, approximately 50 mg of catalyst, 50 μL of furfural and 10 mL of solvent were added into reactor. Then reactor was purged with hydrogen three times for remove the air. After that the reactor was executed at 50°C,2 MPa of H_2 under stirring. Hydrogenation process of furfural was under the conditions of certain temperature in desired time. After completion of the reaction, the reactor was cooled to below room temperature with an ice-water and depressurized carefully. For methanol and toluene solvent, the liquid products were analyzed by a gas chromatograph Shimadzu GC-2014 equipped with a flam ionization detector (FID), the capillary column with 30 M length and 0.32 mm inside diameter were used. Then 0.2 μL was injected into the column and helium was used as a carrier gas. Whereas distilled water solvent, the liquid products were analyzed a high-performance liquid chromatography (Agilent, HPLC 1100 G1361A) equipped with column ZORBAX SB-C18 (80Å, 5 μm, 4.6 mm inner diameter x 250 mm length; Agilent). The injection volume was 20 μL and the absorbance detector wavelength was set at 230.4 nm. The mobile phase flow rate was 0.4 mL min^{-1} using a composed of 80% water and 20% acetonitrile (HPLC grade). The conversion of furfural and selectivity to furfuryl alcohol were calculated as follows:

$$\% \text{ Furfural conversion} = \frac{Mole\ of\ furfural\ (in) - Mole\ of\ furfural(out)}{Mole\ of\ furfural\ (in)} \text{ X } 100$$

$$\%\text{Furfuryl alcohol selectivity} = \frac{Mole\ of\ furfuryl\ alcohol}{Mole\ of\ converted\ furfual} \text{ X } 100$$

4.1.3 Results and Discussion

4.1.3.1 Catalyst characterization

The structural properties of the catalysts prepared by one-pot and impregnation method are shown in **Table 4.1**. Based on the actual amounts of Pt metal contents in the carbon supports were determined by the ICP-OES technique, all the catalysts contained Pt loading between 0.5-0.8 wt%. The Pt/AC showed the highest BET surface area of 804 m^2/g and a pore volume of 0.359 cm^3/g whereas the Pt/MC had the lowest surface area of 208 m^2/g and a pore volume of 0.404 cm^3/g. The BET surface area and pore volume of Pt/OMC-one-pot and Pt/OMC were not significantly different ranging between 591- 623 m^2/g and 0.436-0.509 cm^3/g, respectively. The nitrogen adsorption/desorption isotherm results are shown in **Fig. 4.1a**. The Pt/AC, Pt/OMC-one-pot and Pt/OMC catalysts displayed type IV adsorption isotherms with a H1-type hysteresis loop in the moderate to high relative pressure in the range of 0.3-1.0, indicating the presence of mesoporous structure in carbon supports. Moreover, the H3-type hysteresis loop was observed on Pt/MC because of the absence of any limiting adsorption at high P/P$_0$, suggesting a slit shaped pore structure. The pore size distributions are shown in **Fig. 4.1b**. As clearly seen, Pt/MC had a wide pore size distribution and contained both mesopores and macropore (> 50 nm) with average pore size around 38 nm. The Pt/AC had a pore size around 3.4 nm, corresponding to its mesopore structure, while both Pt/OMC-one-pot and Pt/OMC had a narrow pore size distribution with pore size around 3.4 nm. Such results confirmed that mesoporous structured Pt/OMC catalysts were successfully synthesized by the modified soft-template self-assembly one-pot method. The amounts of Pt active sites were determined from CO chemisorption results assuming Pt:CO atomic ratio = 1. The %Pt dispersion on the various carbon supports varied in the order Pt/MC (23.7%) > Pt/AC (6.1%) > Pt/OMC (5.0%). The CO chemisorption could not be determined on the Pt/OMC-one-pot, probably due to the coverage of carbon species and/or low Pt dispersion.

Table 4. 1 ICP-OES, N_2 physisorption properties, CO chemisorption and H_2 consumption result of Pt/OMC-one-pot, Pt/OMC, Pt/AC and Pt/MC.

Catalyst	Pt actual loading (wt%) [a]	N_2 physisorption properties			Active sites (x10^{18} molecule CO/g cat)	%Pt dispersion [c]	Average Pt particle size (nm)		H_2 consumption[d] (mmol/g_{cat})
		Surface area (m^2/g)	Pore Volume (cm^3/g) [b]	Average pore size (nm)[b]			From CO Chemisorption	From TEM	
Pt/OMC-one-pot	0.6	591	0.436	2.9	n.d.	n.d.	n.d.	5.6	0.0292
Pt/OMC	0.8	623	0.509	3.3	0.62	5.0	22.7	3.2	0.0325
Pt/AC	0.5	804	0.359	1.8	0.95	6.1	18.5	2.5	0.0285
Pt/MC	0.7	208	0.404	7.7	3.65	23.7	4.8	1.2	n.d.

[a] Pt loading measured by ICP-OES.

[b] Calculated from BJH desorption method.

[c] Pt dispersion measured by CO chemisorption.

[d] Total H_2 consumption below the temperature for methanation.

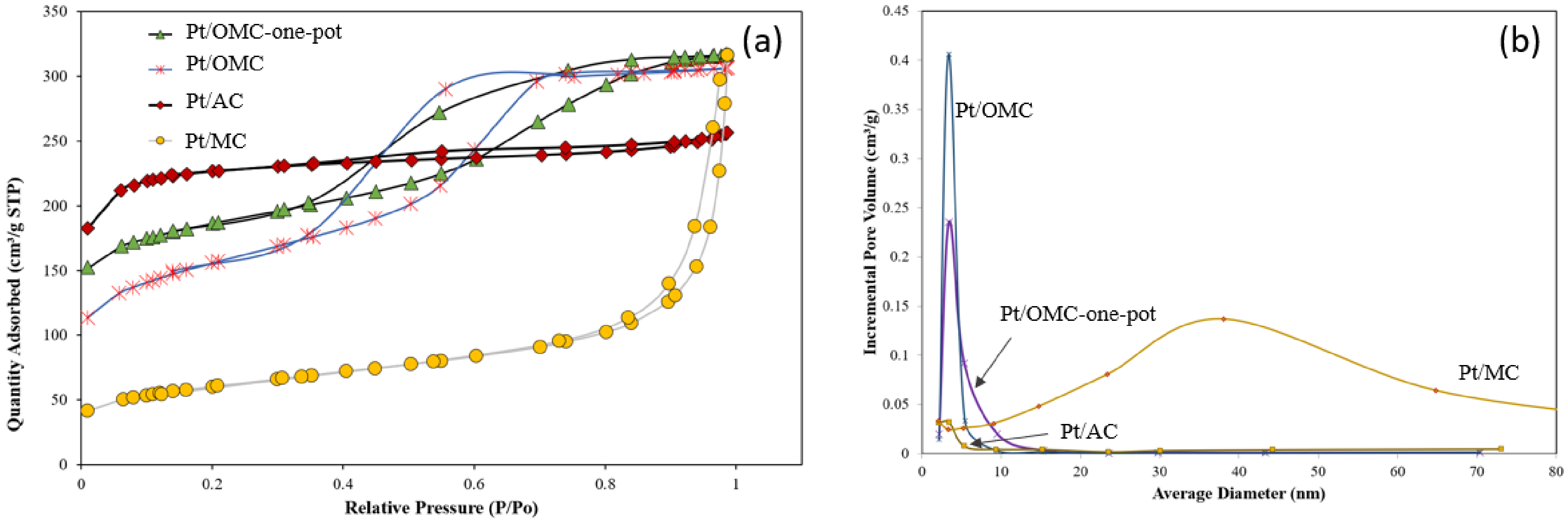

Figure 4. 1 Nitrogen adsorption/desorption (a) and pore size distribution (b) results of Pt/OMC-one-pot, Pt/OMC, Pt/AC and Pt/MC.

Fig. 4.2 shows the TEM images and metal particle size distributions of the Pt catalysts. The dark spots represent the metal species dispersing on all the carbon supports. As illustrated, all the synthesized catalysts displayed good dispersion of Pt nanoparticles. For Pt/OMC-one-pot catalyst, the particle sizes are ranging from 1 to 8 nm with an average value of 5.6 nm. A narrower particle size distribution was found for Pt/OMC, Pt/AC, and Pt/MC with average Pt particle sizes of 3.2 nm, 2.5 nm, and 1.2 nm, respectively. The relatively large Pt particle size on Pt/OMC-one-pot is in agreement with the lowest Pt dispersion as suggested by the CO chemisorption results. However, despite their similar trend, the average particle sizes of platinum obtained from the CO pulse chemisorption and TEM analyses are considerably different. The larger average Pt particle sizes calculated from CO pulse chemisorption could possibly be owing to the fact that some Pt particles were covered with carbon supports from catalyst preparation and/or located deep inside the small pores where CO chemisorption ability could be suppressed. The pore structures of the various carbon supports (e.g. microporous, mesoporous, and non-uniform meso/macroporous carbon) mainly affect the location and particle size of Pt. For Pt/OMC-one-pot and Pt/AC, most Pt particles maybe dispersed on the outer-pores since the average Pt particle sizes (as indicated by TEM) were larger than the pore sizes. On the other hand, the rod-structure pores of the OMC and the larger pore size of the MC could accommodate high dispersion of small Pt particles (1-3 nm) inside the pores.

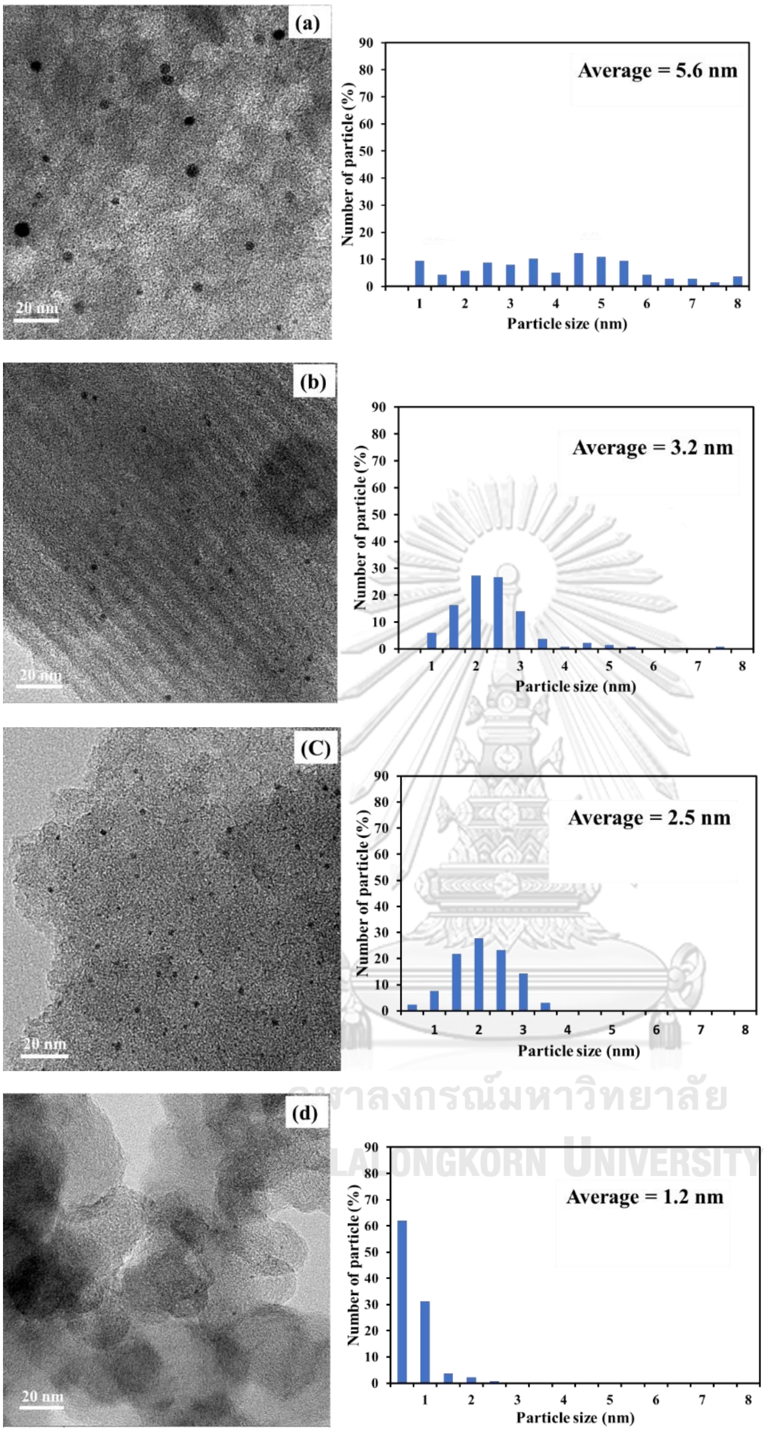

Figure 4. 2 TEM images and particle size distributionof Pt on (a) Pt/OMC-one-pot; (b) Pt/OMC; (c) Pt/AC; and (d) Pt/MC; Average particle size is calculated by the following formula: Average particle size = sigma(nd^3)/sigma(nd^2), where d is the particle size and n is the number of particles with this size.

The XRD patterns at the diffraction angles (2θ) between 20° and 80° of the Pt catalysts and the supported materials are shown in **Fig. 4.3**. For the Pt/OMC-one-pot and OMC which were prepared by the soft-templating method **(Fig. 4.3a)**, the diffraction peaks at 2θ = 15-30° (002) and 40-50° (101), which are attributed to the amorphous carbon structure and the a axis of the graphite structure [62, 63] are detected. The diffraction peaks corresponding to the reflections form the (111), (200) and (220) crystallographic planes of Pt face-centered cubic lattice are detected at 2θ = 39.9°,46.2° and 67.9° on the Pt/OMC-one-pot However, as clearly seen from **Fig. 4.3b-4.3d**, the XRD characteristic peaks of Pt could not be observed for all the impregnated catalysts: Pt/OMC, Pt/AC, and Pt/MC due probably to very small-sized of Pt nanoparticle and/or highly well-dispersed of Pt nanoparticle on the carbon support and/or the low amount of Pt deposited on carbon support.

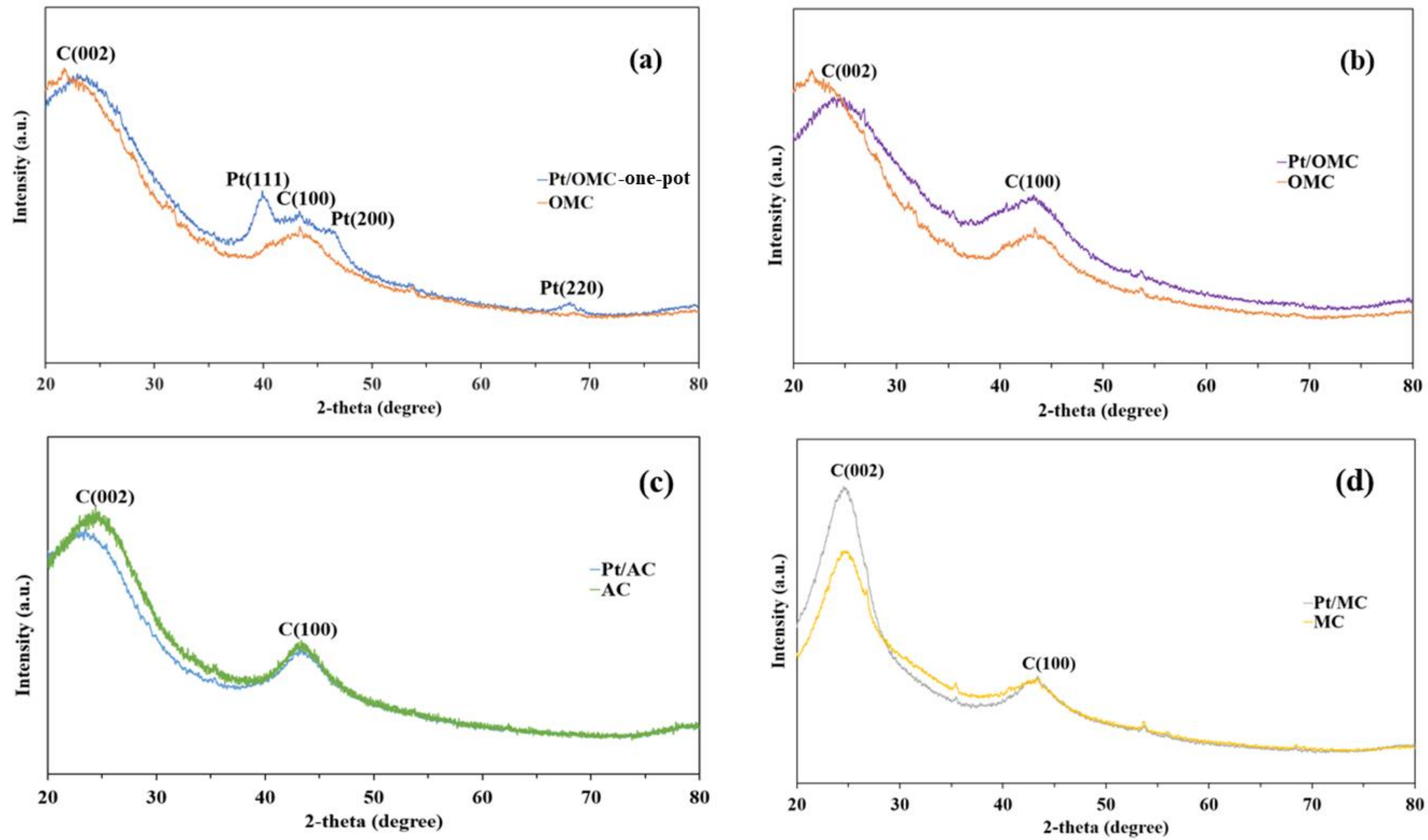

Figure 4. 3 XRD patterns of the catalysts: (a) Pt/OMC-one-pot and OMC; (b) Pt/OMC and OMC; (c) Pt/AC and AC; and (d) Pt/MC and MC.

The H_2-reduction profiles of the prepared catalysts characterized are shown in **Fig. 4.4**. The Pt/OMC- one-pot and Pt/OMC and Pt/AC catalysts showed three reduction peaks at 200-300 °C, 300-370 °C, and 370-700 °C. The reduction peaks at around 200-370°C were associated with the reduction of Pt species interacting strongly with the supports. The reduction behaviors are in good agreement with the other carbon-supported Pt catalysts reported in the literature [20, 56]. Moreover, the possible involvement of the reduction of oxygen-containing functional groups of the carbon support surface itself can also occur at such temperature range. The oxygen groups on the surface of carbon supports have been reported to be bonded with Pt species, therefore strengthening the interactions between the Pt species and support, leading to slightly higher reduction temperatures, but still in the range of 200-370°C [64]. The reduction temperature of Pt/AC was higher than that of Pt/OMC, indicating a stronger interaction between Pt and the carbon support in Pt/AC than in Pt/OMC [20, 61]. The third reduction peak was related to the carbon gasification process to form methane [56]. It is suggested that the formation of methane occurs in the temperature range of 390-800 °C. Nevertheless, Pt/MC catalyst contained only small Pt particles, reduction peaks for Pt species could not be clearly identified and only reduction peak of the gasification was observed. The total H_2 consumption below the temperature for methanation of the supported Pt catalysts decreased in the order: Pt/OMC (0.0325 mmol/g) > Pt/OMC-one-pot (0.0292 mmol/g) > Pt/AC (0.0285 mmol/g) (Table 1), which conformed to Pt actual amount from the ICP-OES.

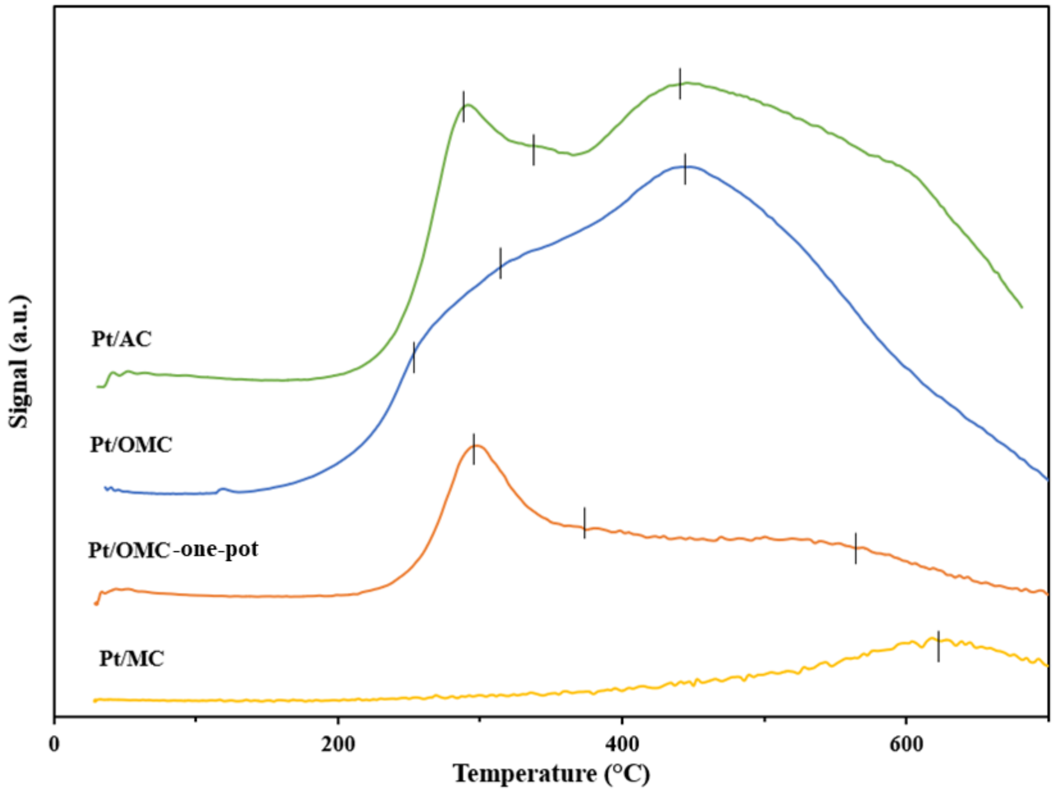

Figure 4. 4 H_2 temperature-programmed reduction profiles of the catalysts.

4.1.3.2 Catalytic reaction study

The catalytic performances of the prepared catalysts were evaluated in the selective hydrogenation reaction of furfural to FA under mild conditions (temperature of 50 °C and H_2 pressure of 2 MPa). Prior to the reaction test, all the wet-impregnated catalysts were reduced at 400 °C for 2 h under H_2 flow. The catalyst prepared via one-pot method was used without the reduction step. However, due to its high content of C element, the carbon precursors can act as “a reducing agent” for the active metal nanoparticles (Pt in this case), so that the conventional reducing using H_2 gas, usually employed for preparation of metal–based catalysts can be totally ignored. In a liquid-phase reaction, the choice of solvent usually has an impact on the catalytic activity [19]. Von Arx et al. [65] demonstrated that the most important solvent effects in the hydrogenation of α, β-unsaturated aldehydes are usually related to solvent polarity, solubility of hydrogen, and interaction between the catalyst and the solvent as well as solvation of reactants in the bulk liquid phase. Thus, methanol and water were used as the solvent in this study. The catalytic test results are shown in **Table 4.2.** When using methanol as the solvent, the conversion of furfural varied in order: Pt/OMC-one-pot (>99.99%) > Pt/MC (95.8%) > Pt/OMC (90.6%) > Pt/AC (53.9%), while FA selectivity was gradually descending in the order: Pt/AC (58.0%) > Pt/OMC (25.0%) > Pt/MC (8.1%) > Pt/OMC-one-pot (0%). Over the Pt/OMC-one-pot catalyst, FA product was not detected. It was found that furfural was completely transformed to 2-furaldehyde dimethyl acetal, which is the side reaction product that occurred from the methanol reacted with furfural, so-called solvent product (SP). A simplified reaction pathway of furfural hydrogenation is shown in **Fig. 4.5** [16]. SP may be observed when using alcohols solvent such as ethanol, methanol, isopropanol, and n-butanol [16, 19, 56]. The other by-products include 2-methylfuran and 1-pentanol, which were formed via hydrogenolysis of FA and ring-opening of 2- methylfuran, respectively [1]. According to Zhu Y. et al., the hydrogenolysis of C–OH is preferred on atomic Pt, affording 2-methyfuran [66].

Table 4. 2 Catalytic reaction of the selective hydrogenation of furfural to furfuryl alcohol over the prepared catalysts.

Catalyst	Solvent	Conversion (%)	Selectivity (%)			FA Yield (%)
			FA	SP	Others[b]	
Pt/OMC-one-pot[a]	Methanol	>99.99	-	>99.99	-	-
Pt/OMC	Methanol	90.6	25.0	75.0	-	22.7
Pt/AC	Methanol	53.9	58.0	4.1	37.9	31.3
Pt/MC	Methanol	95.8	8.1	52.4	39.5	7.8
Pt/OMC-one-pot[a]	Water	93.4	72.1	-	27.9	67.3
Pt/OMC	Water	70.5	37.5	-	62.5	26.4
Pt/AC	Water	81.8	45.2	-	54.8	37.0
Pt/MC	Water	50.1	36.1	-	63.9	18.1

Reaction (50 μL furfural in 10 mL solvent) at 50°C with a 50 mg catalyst under 2 MPa of H_2 for 120 min in methanol and 60 min in water and catalysts were reduced at 400°C, 2h in H_2 flow. [a] Catalyst was used without reduction step.

[b] The by-products include 2-methylfuran and 1-pentanol.

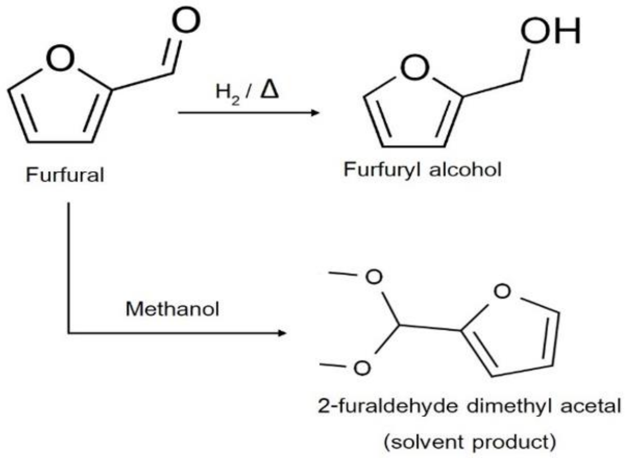

Figure 4. 5 Simplified reaction scheme of the hydrogenation of furfural.

To avoid the side reaction product, water was employed as a green solvent, which has many advantages including low cost, safety, and no environmental impact. The conversion of furfural under aqueous solvent varied in order: Pt/OMC-one-pot (93.4%) > Pt/AC (81.8%) > Pt/OMC (70.5%) > Pt/MC (50.1%), similar trend for FA selectivity was ranged in the order of Pt/OMC-one-pot (72.1%) > Pt/AC (45.2%) > Pt/OMC (37.5%) > Pt/MC (36.1%). In this study, the 5.6 nm Pt particles of Pt/OMC-one-pot gave the highest conversion and selectivity, while the 1.2 nm particles showed the lowest conversion and selectivity. This suggest that the hydrogenation activity increased with increasing Pt nanoparticle size. A similar observation trend was reported by Tsang et al. [67] and Pushkarev et al. [68]. The product selectivity changed as function of size and shape of Pt nanoparticle in vapor-phase furfural hydrogenation in which the Pt particles above 3 nm produced predominately FA. The size effect of Pt was investigated in the selective hydrogenation of cinnamaldehyde [69]. They reported that selectivity to cinnamyl alcohol depend on Pt nanoparticle size, low selectivity was found on small Pt nanoparticles due to the presence of more low coordination. The low coordination sites favor C=C hydrogenation and decrease C=O hydrogenation. The fraction of low coordination sites decreases with increase in the size of Pt nanoparticle, therefore C=O hydrogenation activity was higher on larger size Pt nanoparticle [67, 69]. However, Pt nanoparticle size were not significantly different between Pt/AC and Pt/OMC, the 2.5 nm particles of Pt/AC provided higher conversion and selectivity than the 3.2 nm particle of Pt/OMC. There could be other factors affecting to C=O hydrogenation such as the metal-support interaction. From the TPR results, Pt/AC showed stronger interaction between Pt and C, hence higher FA selectivity was obtained. In addition, for Pt/OMC, most Pt particles may be located deep inside the rod shape structure pores which appeared to favor the pathway for hydrogenation of C=O bond with methanol, resulting in 2-furaldehyde dimethyl acetal solvent product.

Comparing between methanol and water, the reaction in water showed the best activity for furfural hydrogenation over Pt/OMC-one-pot, giving 67.3% yield toward FA with desired FA selectivity of 72.1%. On the other hand, when methanol was used as solvent, 2-furaldehyde dimethyl acetal was detected as solvent product with selectivity >99%. The use of water solvent could provide high furfural conversion and FA selectivity [19]. Moreover, the Pt/OMC-one-pot catalyst was effective in hydrogenation reaction in the polar solvent. A comparison of the performances of the Pt/OMC-one-pot in this study and other previously reported Pt-based catalysts over different carbon supports in the liquid-phase furfural hydrogenation is shown in **Table 4.3**. The catalysts prepared in this study showed relatively high/comparable activities and selectivities of the desired product, compared to those reported in the literature but with lower amount of Pt loading, shorter reaction time under mild condition, and without the reduction step.

Table 4. 3 Comparison of the prepared catalysts and reported in the literature for the liquid phase hydrogenation of furfural on carbon-supported Pt catalysts.

No.	Metal loading (wt%)	Supports	Preparation Method	Reduction Temperature (°C)	Reaction Conditions	Solvent	Reaction Time (h)	Reaction Results		Ref.
								Conversion (%)	Selectivity (%)	
1	0.5	OMC	One-pot	-	50 °C, 2 MPa H_2	H_2O	1	93.4	72.1	This work
2	0.47	MWNT	Impregnation	400	100 °C, 3 MPa H_2	Ethanol	5	64.5	37.6	(38)
3	3	BC	Wet Impregnation	250	210 °C, 10.3 MPa H_2	Toluene	2	60.8	79.2	(42)
	3	BC	Wet Impregnation	250	210 °C, 10.3 MPa H_2	Isopropanol	2	42.9	81.3	
	3	BC	Wet Impregnation	250	250 °C, 10.3 MPa H_2	Isobutanol	2	57.1	88.6	
	3	BC	Wet Impregnation	250	210 °C, 10.3 MPa H_2	Hexane	2	52.3	80.2	
4	0.5	g-C_3N_4 nanosheets	Ultrasound-Assisted	-	100 °C, 1 MPa H_2	H_2O	5	32.1	>99	(15)

			Reduction						
	5	g-C_3N_4 nanosheets	Ultrasound-Assisted Reduction	-	100 °C, 1 MPa H_2	H_2O	5	>99	>99	
	5	g-C_3N_4 nanosheets	Ultrasound-Assisted Reduction	-	100 °C, 1 MPa H_2	H_2O	1	90.3	>99	
	5	g-C_3N_4 nanosheets	Ultrasound-Assisted Reduction	-	100 °C, 2 MPa H_2	H_2O	1	98%	98.9	
5	5	MWNT	Wet Impregnation	250	150 °C, 2 MPa H_2	1wt% tetradecane in propanol	5	94.4	79	(17)
	5	MWNT	Wet Impregnation	250	100 °C, 4 MPa H_2	1wt% tetradecane in propanol	5	75.8	75.8	
6	3	C	Wet Impregnation	400	180 °C, 1 MPa H_2	Isopropyl alcohol	8	100	71	(43)
7	5	Pt/NC-BS-500	Ultrasound-Assisted	-	100 °C, 1 MPa H_2	H_2O	4	>99	>99	(28)

		Reduction						
5	Pt/NC-BS-500	Ultrasound-Assisted Reduction	-	100 °C, 1 MPa H_2	H_2O	1	75.4	>99

4.1.3.3 The recyclability of the catalysts

The recyclability of the catalysts for hydrogenation of furfural to FA is shown in **Fig. 4.6**. The catalysts were recycled for 3 times. After each reaction test, the catalysts were separated, washed by de-ionized water, and then dried in an oven at 110 °C overnight without other treatment steps. All the catalysts showed decrease in furfural conversion by 35-50 %, except Pt/MC that the activity was not significantly dropped after the 3rd run. From the TEM images of the spent catalysts (**Fig.4.7**), the average Pt particle sizes for Pt/OMC-one-pot, Pt/OMC, Pt/AC, and Pt/MC were 5.4, 2.8, 1.9, and 0.9 respectively. Except Pt/MC, the Pt particle sizes were not reduced after recycled for 3 times. Besides, the rod structure of OMC might be destroyed after reaction. Moreover, for any catalyst used, there were no differences in the O/C ratios between the fresh and the spent ones (**Table 4.4**). It suggests that deposition of carbon species from the liquid phase was not the major cause for catalyst deactivation under the conditions used. The actual amount of Pt on the spent catalysts were determined from the ICP-OES to be 0.38-0.49 wt%, which were lower compared to the fresh ones. Among the various prepared catalysts, the Pt/AC showed the least percentage of Pt loss (∼6%). The stronger metal-support interaction on the Pt/AC would be beneficial to lower the metal loss by leaching during the liquid-phase reaction. Some of the large size Pt particles with weak metal-support interaction could be leached out during the liquid-phase reaction. As a consequence, all the catalysts exhibited similar furfural conversion to those of the Pt/MC that contained only small Pt particles after 3 cycles of reaction tests. The significant drop of catalyst activity of the Pt/OMC-one-pot comparing to the other catalysts could be due to the loss (leaching) of larger Pt particles (∼32%) which exhibited higher activity than smaller size Pt particles. Nonetheless, improvement on the stability of catalysts should be done and has recently been carried out in our group. To prevent the loss of active components (especially Pt in our case) from the carbon supports during recyclability, incorporation of N atoms into the OMC matrix could possibly enhance the strong Pt-support interaction. This can result in the better stability of the catalysts even under harsh liquid-phase conditions because of the better dispersion without aggregation and strong attachment of Pt nanoparticles by N heteroatoms [70].

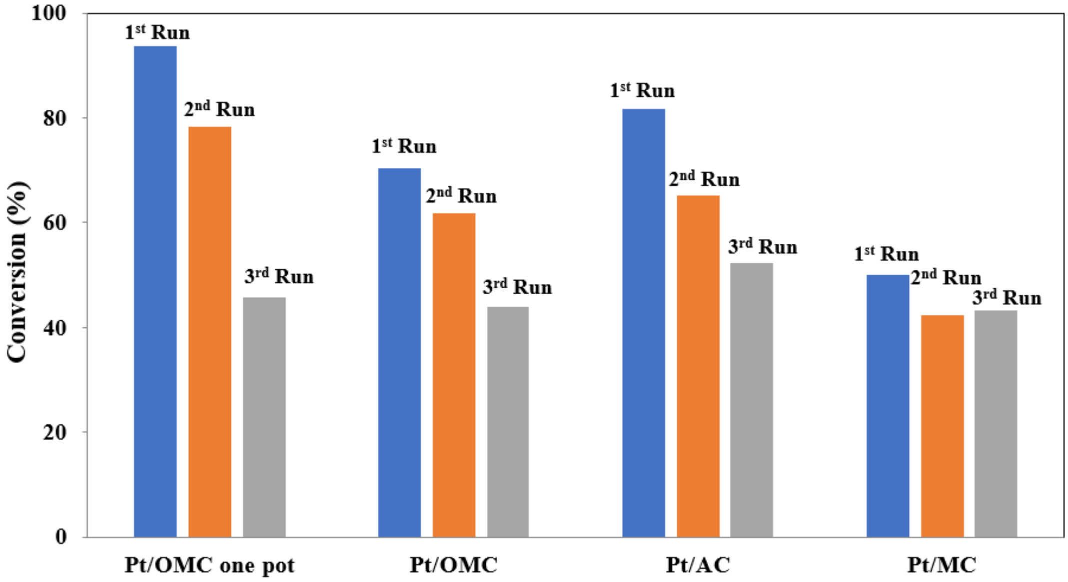

Figure 4. 6 Catalyst recyclability with the catalysts for the conversion of furfural to furfuryl alcohol.

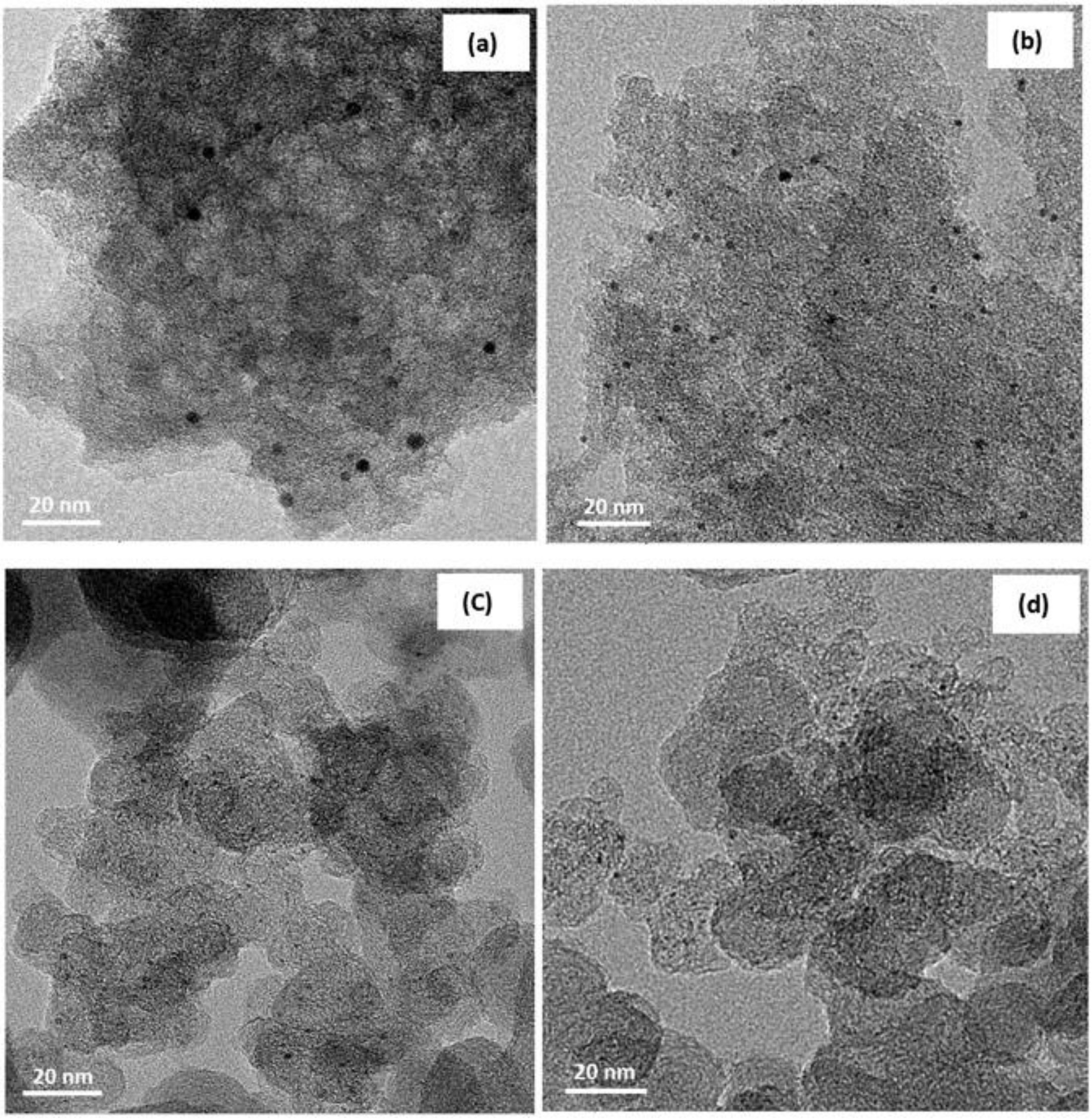

Figure 4. 7 TEM images the used catalysts after third run: (a) Pt/OMC-one-pot; (b) Pt/OMC; (c) Pt/AC; and (d) Pt/MC.

Table 4. 4 Characterization results of the spent catalysts after 3rd run from ICP-OES, TEM, and SEM-EDX.

Catalyst	ICP results (Pt loading, wt%)		TEM results (Pt particle size, nm)		EDX results (wt%)							
					C		O		Pt		O/C ratio	
	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent
Pt/OMC-one-pot	0.56	0.38	5.6	5.4	88.9	86.9	9.8	12	1.3	1.1	11.0	13.8
Pt/OMC	0.78	0.39	3.2	2.8	88.6	87.0	9.5	11.7	1.9	1.2	10.7	13.5
Pt/AC	0.51	0.48	2.5	1.9	88.8	88.6	9.8	9.7	1.4	1.7	11.0	11.0
Pt/MC	0.68	0.49	1.2	0.9	93.8	92.0	4.8	6.2	1.3	1.9	5.1	6.7

4.2 Article II

Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon

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Article II: Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon

Abstract

Ferromagnetic element (x = Fe, Co, Ni, and Nd) promoted Pt/AC catalysts were prepared by co-impregnation method or physical mixing and tested in the liquid-phase hydrogenation of furfural to furfuryl alcohol (FA) under mild conditions (50°C and 20 bar H_2) using water and methanol as the solvent. Among the various catalysts studied, the 0.15FePt/AC exhibited complete conversion of furfural with FA selectivity 74% after only 1 h reaction time in water. The promotional effect of the bimetallic catalysts became less pronounced when methanol was used as the solvent and 2-furaldehyde dimethyl acetal solvent product was formed. The superior catalyst performances were correlated with the higher Pt dispersion, the presence of low coordination Pt sites and the strong Pt-Fe interaction as characterized by X-ray diffraction, H_2-temperature programmed reduction, N_2-physisorption, and infrared spectroscopy of adsorbed CO (CO-IR). However, to simply use a magnet for catalyst separation, 0.5 wt% Fe was the minimum Fe loading on the Pt/AC. The 0.5FePt/AC still exhibited good magnetic properties after the 3rd consecutive runs.

Keywords: furfural; furfuryl alcohol; hydrogenation; water and methanol; platinum-base catalysts

4.2.1 Introduction

Energy crisis and environmental pollution have currently been confronting human life due to increasing global energy consumption. Alternative energy resources such as solar, hydropower, wind, geothermal, and biomass have been extensively explored. Renewable biomass is a promising resource to use as feedstock instead of fossil fuel for production of many petrochemical products. Furfural, a biomass-derived chemical produced by acid-catalyzed dehydration of xylose [4], can be converted into a wide range of value-added derivative molecules [1]. Approximately 62% of furfural produced is transformed into furfuryl alcohol (FA) by selective hydrogenation reaction [2]. FA is an interesting high value chemical and important chemical in the fine chemical industry of lubricants, adhesive, drug intermediates, and dispersing agents and in the polymer industry of phenolic resin, furfural resin, and furan resin [6].

The selective hydrogenation of furfural to FA is an interesting reaction because furfural contains two powerful functional groups, an aldehyde (C=O) and a conjugated system (C=C─C=C) [1]. To produce FA, furfural is hydrogenated at the aldehyde group (C=O) and then transformed to FA. The catalytic hydrogenation of furfural to FA is usually performed either in the gas or liquid phase [8-11]. Compared to gas-phase hydrogenation process, liquid phase hydrogenation of furfural has the advantages of high selectivity and low energy consumption [12]. In the present industrial processes of furfural production, copper chromite (Cu–Cr) is being used as the catalyst for both liquid-phase and gas-phase furfural hydrogenation [13], performing under high temperature (between 130 and 200^{o}C), and high pressure (up to 30 bar) conditions. Although copper chromite exhibits good activity and selectivity toward FA, serious environmental pollution due to toxicity of Cr species is being concerned [16]. A variety of Cr-free catalysts have been investigated, including precious metal catalysts such as Pt [16-21], Ru [24, 55], and Pd [25, 26] and nonprecious metal catalysts such as Co[71] , Cu [5, 30] and Ni [31, 32]. Among these catalysts, Pt exhibits good catalytic performances for selective hydrogenation of furfural to FA under mild conditions. Addition of a second metal including Co, Ni, Fe has resulted in significant improvement of Pt-based catalysts for FA production. Liu et al.[56] prepared bimetallic catalyst by adding Fe, Co, and Ni as promoter by co-impregnation method and tested in the hydrogenation of furfural at 100 ^{0}C, 30 bar H_2 for 5 h. All the promoters exhibited positive effect on furfural hydrogenation, especially Fe and Ni in which furfural conversion and FA and tetrahydrofurfuryl alcohol (THFA) selectivity were significantly improved. Tolek et al. [72] reported the performances of bimetallic PtCo/TiO_2 with 0.7wt%Pt and 0-0.4 wt%Co selective furfural hydrogenation to FA. The Pt-0.2Co/TiO_2 catalyst showed the best performance with 100% conversion of furfural and 97.5% selectivity towards FA. Dohade and Dhepe [58] also indicated that Pt-Co supported on activated carbon presented the improved activity compared to monometallic catalyst when the reaction was carried out at 180^{o}C for 8 h. Although the improvement of Pt catalysts promoted by ferromagnetic element such as Fe and Ni as promoter for Pt catalysts in the hydrogenation of furfural to FA has been demonstrated, the comparison of the catalytic performances among them as well as their magnetic properties have been reported to a less extent, especially under different solvents. In liquid phase reaction, carbon powders are extremely difficult to separate from solution and typically require complex and expensive steps such as filtration or centrifugation. The magnetic properties of catalysts make catalyst separation easy by using a simple external magnet. The magnetic properties of catalysts have been utilized in the hydrogenation of furfural to furfuryl alcohol over Ni-Fe alloy [50] and Fe(NiFe)O_4–SiO_2 nanoparticles catalysts [7]. Both catalytic and magnetic properties of carbon supported Pt catalysts with ferromagnetic element promoters have not yet been reported.

In this work, we aimed to compare the liquid phase hydrogenation of furfural to FA using various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts under relatively mild reaction conditions (50 ^{o}C and 20 bar H_2) using water and methanol as the solvent. The structural-activity relationship was investigated by means of X-ray diffraction, H_2-temperature programmed reduction (H_2-TPR), N_2-physisorption, and infrared spectroscopy of adsorbed CO (CO-IR). Magnetic property and reusability of the catalysts were also discussed.

4.2.2 Experimental

4.2.2.1 Catalyst preparation

The Pt/AC (0.5 wt%) , FePt/AC (0.5 wt%Pt and 0.1-10 wt%Fe), and 0.15MPt/AC (0.5 wt%Pt and 0.15wt%M: Ni and Co) were prepared by co-impregnation method using commercial activated carbon (C=90.81%, O=9.02% and P=0.18%), tetraammineplatinum (II) chloride hydrate ($(Pt (NH_3)_4Cl_2{\cdot}xH_2O)$, 99.99%, Sigma-aldrich, Darmstadt, Germany), ferric nitrate nonahydrate ($FeN_3O_9.9H_2O$, ≥ 97.0%, Fluka, Buchs, Switzerland), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, ≥ 98.0%, Carlo Erba, Milano, Italy), and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, ≥ 98.0%, ACS, Darmstadt, Germany), as C, Pt, Fe, Co, and Ni precursors, respectively.The Pt and the second metal precursors were dissolved in deionized water and then the aqueous solution was slowly dropped onto the activated carbon. The impregnated catalysts were dried overnight at 110 ^{o}C in an oven. Finally, the catalysts were calcined in N_2 at 500 ^{o}C for 2 h. The catalysts were denoted as Pt/AC and xMPt/AC when x was wt% and M was the second metal. The 0.15NdPt/AC (0.5 wt%Pt and 0.15wt%Nd) was prepared by physical mixing. Firstly, the Pt/AC catalyst from impregnation was mixed with neodymium powder (< 400 mm, Nd ≥ 99.0%, Aldrich) in toluene at room temperature and stirred for 40 min for uniform mixing. The solvent was removed from the mixture by centrifugation and washed by DI water. Then, the solid catalyst was dried at 110 ^{o}C overnight and calcined at 500 ^{o}C for 2 h in N_2 flow. The catalysts were denoted as 0.15NdPt/AC.

4.2.2.2 Catalyst Characterization

The H_2-TPR measurements were carried to determine reducibility and reduction temperature of the Pt-based catalysts. A quartz U-tube reactor was used, and all the catalyst samples were pretreated with a N_2 flow (25 mL/min, 1 h, 150°C). The TPR profiles were obtained by passing carrier gas (10% H_2 in nitrogen) through the catalyst samples (25 mL/min, ramping from room temperature to 800°C at 10°C/min). The BET (Brunauer–Emmett–Teller) surface area, average pore size diameter, and pore size distribution were determined by physisorption of N_2 using a

Micrometrics ASAP 2020 instrument. The morphologies of the catalysts were determined by JEOL-6400 scanning electron microscope and the elemental distribution over the catalyst surface were determined by Link Isis Series 300 program energy dispersive X-ray spectroscopy, respectively. The XRD patterns were collected using a Bruker D8 Advance with a Ni filter and Cu K_α radiation. The platinum active sites were determined by CO pulse chemisorption technique using a Micromeritics ChemiSorb 2750 (pulse chemisorption system). The FT-IR spectra of adsorbed CO were collected using FTIR-620 spectrometer (JASCO) with a MCT detector at a wavenumber resolution of 2 cm^{-1}. The sample was heated to 500°C and reduced by H_2 for 2 h. The actual metal loadings were determined by inductive coupled plasma-optical emission spectroscopy (ICP-OES) technique.

4.2.2.3 Catalyst activity

The catalyst activity was tested in liquid phase selective hydrogenation of furfural to furfuryl alcohol. Reactions were performed in a 100 mL stainless steel autoclave reactor (JASCO, Tokyo, Japan). Prior to the catalyst test, the catalysts were reduced under H_2 flow (25 cm^3/min) at 500 ^oC for 2 h. For the furfural hydrogenation reaction, approximately 50 mg of catalyst, 50 μL of furfural and 10 mL of solvent were added into reactor. Then reactor was purged with hydrogen three times for removing the air. After that the reaction was performed at 50^{o}C, 2 MPa of H_2 under stirring. The hydrogenation of furfural was carried out at 50^{o}C for 2 h in methanol and 1 h in water. After completion of the reaction, the reactor was cooled to below room temperature with an ice-water mixture and depressurized carefully. For methanol solvent, the liquid products were analyzed by a gas chromatograph Shimadzu GC-2014 equipped with a flame ionization detector (FID), the Rxt-5 capillary column with 30 M length and 0.32 mm inside diameter were used. Then 0.2 μL was injected into the column and helium was used as a carrier gas. In the case of distilled water solvent, the liquid products were analyzed a high-performance liquid chromatography (Shimadzu 20A) equipped with column Aminex HPX-87H (300 × 7.8 mm). The injection volume was 10 μL and the absorbance detector wavelength was set at 215 nm. The mobile phase was composed of 86% H_3PO_4 0.1N and 14% acetonitrile (HPLC grade) and the flow rate was 0.4 mL min^{-1}.

4.2.3 Results and Discussion

4.2.3.1 Catalyst characterization

The XRD patterns of Pt/AC and Pt-based bimetallic catalysts prepared by impregnation and physical mixing in the range of diffraction angles (2θ) between 20^o and 80^o are shown in **Fig. 4.8.** The characteristic diffraction peaks at 2θ = 24.4°, 35.5° and 43.3° could be attributed to graphitized activated carbon [62, 63]. However, higher intensity of the diffraction peak at 2θ = 35.5° was clearly observed on 5FePt/AC and 10FePt/AC, which could possibly due to the overlap of diffraction peak of iron, which occurred at around 35.7° [73]. There were no characteristic diffraction peaks corresponding to platinum, cobalt, nickel, and neodymium species detected for all the catalysts due probably to the low amounts of metal present and/or high dispersion of these metals on the carbon supports and/or very small crystallite size of these metal particles.

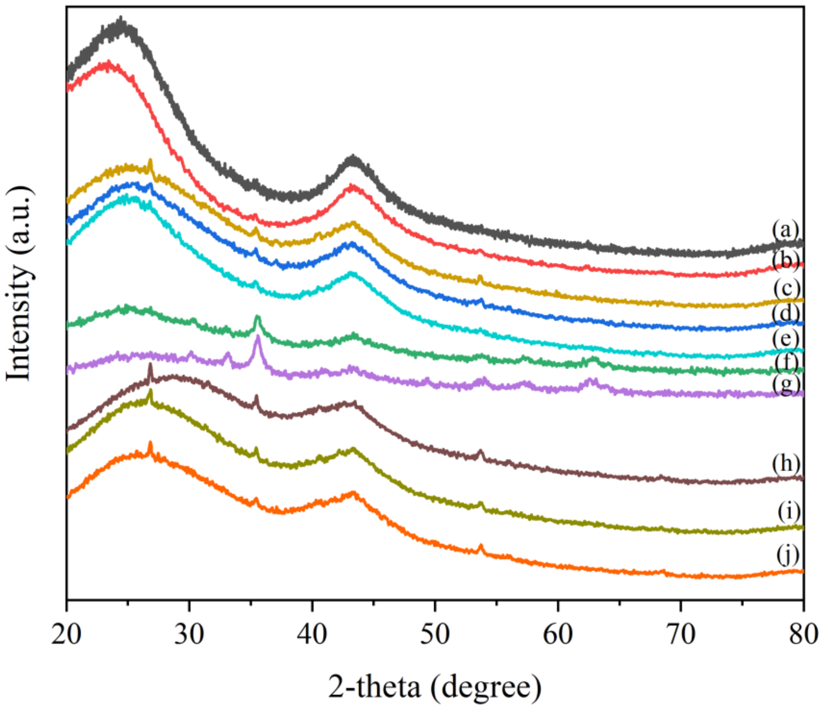

Figure 4. 8 XRD pattern of Pt-based catalyst: (a) AC, (b) Pt/AC, (c) 0.1FePt/AC, (d) 0.15FePt/AC, (e) 0.2FePt/AC, (f) 5FePt/AC, (g) 10FePt/AC, (h) 0.15CoPt/AC, (i) 0.15NiPt/AC and (j) 0.15NdPt/AC.

Nitrogen adsorption isotherms for the Pt/AC and Pt based bimetallic catalysts are shown in **Fig. 4.9**. All the catalysts samples exhibited type I isotherm, and the stepwise increase in the adsorption branch expressed the presence of both micropores and mesopores. The ICP-OES, N_2 physisorption, and CO chemisorption results are given in **Table 4.5**. The actual loadings of Pt and the second metals were close to their nominal values. For a similar second metal loading (e.g. 0.15MPt/AC), the calculated atomic ratios of Pt:M were in the range of 0.66-1.57. The BET surface area, the pore volume and the pore diameters are summarized in **Table 4.5.** All the prepared supported carbon catalysts exhibited high surface area in the range of 755 – 988 m^2/g with the 0.15FePt/AC had the highest surface area of 988 m^2/g. For the lowest Fe loading 0.1FePt/AC, the BET surface area was not significantly different from the monometallic Pt/AC (804 and 793 m^2/g, respectively). The BET surface area of the bimetallic xMPt/AC (M = Fe, Co, and Ni) with x = 0.15-5 wt% was higher than that of Pt/AC. Such results suggest that the second metal may be highly dispersed as small particles on the external surface of the AC supports, which could create heterogeneity and roughness that led to an increased BET surface area. The Fe dispersion would be maximized on the 0.15FePt/AC so that it exhibited the highest BET surface area (smallest Fe particles). As the Fe loading increased, larger Fe particles would form and as the consequence the surface area decreased. The lowest BET surface area 755 m^2/g was observed on the highest Fe loading 10FePt/AC.

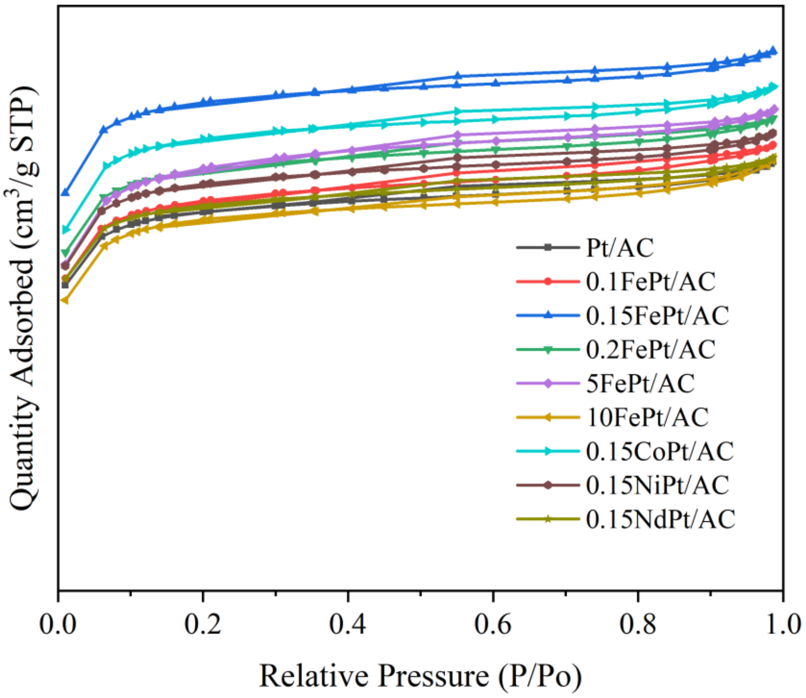

Figure 4. 9 Nitrogen adsorption/desorption results of Pt-based catalyst.

Table 4. 5 Atomic ratio, N_2 physisorption properties, CO-IR analysis, and Active sites of Pt-based catalyst.

Catalyst	ICP results (Metal loading, wt%)[a]		Atomic ratio (Pt/M)[b]	N_2 physisorption properties			The ratio of CO adsorption on Pt atom at edge sites and Pt terrace[d]	Active sites ($\times 10^{18}$ molecule CO/g cat.)[e]
	Pt	M (M = Fe, Co, or Ni)		Surface area (m^2/g)	Pore Volume (cm^3/g)[c]	Average pore size (nm)[c]		
Pt/AC	0.51	-	-	804	0.092	3.5	0.09	0.95
0.1FePt/AC	n.d.	n.d.	n.d.	793	0.110	3.4	n.d.	n.d.
0.15FePt/AC	0.53	0.23	0.66	988	0.102	3.2	0.47	5.69
0.2FePt/AC	n.d.	n.d.	n.d.	852	0.106	3.3	n.d.	n.d.
5FePt/AC	0.50	4.70	0.03	860	0.129	3.1	n.d.	n.d.
10FePt/AC	0.42	9.50	0.013	755	0.109	3.9	n.d.	n.d.
0.15CoPt/AC	0.52	0.10	1.57	915	0.104	3.4	0.21	2.94
0.15NiPt/AC	0.47	0.16	0.88	826	0.110	3.4	0.34	0.82
0.15NdPt/AC	0.48	n.d.	n.d.	780	0.094	3.5	0.16	1.85

n.d. = not determined

[a] Metal loading measured by ICP-OES

[b] Calculated from percentage of metal loading

[c] Calculated from BJH desorption method

[d] Based on CO-IR result

[e] Based on CO-chemisorption

The morphologies and elemental distribution of the catalyst samples were investigated by SEM and EDX. The SEM images of Pt/AC and xMPt/AC are shown in **Fig. 4.10.** All the catalysts showed non-uniform particle size and shape. There were no significant differences in the catalyst morphology when a second metal was added by co-impregnation and physical mixing technique. Moreover, the EDX results from the various 0.15MPt/AC catalysts confirmed the existence of Pt, Fe, Co, Ni, and Nd on the catalyst surface and that the metal could be highly dispersed on the surface.

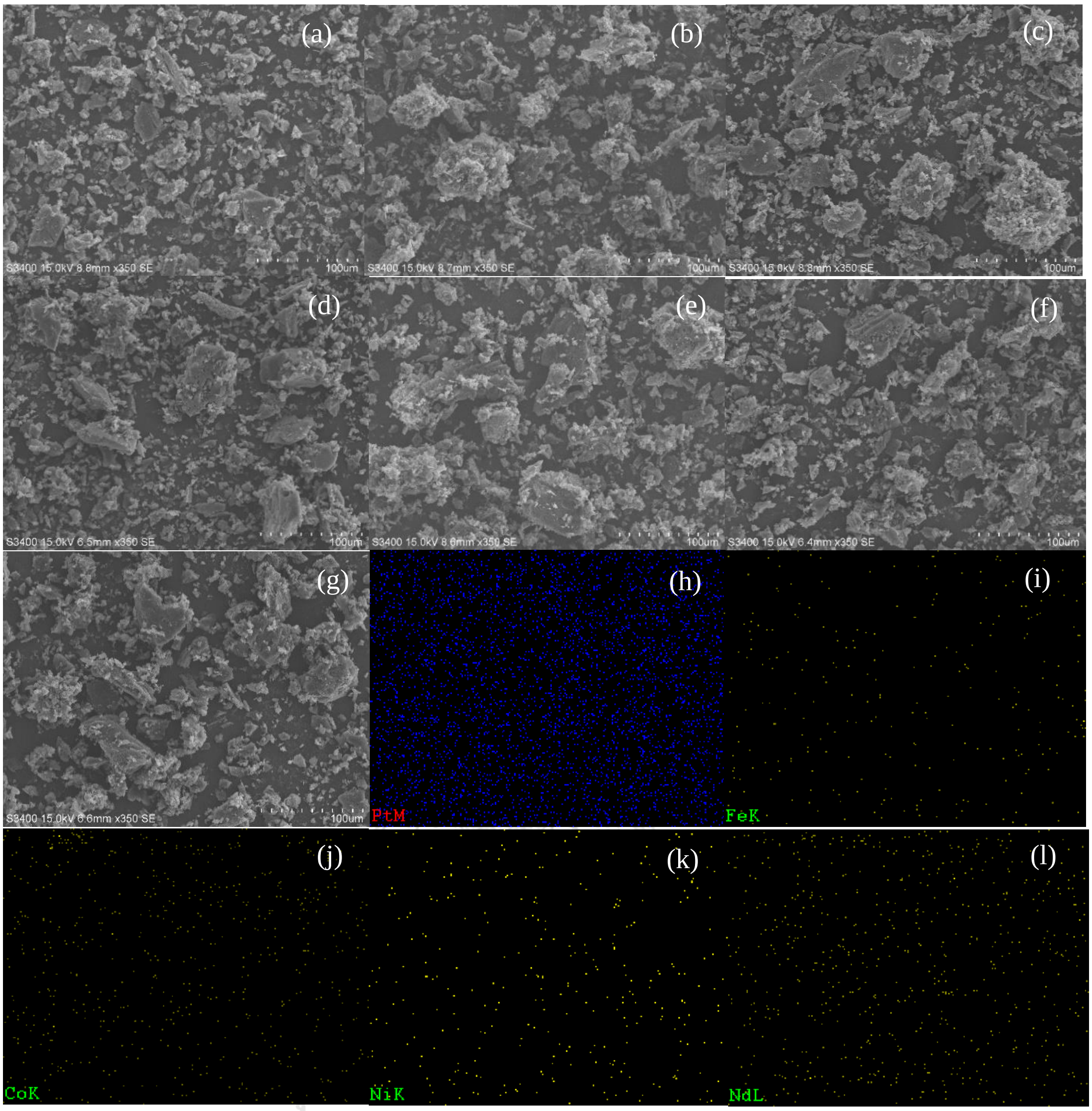

Figure 4. 10 SEM image of (a) Pt/AC; (b) 0.15FePt/AC; (c) 5FePt/AC; (d) 10FePt/AC; (e) 0.15CoPt/AC; (f) 0.15NiPt/AC; (g) 0.15NdPt/AC catalysts and the corresponding elemental mapping images of (h) Platinum; (i) Iron; (j) Cobalt; (k) Nikel; and (l) Neodymium on 0.15MPt/AC.

Magnetic properties were tested by using a simple external magnet to separate the catalyt from liquid media (**Fig. 4.11**). The efficiency of the magnetic separation is highly dependent on the amount of ferromagnetic elements. The minimum %wt. of Fe loading on the Pt/AC to make the catalyst separable from the liquid by a magnet was determined to be 0.5 wt% Fe. The superior catalyst separation by magnet are demonstrated for higher Fe loadings such as 5% and 10% of Fe loadings.

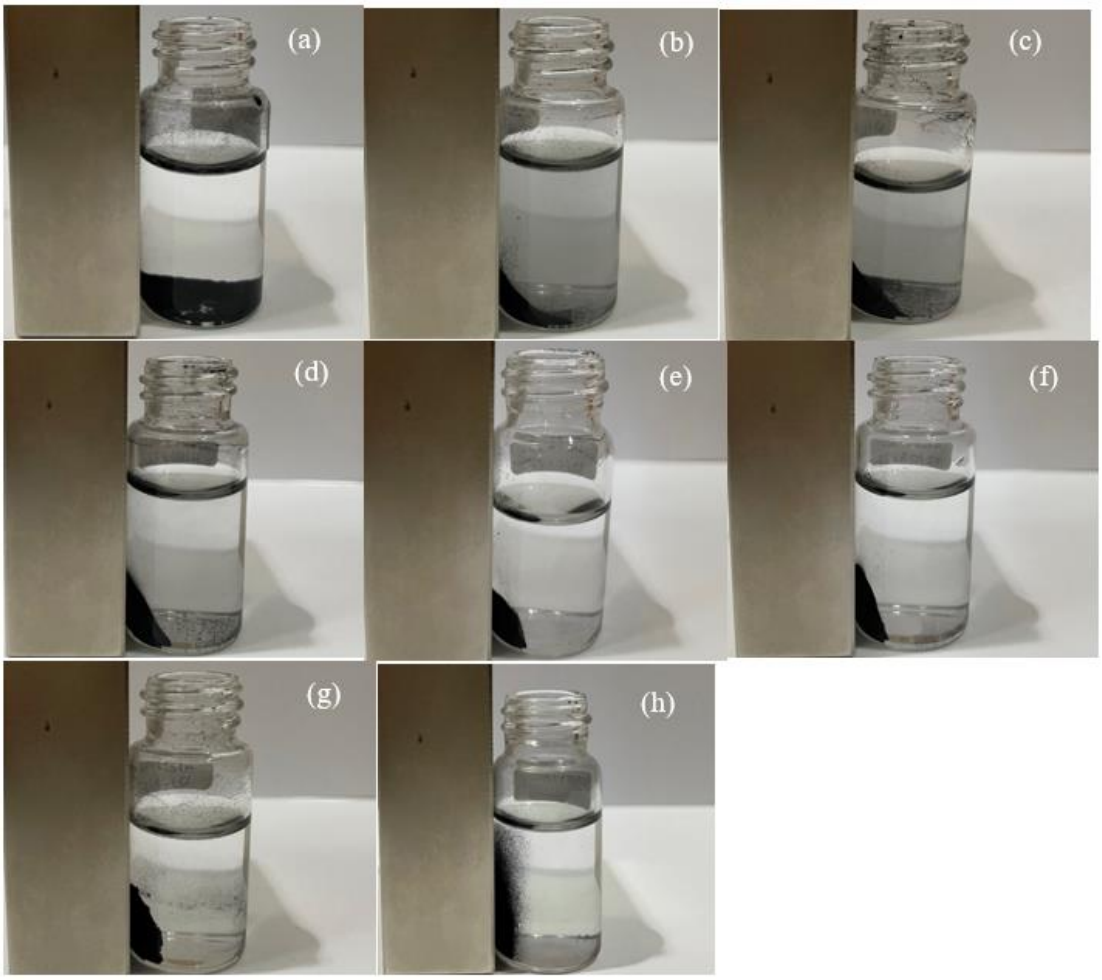

Figure 4. 11 Magnetic separation of (a) 0.15FePt /AC; (b) 0.5FePt/AC; (c) 1FePt/AC; (d) 2FePt/AC; (e) 3FePt/AC; (f) 4FePt/AC; (g) 5FePt/AC; (g) 10FePt/AC.

The characteristic of the surface of dispersed Pt particles was further studied by FT-IR of adsorbed CO on the Pt/AC and Pt-based bimetallic catalysts (**Fig. 5**). The CO adsorption band at around 2,070 – 2,100 cm^{-1} suggests a linear-type of CO adsorption [74] and it has been reported that linear-type adsorbed CO dominated on small Pt particles [75]. For the Pt/AC, the adsorption band at 2108 cm^{-1} could be attributed to the CO adsorbed on coordinated Pt surface like Pt(111) and Pt(100) whereas the band at 2070 cm^{-1} was attributed to the low coordinated Pt sites like edge, kink, and corner ones. For all the bimetallic catalysts, the adsorption bands of both positions were slightly shifted towards higher wavenumber compared to that of Pt/AC. The ratios of CO adsorption on low coordination Pt atoms at edge sites and Pt terrace (111) and (100) are given in **Table 4.5**. It can be seen that all the bimetallic catalysts exhibited larger relative quantity of less-coordinated Pt atoms on edge, kink, and corner, especially for the 0.15 FePt/AC catalyst. In addition, the IR spectra relating to CO adsorbed species on Fe, Co, Ni, and Nd were not detected. Such results are similar to those previously reported by Einaga et al.[76] and Pisduangdaw et al. [77].

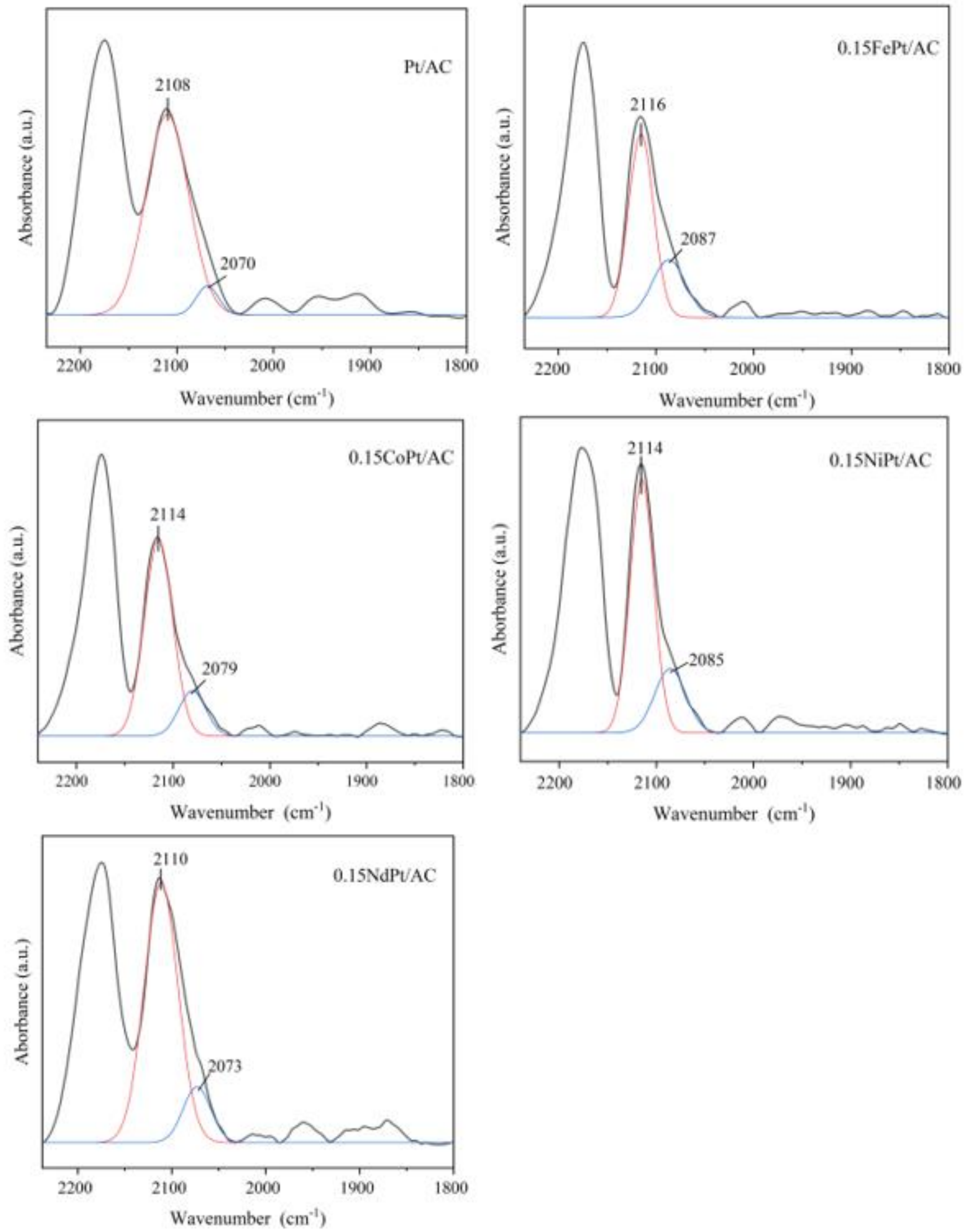

Figure 4. 12 CO-IR result of the Pt-base catalysts.

The amounts of CO chemisorption on the Pt/AC and 0.15MPt/AC catalyst are demonstrated in **Table 4.5**. The number of surface Pt active atoms on all the Pt catalysts derived from CO uptake are ranging between 0.82–5.69 x 10^{18} molecules CO in the order: 0.15FePt/AC > 0.15CoPt/AC > 0.15NdPt/AC > Pt/AC > 0.15NiPt/AC. The relatively low CO uptake on 0.15NiPt/AC maybe due to the partial coverage of second metal on Pt surfaced and/or alloy formation, resulting in low amount of active Pt surface.

The H_2-TPR measurements were carried out to study the reduction behaviors of the monometallic Pt/AC and bimetallic 0.15MPt/AC catalysts and the results are shown in **Fig. 4.13**. Both monometallic Pt/AC and bimetallic 0.15MPt/AC catalysts exhibited three reduction peaks at 230- 270 ^{o}C, 300-350 ^{o}C, and 370-700 ^{o}C. The first reduction peak of Pt/AC catalyst was associated to reduction of Pt oxide to Pt metal [20]. When the second metal Fe, Co, Ni, and Nd were introduced into the monometallic Pt catalysts, the reduction temperature for PtO_x was lower due probably to the formation of smaller Pt oxides particles (higher Pt dispersion) and/or the interaction between the second metal and Pt in the bimetallic catalysts [12]. The second reduction peak was typically correlated to reduction of Pt species interacting with the carbon support. Among the various ferromagnetic element promoted Pt/AC catalysts, the second reduction peak was higher and shifted to higher reduction temperature only when Fe was added, which indicated a stronger interaction between metal and carbon support and/or a Pt-Fe alloy [56]. The third reduction peaks were the carbon gasification process to form CH_4. It had been reported the formation of methane generally occurs in the temperature range 390-800 ^{o}C [56].

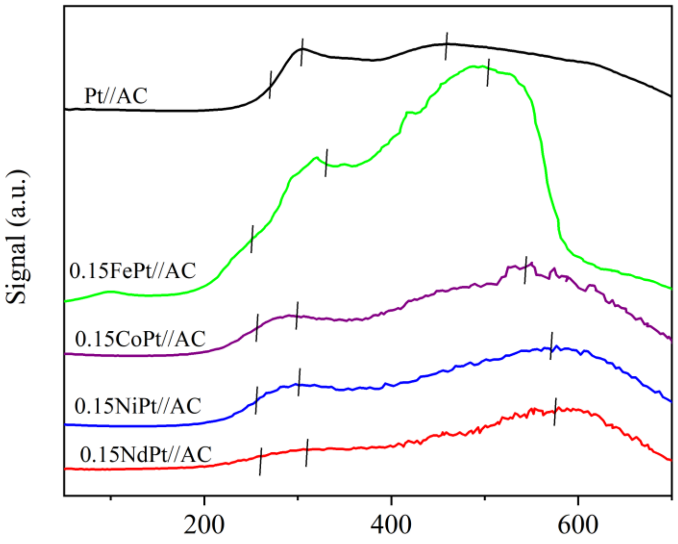

Figure 4. 13 H_2 temperature-programmed reduction profiles of the catalysts.

4.2.3.2 Catalytic reaction study

The catalytic activities of the prepared catalysts were evaluated in the liquid phase hydrogenation of furfural to furfuryl alcohol under mild reaction conditions (temperature of 50 °C and H_2 pressure of 2 MPa). All the catalysts were reduced at 500 ^{o}C in H_2 flow for 2 h before reaction test. In a liquid-phase reaction, the choice of solvent usually has an impact on the catalytic activity [19]. In this study methanol and water were used as the medium to investigate the solvent effect in the hydrogenation of furfural and the results are summarized in **Table 4.6.** The addition of ferromagnetic metal on the Pt/AC catalysts showed different effects on the catalytic performances in the furfural hydrogenation, depending on the solvent used. Using methanol as the solvent, a slight improvement on the FA yield was found on the 0.15%FePt/AC catalyst (36.4%) compared to the Pt/AC (31.3%). Whilst, the other bimetallic 0.15%CoPt/AC and 0.15%NiPt/AC catalysts exhibited much lower FA yield at 22.3% and 11.3%, respectively. In addition, the furfural conversion and FA selectivity decreased with increasing Fe loading from 0.15 to 5 and 10 wt%, especially for the 10FePt/AC that showed the lowest performance. Besides, the 2-furaldehyde dimethyl acetal, solvent product (SP), which is the side reaction product that occurred from the methanol reacted with furfural was found when using methanol as solvent. SP was normally observed in alcohols solvent, not only methanol but also ethanol, isopropanol, etc. [16, 19]. The other by-products include 2-methylfuran and 1-pentanol, which were formed via hydrogenolysis of FA and ring-opening of 2- methylfuran, respectively [2].

Table 4. 6 Catalytic reaction of the selective hydrogenation of furfural to furfuryl alcohol over the prepared catalysts.

	Solvent	Reaction time (h)	Conversion (%)	Selectivity (%)		
				FA	SP	Others[a]
Pt/AC	Methanol	2	53.9	58.0	4.1	37.9
0.15FePt/AC	Methanol	2	64.1	56.8	6.0	37.2
5FePt/AC	Methanol	2	47.6	10.4	1.1	88.5
10FePt/AC	Methanol	2	14.1	0	7.0	93.0
0.15CoPt/AC	Methanol	2	62.9	35.4	1.5	63.1
0.15NiPt/AC	Methanol	2	26.7	42.4	21.3	36.3
Pt/AC	Water	1	81.8	45.2	-	54.8
0.1FePt/AC	Water	1	100	57.4	-	42.6
0.15FePt/AC	Water	1	100	74.1	-	25.9
0.2FePt/AC	Water	1	91.9	65.6	-	34.4
0.5FePt/AC	Water	1	95.9	58.1	-	41.9
5FePt/AC	Water	1	83.6	56.6	-	43.4
10FePt/AC	Water	1	58.4	41.4	-	58.6
0.15CoPt/AC	Water	1	88.1	47.6	-	52.4
0.15NiPt/AC	Water	1	96.7	32.6	-	67.4
0.15NdPt/AC	Water	1	75.5	32.6	-	67.4

Reaction (50 μL furfural in 10 mL solvent) at 50°C with a 50 mg catalyst under 2 MPa of H_2 for 120 min in methanol and 60 min in water and catalysts were reduced at 500°C, 2h in H_2 flow

[a] Based on GC-MS analysis, the by-products include 2-methylfuran and 1-pentanol

The catalytic activity of various amounts of Fe loading and other bimetallic 0.15MPt/AC catalysts were also examined in the aqueous phase hydrogenation of furfural to FA at 50 °C and 2 MPa H_2, 1 h reaction time using water as the solvent (**Table 4.6**). Unlike the use of methanol solvent, when the reaction was carried out in water, all the PtFe/AC showed higher furfural conversion than the monometallic Pt/AC except for the 10FePt/AC. The conversion of furfural varied in the order: 0.15FePt/AC (100%) = 0.1FePt/AC (100%) > 0.2FePt/AC (91.9%) > 5FePt/AC (83.6%) > Pt/AC (81.8%) >> 10FePt/AC (58.4%). And the FA selectivity decreased in the order: 0.15FePt/AC (74.1%) > 0.2FePt/AC (65.6%) > 0.1FePt/AC (57.4%) > 5FePt/AC (56.6%) > Pt/AC (45.2%) ~ 10FePt/AC (41.4%). The results indicated that the xFePt/AC series with small amount of Fe (0.1-0.2 wt%) could improve both furfural conversion and FA selectivity of the Pt/AC catalysts, especially in water solvent. The superior catalyst performances were attributed to high Pt dispersion and a strong interaction between Pt and carbon support and/or the formation of a Pt-Fe alloy [56, 78]. The role of Fe to enhance selectivity of carbonyl compound (C=O) reduction has been suggested by Ananthan S.A. et al. that Pt-Fe sites favoured the di- σCO adsorption, which promoted the activation of the C=O group over the supported Pt-Fe catalysts [79].

Furthermore, the catalytic performances of Pt/AC, 0.15FePt/AC, 0.15CoPt/AC, 0.15NiPt/AC, and 0.15NdPt/AC were also investigated in water solvent. The hydrogenation of furfural to FA can occur from hydrogenation of aldehyde group (C=O). The conversion of furfural of the Pt-based bimetallic catalysts were ranged between 75.5-100%. Improvement in furfural conversion by co-impregnation was correlated to high Pt dispersion with higher Pt active sites as determined by CO chemisorption. Surprising, 0.15NdPt/AC with higher Pt sites results revealed lower hydrogenation activity in the furfural hydrogenation than the monometallic Pt/AC. It is likely that the physical mixing of Nd power and Pt/AC catalyst led to poor Pt-Nd interaction. From the H_2-TPR, the second reduction peak which was attributed to the Pt species strongly interact with the support became flattened on the 0.15NdPt/AC. In other words, addition of Nd could weaken the Pt-support interaction. Hence, the catalyst was less active under the reaction conditions despite its high dispersion. The

FA selectivities of all the other 0.15 MPt/AC catalysts (Co, Ni, Nd) were not much different at around 32.6- 47.6% and were similar to those obtained on the monometallic Pt/AC catalyst (45.2%). The highest conversion of furfural and FA selectivity on the 0.15FePt/AC were in accordance to the high dispersion with high Pt active sites and the strongest Pt-Fe or Pt-C interaction and/or a Pt-Fe alloy as indicated by the shift of the reduction temperature in the H_2-TPR profiles. Moreover, the hydrogenation of the aldehyde group (C=O) would preferentially proceed on less-coordinated Pt sites as edge, corner, and kink.

Considering the solvent effect between methanol and water on all the Pt-based bimetallic catalysts, the use of water exhibited higher conversion and selectivity than methanol, although a shorter reaction time was used (1 h). It can be concluded that the activity and product selectivity in furfural hydrogenation over Pt-based bimetallic catalysts was promoted by the higher polar solvent. It is generally be accepted that hydrogenation of α, β-unsaturated aldehydes are controlled by hydrogen solubility, solvent polarity, and interaction between the catalyst and solvent[80]. A comparison between the Pt-based catalyst in this study and those reported in the literature are summarized in **Table 4.7.** At state-of the art, the highest furfural conversion (>99%) with FA selectivity (>99%) could be obtained on the Pt/NC-BS-500 catalyst, in water solvent but under more severe conditions (100°C and 2 MPa $H_{2)}$, longer reaction time (4 h), and higher amount of Pt loading (5 wt%) [20]. The carbon support material from bamboo shoots were prepared in two- steps, including a hydrothermal treatment and a carbonization process and Pt supported on carbon were prepared using an ultrasound-assisted reduction method. The catalysts in this study achieved similar conversion with relatively high FA selectivity under milder reaction conditions. The beneficial effect of water solvent was also emphasized.

Table 4. 7 Comparison of the prepared catalysts and reported in the literature for the liquid phase hydrogenation of furfural.

No.	Catalysts	Preparation Method	Reaction Conditions	Solvent	Reaction Time (h)	Reaction Results		Ref.
						Conversion (%)	Selectivity (%)	
1	0.15FePt/AC	Co-impregnation	50 °C, 2 MPa H_2	H_2O	1	100	74.1	This work
2	Pt-Fe/MWNT	Co-impregnation	100 °C, 3 MPa H_2	Ethanol	5	95.2	91.8	[56]
	Pt-Fe/H-AC	Co-impregnation	100 °C, 10.3MPa H_2	Ethanol	5	35.5	33.4	
	Pt-Fe/AC	Co-impregnation	100 °C, 10.3MPa H_2	Ethanol	5	52.9	28.6	
	Pt-Ni/MWNT	Co-impregnation	100 °C, 10.3MPa H_2	Ethanol	5	95.9	84.1	
	Pt-Co/MWNT	Co-impregnation	100 °C, 10.3MPa H_2	Ethanol	5	86.7	80.3	
3	5%Pt@TECN	Ultrasound-assisted reduction	100 °C, 1 MPa H_2	H_2O	5	>99	>99	[19]
	5%Pt@TECN	Ultrasound-assisted reduction	100 °C, 2 MPa H_2	H_2O	1	98	98	
4	3%Pt/BC	Wet impregnation	210 °C, 10.3 MPa H_2	Toluene	2	60.8	79.2	[57]
5	3%Pt/AC	Wet impregnation	180 °C, 1 MPa H_2	Isopropanol	8	100	71	[58]
6	Pt/NC-BS-500	Ultrasound-assisted reduction	100 °C, 1 MPa H_2	H_2O	4	>99	>99	[20]
7	Pt-$Sn_{0.3}$/SiO_2	Controlled surface reaction	100 °C, 1 MPa H_2	2-propanol	8	>90	96.2	[17]
8	Pt-Re/TiO_2-ZrO_2	Co-impregnation	130 °C, 5 MPa H_2	Ethanol	8	100	95.7	[81]
	Pt-In/TiO_2-ZrO_2	Co-impregnation	130 °C, 5 MPa H_2	Ethanol	8	73.3	74.9	
	Pt-Sn/TiO_2-ZrO_2	Co-impregnation	130 °C, 5 MPa H_2	Ethanol	8	98.3	47.8	

The 0.5FePt/AC catalyst was chosen for recyclability tests because it contained the minimum loading of Fe that made the catalyst separable from the liquid by a magnet. The results are shown in **Fig. 4.14**. After the reaction, the catalyst was separated by a magnet, washed with DI water for 3 times, dried in an oven at 110 °C overnight and used under the same reaction conditions in water solvent. It was found that the conversion of furfural and FA selectivity decreased after the first run but were not significantly changed in the consecutive run. During the first run, some large Pt particles with weak metal-support interaction could be leached out from the carbon support. Comparison of the EDX of the fresh and spent catalyst after the 3rd run is shown in **Table 4.8**. The differences in the O/C ratios suggests the deposition of carbon species from the liquid phase under the conditions used. The XPS results (**Table 4.9**) of C 1s suggest the increase of C─O─C and O─C═O species on the spent catalysts compared to the fresh one, which more than 90% was C─C species [82]. The Fe 2p peaks on both fresh and spent catalysts at around 711.2-711.4 eV were attributed to Fe^{3+} in Fe_2O_3 [83] and the amounts were not significantly different (< 1 wt%). After the 3rd cycle run, the 0.5FePt/AC catalyst still maintain the magnetic properties and can be separated by a magnet (**Fig. 4.15**).

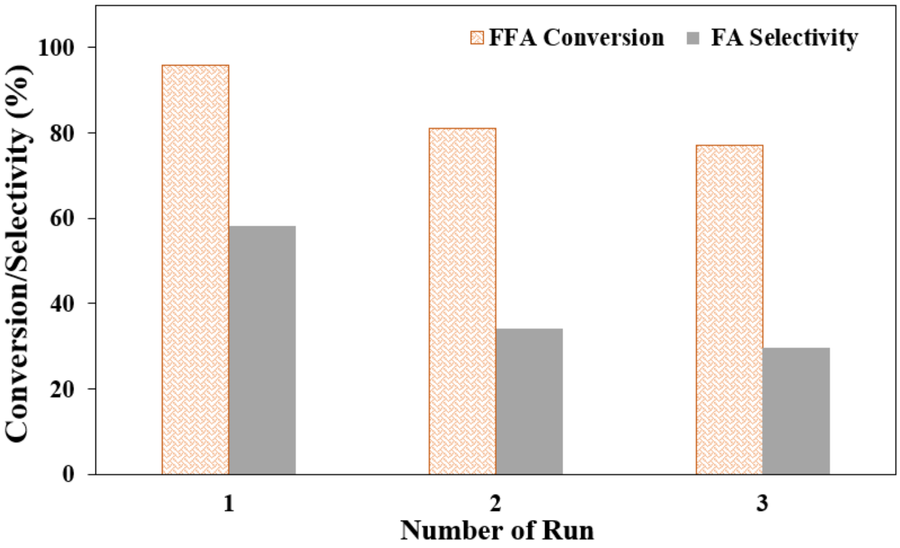

Figure 4. 14 Catalyst recyclability with the 0.5FePt/AC catalysts for the conversion of furfural to furfuryl alcohol.

Table 4. 8 EDX results of fresh and spent 0.5 FePt/AC catalysts after 3rd cycle

0.5FePt/AC	EDX (wt%)				Ratio O/C
	C	O	Pt	Fe	
Fresh	90.57	6.42	1.86	1.9	0.066
Spent 3rd cycle	94.2	3.41	1.64	0.79	0.036

Table 4. 9 XPS results of fresh and spent 0.5 FePt/AC catalysts after 3rd cycle

	Fresh		After 3rd cycle	
	Binding energy (eV)	Mass (%)	Binding energy (eV)	Mass (%)
C 1s	285.0	68.71	285.0	43.39
	288.9	6.57	286.6	26.89
			289.7	12.60
O 1s	533.7	24.30	533.4	16.23
Fe 2p	711.4	0.42	711.2	0.90
Ratio O/C		0.323		0.196

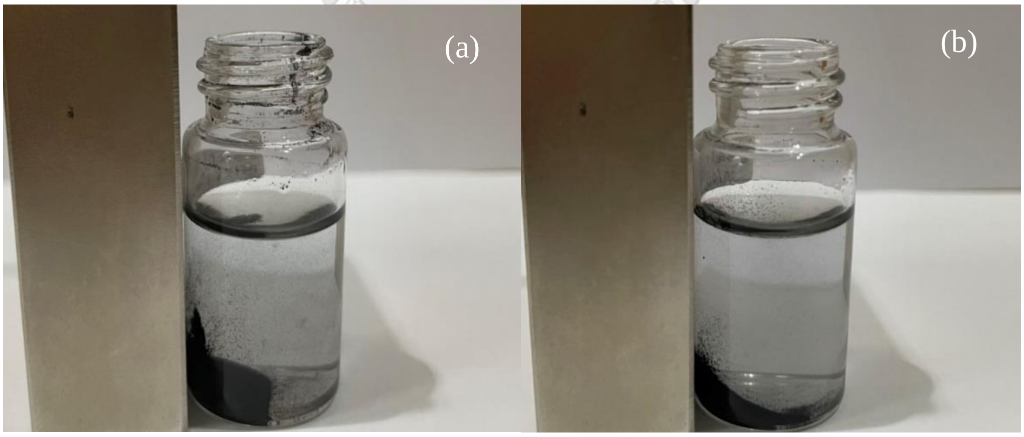

Figure 4. 15 Magnetic separation of 0.5FePt /AC catalyst (a) After 1st cycle run; (b) After 3rd cycle run.

CHAPTER V
CONCLUSIONS AND REXOMMENDATIONS

5.1 General summary

This dissertation focused on platinum-based catalyst for hydrogenation of furfural to FA under mind conditions (50°C and 20 bar H_2) using water and methanol as solvent. The study was divided into 2 parts. In the first part, various types of carbon supports were used for preparation of supported Pt catalysts with 0.5 wt% Pt loading. The results showed that Pt incorporated in order mesoporous carbon by soft the soft-templating method exhibited the highest activity comparing to the other supports which prepared by impregnation method. For the second part, various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts were studied. The 0.15FePt/AC showed the best improvement of catalyst performances with complete furfural conversion and high selectivity of FA (74%). In addition, solvent product (2-furaldehyde dimethyl acetal) was formed when the methanol was used as the solvent.

5.2 Conclusions

Part I: Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method

Various carbon materials containing micro-, meso-, and macro-porous structures (ordered mesoporous carbon, activated carbon, meso/macroporous carbon) were employed as the supports for Pt catalysts for aqueous-phase selective hydrogenation of furfural to furfuryl alcohol (FA) at 50°C and 20 bar H_2. Regardless of the pore size of the carbon supports, high dispersion of Pt particles with average Pt size 0.5-2 nm could be obtained on all the impregnated catalysts. However, when Pt was incorporated in the ordered mesoporous carbon by the soft-templating method (Pt/OMC-one-pot), fairly large Pt particle size (∼4-5 nm) with poor CO chemisorption ability were obtained. The Pt/OMC-one-pot exhibited the highest furfural conversion and highest FA selectivity under aqueous conditions while only solvent products were obtained when methanol was used as the solvent. Comparing to other carbon supported Pt catalysts in the literature, the Pt/OMC-one-pot in this study exhibited comparable high FA yield with lower amount of Pt presented and milder reaction conditions. Larger Pt particles with weak metal-support interaction, however, were susceptible for deactivation by leaching under the liquid-phase reaction. N-doping of the Pt/OMC-one-pot is recommended to inhibit leaching of large Pt particles from the carbon supports.

Part II: Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon

The liquid-phase selective hydrogenation of furfural to FA under mild condition (50°C and 20 bar H_2) was studied over various ferromagnetic elements (x = Fe, Co, Ni, and Nd) promoted Pt/activated carbon catalysts. Among the ferromagnetic element, the 0.15FePt/AC catalyst exhibited the best improvement of catalyst performances in terms of FA yield in both methanol and water solvent, which was attributed to the highest Pt dispersion with low coordinated Pt sites, and the strong Pt-Fe interaction as revealed by CO chemisorption and FT-IR of adsorbed CO results. The highest FA yield was 74% in water. For all the Pt-based bimetallic catalysts, the use of water medium showed higher furfural conversion and FA selectivity than methanol despite a shorter reaction time used (1 h). The minimum Fe loading was 0.5 wt% to make the bimetallic catalysts separable by a simple magnet. The activities and selectivities of the 0.5FePt/AC slight dropped after the first cycle but remained stable afterward. The catalysts, however, still exhibited magnetic properties after the consecutive runs.

5.3 Recommendations

1. The improvement on the stability of catalyst should be done. To prevent the loss of active components from the carbon supports during recyclability, incorporation of N atoms into the OMC matrix could possibly enhance the strong Pt-support interaction.

2. Characteristic of bimetallic catalysts supported on activated carbon should be investigated by TEM.

3. The other products in hydrogenation of furfural should be classified.

APPENDIX A
CALCULATION FOR CATALYST PREPARATION

For monometallic catalyst, the 0.5 wt%Pt supported on carbon catalyst prepared by impregnation method was shown.

Reagent: Platinum (II)acetyl-acetonate 97%, MW = 195.078 g/ mol

Carbon support

Based on 3 g of catalysts used, the composition of catalysts will be as follows:

Platinum required = (3 x 0.5)/100 = 0.015 g

Carbon required = 3-0.015 = 2.985 g

Platinum 0.015 g was prepared by using platinum (II) acetyl-acetonate 97%

$$= \frac{\text{MW. of platinum (II) acetyl-acetonate x weight of platinum required}}{\text{MW. of platinum}}$$

$$= \frac{323.29 \text{ g/mol} \times 0.015 \text{ g}}{195.078 \text{ g/mol}}$$

= 0.0249 g

For bimetallic catalyst, FePt/AC (0.5 wt%Pt and 0.1-10 wt%Fe) and 0.15MPt/AC (0.5 wt%Pt and 0.15wt%M: Ni and Co) catalysts prepared by Co-impregnation method was shown.

Reagent: Tetraammineplatinum (II) chloride hydrate 99.99%, MW = 334.11 g/mol

Ferric nitrate nonahydrate 97%, MW = 404.00 g/mol

Cobalt (II) nitrate hexahydrate 98%, MW = 291.03 g/mol

Nickel (II) nitrate hexahydrate, 98%, MW = 290.79 g/mol

Carbon support

Example: based on 3 g of 0.15FePt/ AC catalyst, the composition of catalysts will be as follows:

Platinum required = (3 x 0.5)/100 = 0.015 g

Iron required = (3 x 0.15)/100 = 0.0045 g

Carbon required = 3-0.015-0.0045 = 2.9805 g

Platinum 0.015 g was prepared by using Tetraammineplatinum (II) chloride hydrate 99.99%

$$= \frac{\text{MW. of Tetraammineplatinum (II) chloride hydrate} \quad \text{x weight of platinum required}}{\text{MW. of platinum}}$$

$$= \frac{334.11\ \text{g/mol x } 0.015\ \text{g}}{195.078\ \text{g/mol}}$$

= 0.0257 g

Iron 0.0045 g was prepared by using Ferric nitrate nonahydrate 97%

$$= \frac{\text{MW. of Ferric nitrate nonahydrate} \quad \text{x weight of iron required}}{\text{MW. of iron}}$$

$$= \frac{404.0\ \text{g/mol x } 0.0045\ \text{g}}{55.845\ \text{g/mol}}$$

= 0.0306 g

APPENDIX B

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

Calculation of Pt active sites and Pt dispersion of the catalyst by CO-chemisorption is as follows:

$$\text{Volume of CO adsorption on catalyst, } V_{ads} = \frac{V_{inj}}{m} \times \sum_{i-1}^{n} \left(1 - \frac{A_i}{A_f}\right)$$

Where V_{inj} = volume injected, 0.01 cm3

m = mass of catalyst used, g

A_i = area of peak i

A_f = area of last peak

Pt active sites

$$\text{Pt active site} = S_f \times \frac{V_{ads}}{V_g} \times N_A$$

Where Sf = stoichiometry factor, H_2 adsorbed on Pt, CO: Pt = 1: 1

V_{ads} = volume adsorbed

V_g = molar volume of gas at STP, 22414 cm^3/mol

N_A = Avogadro’s number, 6.023x1023 molecules/mo

Metal dispersion

$$\text{Metal dispersion }(\%) = 100 \times \frac{\text{molecule of Pt loaded}}{\text{molecule of Pt from CO adsorption}}$$

$$\%D = S_f \times \frac{V_{ads}}{V_g} \times \frac{MW}{\%M} \times 100\% \times 100\%$$

Where:

Sf = stoichiometry factor, H_2 adsorbed on Pt, CO: Pt = 1: 1

V_{ads} = volume adsorbed

V_g = molar volume of gas at STP, 22414 cm^3/mol

MW = molecular weight of the metal

%M= weight percent of the active metal

APPENDIX C

CALCULATION OF AVERAGE CRYSTALLITE SIZE

Average Crystallite Size of Platinum metal can be calculated, based on active metal surface area per gram of metal

$$d = \frac{F_g}{\rho x MSA_m} x \frac{m^3}{10^6 cm^3} x \frac{10^9 nm}{m} \qquad \text{---------- (1)}$$

Where:

d = average crystallite size of platinum metal

F_g = crystallite geometry factor (hemisphere = 6)

ρ = specific gravity of the active metal (Platinum = 21.4 g/cm^3)

MSA_m = active metal surface area per gram of metal 77.52 m^2/g$_{metal}$

Example: Average Crystallite Size of 0.5%Pt/MC

Calculation of active metal surface area

$$MSA_m = S_f x \left[\frac{V_{ads}}{V_g}\right] x \left[\frac{100\%}{\%M}\right] x N_A x \sigma_m x \left[\frac{m^2}{10^{18} nm^2}\right] \qquad \text{---------- (2)}$$

Where:

S_f = stoichiometry factor, (CO on Pt*1)

V_{ads} = volume adsorbed (0.15%Pt/MC = 0.136 cm^3/g)

V_g = molar volume of gas at STP 22414 cm^3/mol

N_A = Avogadro's number (6.023 x 10^{23} molecules/mol)

σ_m = cross-sectional area of active metal atom (Platinum = 0.08 nm^2)

To replace values in equation (1) and (2);

$$MSA_m =$$

$$1x\left[\frac{0.136cm^3/g}{22414\ cm^3/mol}\right]x\left[\frac{100\%}{0.5\%}\right]x6.02x10^{23}\,\frac{Molecules}{mol}\,x0.08\ nm^2x\left[\frac{m^2}{10^{18}nm^2}\right]$$

= 58.464 m^2/g

$$d = \frac{6}{21.4\ g/cm^3x58.464\ m^2\ /g}\,x\,\frac{m^3}{10^6cm^3}\,x\,\frac{10^9nm}{m} = 4.8\ nm$$

Average crystallite size of Platinum metal equal to 4.8 nm.

APPENDIX D
CALCULATION FOR CATALYTIC PERFORMANCE

The catalysts performances for the furfural hydrogenation are shown in this below.

$$\%\text{Conversion}=\frac{\text{Mole (in)-Mole (out)}}{\text{Mole (in)}}\times 100$$

$$\%\text{Selectivity}=\frac{\text{Mole of product}}{\text{Mole of convert reactant}}\times 100$$

%Yield = conversion × selectivity

Example:

$$\%\text{Furfural conversion}=\frac{\text{Mole of furfural (in)-Mole of furfural (out)}}{\text{Mole of furfural (in)}}\times 100$$

$$\%\text{Furfuryl alcohol selectivity}=\frac{\text{Mole of furfuryl alcohol}}{\text{Mole of converted furfural}}\times 100$$

% Furfuryl alcohol Yield = Furfural conversion × Furfuryl alcohol selectivity

For methanol solvent, the liquid products were analyzed by a gas chromatograph, Shimadzu GC-2014 and the calibration curves of furfural, and furfuryl alcohol are shown in Figure D1, and Figure D2, respectively.

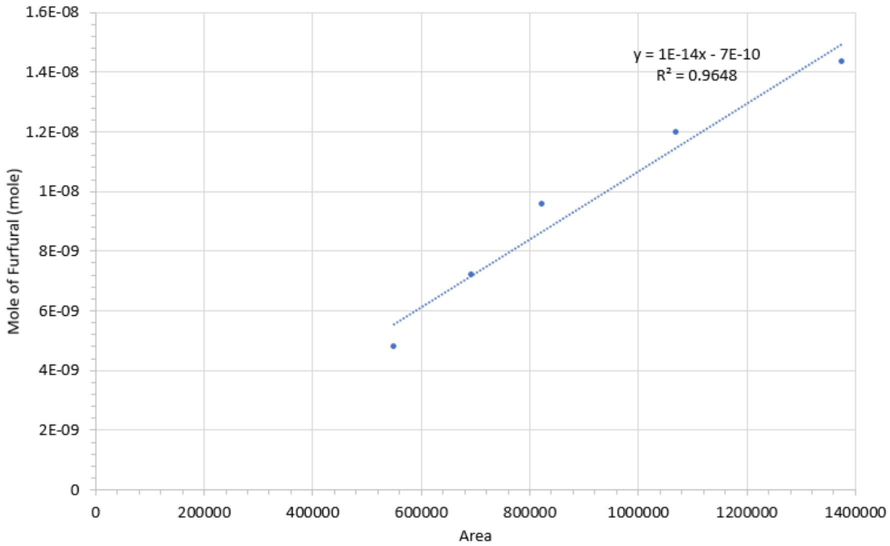

Figure D 1 The calibration curve of furfural for a gas chromatograph, Shimadzu GC-2014.

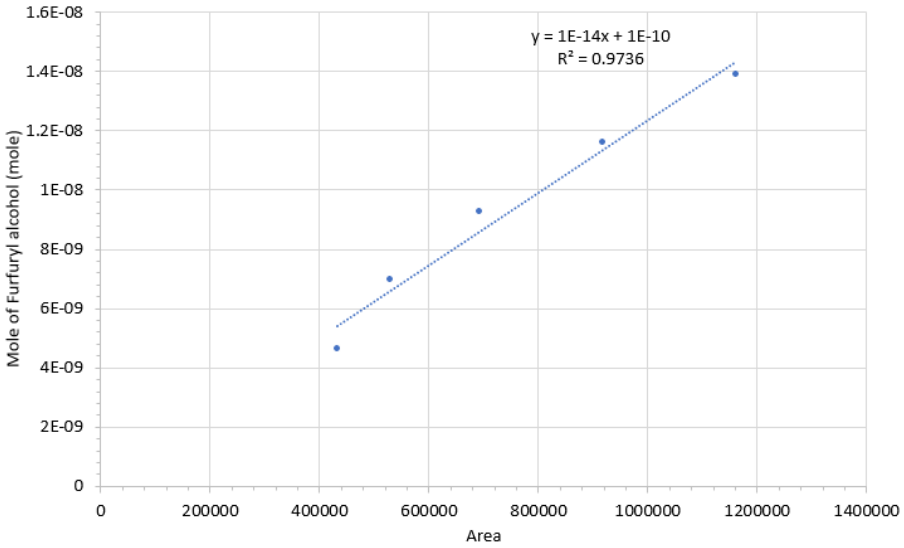

Figure D 2 The calibration curve of furfuryl alcohol for a gas chromatograph, Shimadzu GC-2014.

For water solvent of part I, the liquid products were analyzed by a high-performance liquid chromatography, Agilent HPLC 1100 G1361A and the calibration curves of furfural, and furfuryl alcohol are shown in Figure D3, and Figure D4, respectively.

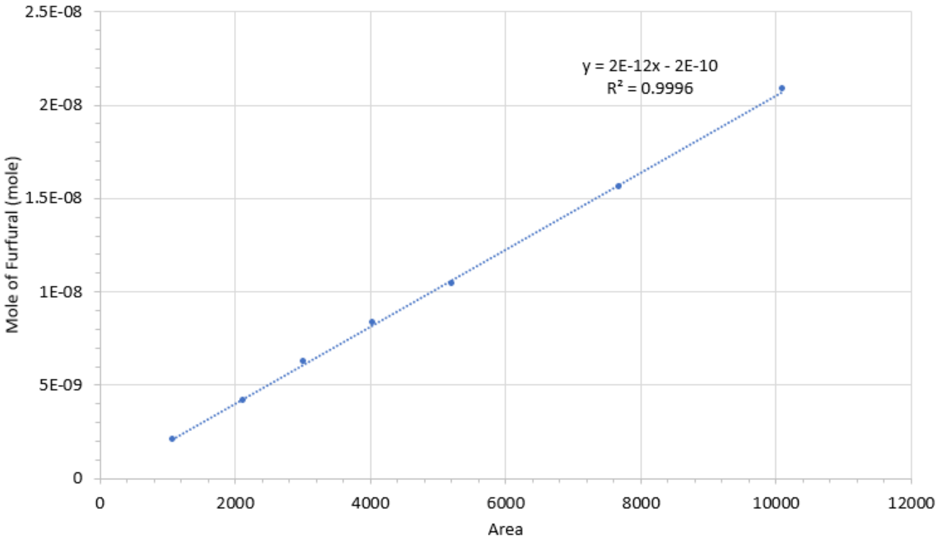

Figure D 3 The calibration curve of furfural for a high-performance liquid chromatography, Agilent HPLC 1100 G1361A.

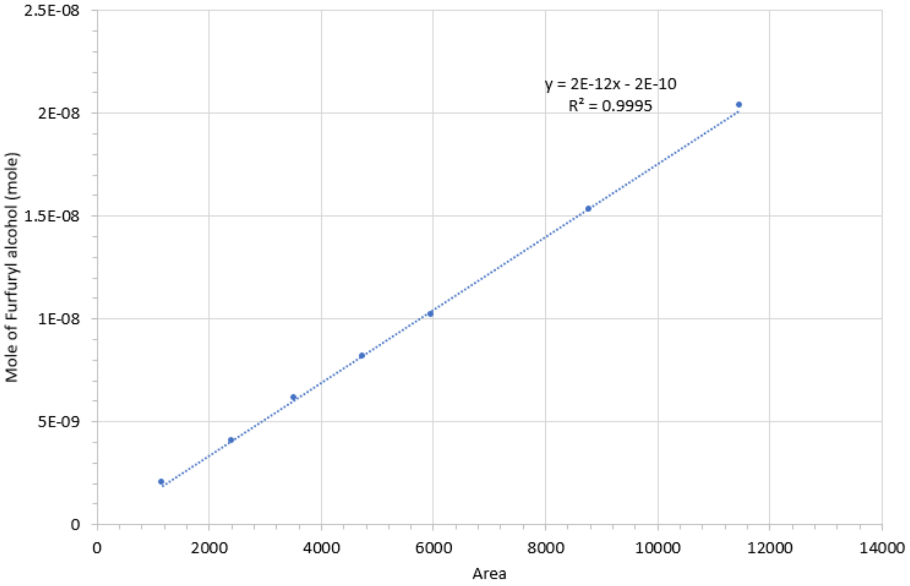

Figure D 4 The calibration curve of furfuryl alcohol for a high-performance liquid chromatography, Agilent HPLC 1100 G1361A.

For water solvent of part II, the liquid products were analyzed by a high-performance liquid chromatography, Shimadzu 20A and the calibration curves of furfural, and furfuryl alcohol are shown in Figure D5, and Figure D6, respectively.

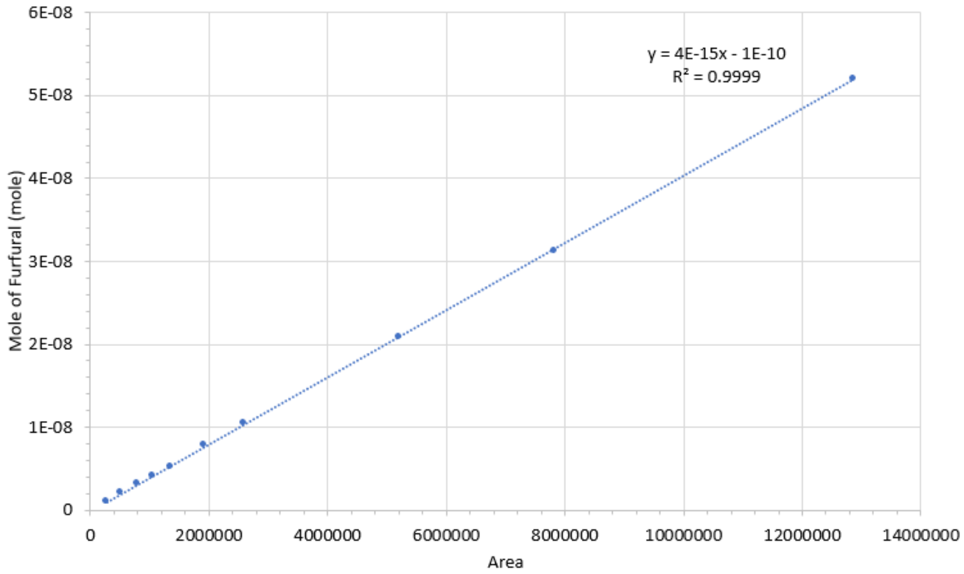

Figure D 5 The calibration curve of furfural for a high-performance liquid chromatography, Shimadzu 20A.

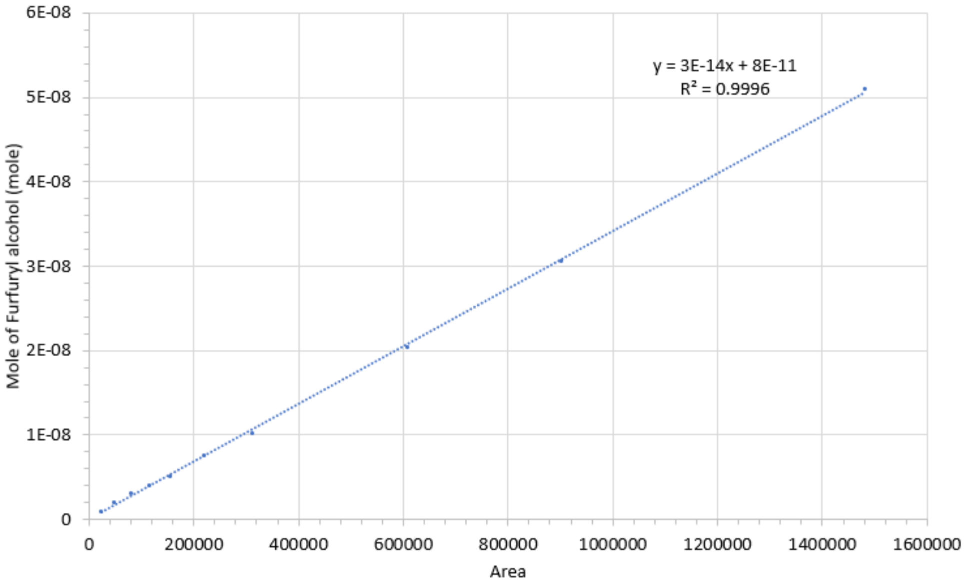

Figure D 6 The calibration curve of furfuryl alcohol for a high-performance liquid chromatography, Shimadzu 20A.

APPENDIX E

LIST OF PUBLICATIONS

B-1 Publications

1. S. Saknaphawuth, B. Pongthawornsakun, P. Toumsri, L. Chuenchom, and J. Panpranot, “Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method”, Journal of Oleo Science **2020**, 71(8).

2. S. Saknaphawuth, P. Weerachawanasak, L. Chuenchom, P. Praserthdam, and J. Panpranot, “Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon” Catalysts **2022**, 12(4), 393.

B-2 Conference contributions

1. Oral presentation: Sureeporn Saknaphawuth, Boontida Pongthawornsakun, Piyamit Toumsri, Laemthong Chuenchom, Joongjai Panpranot, One-pot synthesis of Pt incorporated mesoporous carbon for selective hydrogenation of furfural to furfuryl alcohol, Third edition of International Conference on Catalysis and Chemical Engineering 2019 (CCE-2019), Houston, Texas, United States, February 25-27, 2019.

2. Oral presentation: Sureeporn Saknaphawuth, Boontida Pongthawornsakun, Piyamit Toumsri, Laemthong Chuenchom, Joongjai Panpranot, Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over Pt-incorporated ordered mesoporous carbon, The eighth Asia-Pacific Congress on Catalysis 2019 (APCAT-8), Bangkok, Thailand, August 4-7,2019.

3. Oral presentation: Sureeporn Saknaphawuth and Joongjai Punpranot, Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni) - promoted Pt catalysts supported on activated carbon, Fifth edition of International Conference on Catalysis and Chemical Engineering 2021 (CCE-2021), Virtual Catalysis, February 22-26, 2021.

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PUBLICATION	1. S. Saknaphawuth, B. Pongthawornsakun, P. Toumsri, L. Chuenchom, and J. Panpranot, “Aqueous-phase selective hydrogenation of furfural to furfuryl alcohol over ordered-mesoporous carbon supported Pt catalysts prepared by one-step modified soft-template self-assembly method”, Journal of Oleo Science, 71(8/9) 2020 (In press). 2. S. Saknaphawuth, P. Weerachawanasak, L. Chuenchom, P. Praserthdam, and J. Panpranot, “Liquid-phase selective hydrogenation of furfural to furfuryl alcohol over ferromagnetic element (Fe, Co, Ni, Nd) - promoted Pt catalysts supported on activated carbon” Catalysts 2022, 12(4), 393.