

SELECTIVE HYDROGENATION OF ACETOPHENONE TO 1-PHENYLETHANOL ON Pt/TiO₂
CATALYSTS PREPARED BY PULSED DC MAGNETRON SPUTTERING



A Thesis Submitted in Partial Fulfillment of the Requirements
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ปฏิกิริยาไฮโดรจีนชั้นแบบเลือกเกิดของอะซีไตฟิโนนเป็น 1-ฟีนิลเอทานอลบนตัวเร่งปฏิกิริยา
แพลทินัมบนตัวรองรับไททานเนียมไดออกไซด์ที่เตรียมโดยวิธีแมกนีตรอนสปัตเตอริงแบบกระแสดตรง
ประเภทพัลส์



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คุณานนต์ ดิฐสถาพรเจริญ : ปฏิกริยาไฮโดรจิเนชันแบบเลือกเกิดของอะซีโตฟีโนนเป็น 1-ฟีนิลเอทานอลบนตัวเร่งปฏิกริยาแพลทินัมบนตัวรองรับไททานเนียมไดออกไซด์ที่เตรียมโดยวิธีแมกนีตรอนสเปตเตอร์แบบกระแสตรงประเภทพัลส์. (SELECTIVE HYDROGENATION OF ACETOPHENONE TO 1-PHENYLETHANOL ON Pt/TiO₂ CATALYSTS PREPARED BY PULSED DC MAGNETRON SPUTTERING) อ.ที่ปรึกษาหลัก : ศ. ดร.จุงใจ ปั้นประณต

1-ฟีนิลเอทานอลเป็นสารเคมีมูลค่าสูงและใช้งานได้ในอุตสาหกรรมหลายอย่าง ในอุตสาหกรรมเครื่องหอม 1-ฟีนิลเอทานอลใช้เป็นสารแต่งกลิ่นที่ให้รสต่อเบอร์ซึ่งนิยมใช้ในโยเกิร์ตและหมากฝรั่ง ในอุตสาหกรรมยา 1-ฟีนิลเอทานอลใช้เป็นสารมัธยตร์ในการผลิตยาแก้ปวดและยาแก้แสบ เช่น ยาไอบูโพรเฟน สำหรับปฏิกริยาไฮโดรจิเนชันแบบเลือกเกิดของอะซีโตฟีโนนเป็น 1-ฟีนิลเอทานอลสามารถใช้ตัวเร่งปฏิกริยาแพลทินัมบนตัวรองรับไทเทเนียมไดออกไซด์ โครงงานนี้มีวัตถุประสงค์เพื่อทำการศึกษาและวิเคราะห์ตัวเร่งปฏิกริยาที่มีโครงสร้างผลึกของไทเทเนียมแบบต่างๆ ได้แก่ PC500 (อนาเทส) และ P25 (อนาเทสผสมรูไทล์) บนตัวเร่งปฏิกริยาแพลทินัมบนไทเทเนียมที่เตรียมด้วยวิธีแมกนีตรอนสเปตเตอร์แบบกระแสตรงประเภทพัลส์ โดยปรับเวลาเคลือบที่ 3 6 และ 9 นาที และทำการเปรียบเทียบกับตัวเร่งปฏิกริยาที่เตรียมด้วยวิธีเคลือบผงที่มีปริมาณแพลทินัมใกล้เคียงกัน ทำการวิเคราะห์ลักษณะตัวเร่งปฏิกริยาโดยเครื่องมือวิเคราะห์ต่างๆ ได้แก่ เทคนิคการเลี้ยวเบนของรังสีเอกซ์ การดูดซับทางกายภาพด้วยแก๊สไนโตรเจน เอ็กซ์เรย์โฟโตอิเล็กตรอนสเปกโตรสโกปี เครื่องวิเคราะห์ชนิดและปริมาณธาตุโดยหลักการคายแสงของธาตุด้วยการกระตุ้นจากพลาสมา กล้องจุลทรรศน์แบบส่องผ่าน การดูดซับทางเคมีด้วยแก๊สคาร์บอนมอนอกไซด์และเทคนิคการรีดักชันของไฮโดรเจนด้วยการโปรแกรมอุณหภูมิ ปฏิกริยาไฮโดรจิเนชันแบบเลือกเกิดของอะซีโตฟีโนนเป็น 1-ฟีนิลเอทานอลถูกดำเนินการที่ ความดัน 1 บาร์ อุณหภูมิ 80 องศาเซลเซียส โดยใช้เวลา 2 ชั่วโมงและใช้ 2-โพรพานอลเป็นตัวทำละลาย พบว่า เมื่อใช้เวลาในการเคลือบแพลทินัมบนตัวรองรับไททานเนียมด้วยวิธีแมกนีตรอนสเปตเตอร์แบบกระแสตรงประเภทพัลส์นานขึ้น จะทำให้ขนาดของแพลทินัมบนพื้นผิวของตัวรองรับไททานเนียมมีขนาดใหญ่ขึ้นและมีปริมาณแพลทินัมมากขึ้น ตัวเร่งปฏิกริยาที่มีตัวรองรับไททานเนียมแบบ PC500 จะให้ค่าร้อยละการเลือกเกิดเป็น 1-ฟีนิลเอทานอลสูงกว่าตัวรองรับไททานเนียมแบบ P-25 และให้ค่าร้อยละการเปลี่ยนไปของอะซีโตฟีโนนใกล้เคียงตัวรองรับไททานเนียมแบบ P25 เนื่องจากตัวเร่งปฏิกริยาที่ใช้ตัวรองรับไททานเนียมแบบ PC500 มีปริมาณแพลทินัมต่อไททานเนียมบนพื้นผิวของตัวรองรับไททานเนียมและมีการกระจายตัวของแพลทินัมสูงกว่า อย่างไรก็ตามตัวเร่งปฏิกริยาที่มีปริมาณแพลทินัมบนตัวรองรับไททานเนียมสูงจะช่วยเร่งปฏิกริยาไฮโดรจิโนไลซิสของ 1-ฟีนิลเอทานอลเป็นเอทิลเบนซีนให้เกิดดีขึ้นซึ่งส่งผลให้เกิด 1-ฟีนิลเอทานอลน้อยลง ยิ่งไปกว่านั้นเมื่อใช้อุณหภูมิในการทำปฏิกริยาที่ 80 องศาเซลเซียสสามารถส่งเสริมให้ปฏิกริยาไฮโดรจิเนชันของอะซีโตฟีโนนเป็น 1-ฟีนิลเอทานอลเกิดขึ้นและช่วยยับยั้งปฏิกริยาไฮโดรจิโนไลซิสของ 1-ฟีนิลเอทานอลเป็นเอทิลเบนซีน

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Khunarnon Ditsataporncharoen : SELECTIVE HYDROGENATION OF ACETOPHENONE TO 1-PHENYLETHANOL ON Pt/TiO₂ CATALYSTS PREPARED BY PULSED DC MAGNETRON SPUTTERING. Advisor: Prof. JOONGJAI PANPRANOT, Ph.D.

1-Phenylethanol (PHE) is a high-value chemical with various applications in fragrance and pharmaceutical industries. It is extensively used as strawberry fragrance additives in yogurts and chewing gums and an intermediate of anti-inflammatory drugs such as Ibuprofen. In this study, selective hydrogenation of acetophenone (AP) to PHE was investigated using platinum catalysts supported on different types of titanium dioxide including PC500 (pure anatase) and P25 (anatase mixed rutile). Pt was deposited on the titanium dioxide supports by pulsed direct current magnetron sputtering (PDC-MSD) method with deposition time spent on Pt coating at 3, 6, and 9 minutes. For comparison purposes, Pt/TiO₂ catalysts were also prepared by incipient wetness impregnation method with similar Pt loadings (%). The characteristics and catalyst properties were analyzed by XRD, N₂-physisorption, XPS, ICP-OES, TEM, CO-chemisorption, and H₂-TPR. Hydrogenation of AP was carried out in a batch reactor at the pressure of 1 bar H₂ and the temperature of 80°C for 2 hours using 2-propanol as the solvent. It was found that increasing sputtering time resulted in a larger average Pt particle size deposited on the TiO₂ surface and increased amount of Pt loading (%). For any sputtering time used, platinum catalysts on PC500 TiO₂ support provided higher selectivity of PHE than on P25 because of higher atomic ratio of Pt/Ti on the catalyst surfaces and higher Pt dispersion (%) on the PC500 TiO₂ surface. However, increasing Pt loading (%) may also catalyze the hydrogenolysis of PHE to ethylbenzene (EB), resulting in lower PHE product. Moreover, at the reaction temperature of 80 °C could promote the hydrogenation of AP to PHE and inhibit hydrogenolysis of PHE to EB in 2-propanol solvent.

Field of Study: Chemical Engineering

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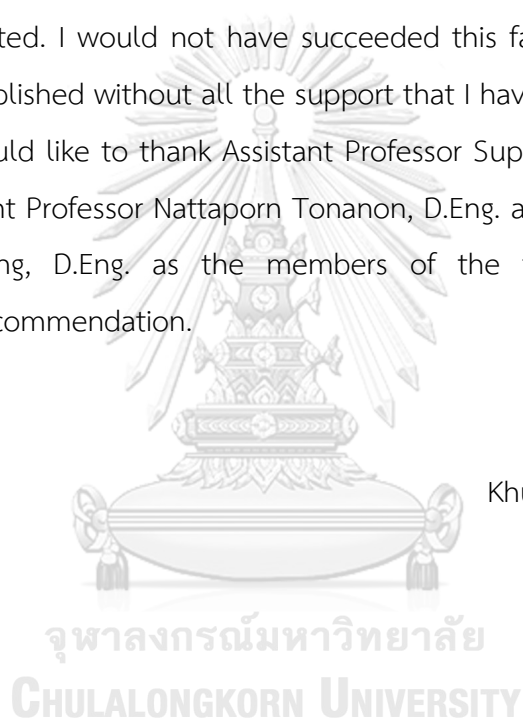
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CHAPTER I

INTRODUCTION

1.1 Introduction

The selective hydrogenation of aromatic ketones to aromatic alcohols is a significant reaction in the fine chemical industry because of increasing high-value added chemicals [1]. The hydrogenation of acetophenone (AP) has reaction pathways to produce many products such as 1-phenylethanol (PHE), ethylbenzene (EB), cyclohexylmethylketone (CHMK), cyclohexylethanol (CHE), and ethylcyclohexane (ECH). PHE is the main product from the selective hydrogenation of AP. PHE is a high-value chemical with various applications including fragrance and pharmaceutical industries [2, 3]. In fragrance industries, PHE is extensively used as strawberry fragrance additives in yogurts and chewing gums [2]. In pharmaceutical industries, PHE is an intermediate of analgesic and anti-inflammatory drugs such as Ibuprofen [2, 4].

Considering the selective hydrogenation of AP to PHE in liquid-phase hydrogenation, various pressures, temperatures, and types of solvents have been employed over supported noble metal and non-noble metal catalysts [5]. Noble metal catalysts that have been used are Pt [6-10], Ag [11], Pd [10, 12, 13], Rh [12, 14], Ru [15] and non-noble metals such as Cu [2, 4, 5], Ni [5, 16], Co [1, 3, 5], Zr [17], Fe [8, 18], Cr [18]. Pt-supported catalysts are used in the hydrogenation of AP because of high catalytic activity but Pt-supported catalysts can catalyze hydrogenation of carbonyl (C=O) and phenyl groups of the AP molecule to produce comparable products of PHE and CHMK respectively. After that, both products are simultaneously hydrogenated to CHE [2, 4]. Therefore, it is difficult to obtain high selectivity of PHE product and high activity of AP under mild reaction conditions. So, improving catalytic performance under mild conditions are of special challenge to reduce

operating costs. This could be achieved by changing catalyst support and reducing operating conditions.

Titanium dioxide (TiO_2) is used as catalyst supports in many reactions such as hydrogenation, dehydrogenation, and photocatalyst. TiO_2 presents fascinating characteristics such as nontoxicity, high effectiveness, and low costs. At high reduction temperature, it shows the strong metal-support interaction [19]. TiO_2 exists in three crystalline forms: anatase, rutile, and brookite. The properties of TiO_2 such as surface area, crystallite size, crystalline phase composition, crystallite size, and morphology of particles depend on the catalyst synthesis method and post-synthesis treatment conditions [20]. Pt/TiO_2 has been widely used in the hydrogenation reaction. TiO_2 has been shown to promote the hydrogenation of the carbonyl group [21].

Pulsed direct current magnetron sputtering deposition (PDC-MSD) method is a famous deposition technique applicable to produce thin films layer for packaging coating. This deposition technique has been employed in the industry due to its easy to scale up, high ability, high stability, controllability, repeatability, uniformity, low environmental effect, and high efficiency in coatings. Nowadays, PDC-MSD method has been applied on the laboratory scale for the deposition of metal nanoparticles on solid and liquid surface supports [22, 23]. Importantly, the PDC-MSD method deposits atoms and atomic clusters with high pure targets (99.99%) on the substrate [24].

In the present study, the selective hydrogenation of AP to PHE was carried out using Pt-based catalysts prepared on TiO_2 supports by PDC-MSD method on various TiO_2 polymorphs such as PC500 (pure anatase) and P25 (mixed anatase and rutile phase). For each type of support, the deposition time spent on Pt coating was adjusted to be 3, 6, or 9 minutes. For comparison purposes, Pt/TiO_2 catalysts were also prepared by an incipient wetness impregnation method with similar Pt loadings

(%). Finally, the effect of reaction temperature on the hydrogenation of AP to PHE was investigated.

1.2 Objectives of the Research

To study the characteristics and catalytic properties of TiO₂ supported Pt nanoparticles prepared by PDC-MSD method on PC500 and P25 TiO₂ in the liquid phase selective hydrogenation of AP to PHE in comparison to those prepared by the incipient wetness impregnation method.

To study the effect of reaction temperature on the catalytic performances of TiO₂ supported Pt nanoparticles prepared by PDC-MSD method in the liquid phase selective hydrogenation of AP to PHE.

1.3 Scope of the Research

1. Characterization of catalysts prepared by the PDC-MSD method using X-ray diffraction (XRD), N₂-physisorption, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma optical emission spectrometer (ICP-OES), transmission electron spectroscopy (TEM), CO-pulse chemisorption, and H₂ temperature-programmed reduction (H₂-TPR).

2. Testing of the Pt/TiO₂ catalysts prepared by the PDC-MSD method (Pt coating time 3, 6, 9 minutes on PC500 and P25 supports) in the liquid phase selective hydrogenation of AP to PHE. The reaction was carried out in a batch reactor at 60, 80, 100°C, 1 bar hydrogen pressure, and 120 minutes using 2-propanol as a solvent.

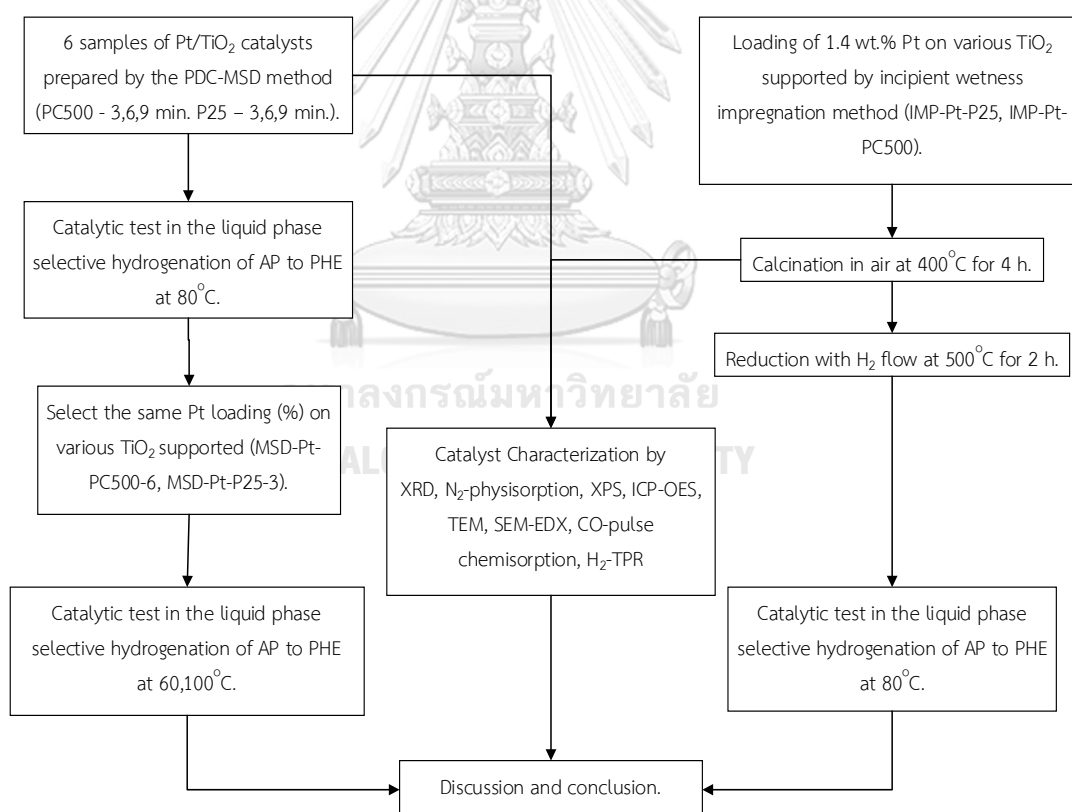
3. Preparation of TiO₂ supported Pt catalysts by the conventional impregnation method with Pt content 1.4 wt% support with different TiO₂ polymorphs (PC500 and P25 support) by using incipient wetness impregnation

method and calcined at 400°C under air atmospheres for 4 h. and followed by reduction under H₂ flow (30 cm³/min) at 500 °C for 2 h.

4. Characterization of catalysts prepared by the incipient wetness impregnation method using the same technique.

5. The Pt/TiO₂ catalysts prepared by the incipient wetness impregnation method were tested in the liquid phase selective hydrogenation of AP to PHE in a batch reactor under the same conditions.

1.4 Research Methodology



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogenation Reaction

Hydrogenation is a chemical reaction that indicates the treatment of substances with molecular hydrogen (H_2), adding pairs of hydrogen atoms to compounds (unsaturated compounds except for an alkane). Under normal temperature and pressure conditions, a catalyst is needed for the reaction to take place. Most hydrogenation reactions employ gaseous hydrogen as the hydrogen source. In the future, other hydrogen sources could be provided. Hydrogenation reduces double and triple bonds of hydrocarbons to single bonds hydrocarbons. Hydrogenation differs from protonation or hydride addition because in hydrogenation the products have the same charge as the reactants. The reverse of hydrogenation, where hydrogen is removed from the compounds, is known as dehydrogenation. [25, 26].

Generally, there are three components in hydrogenation reactions consisting of substrate, hydrogen source, and a catalyst. The reaction can be operated at different temperatures and pressures based on the catalyst and substrate used. Commonly, The hydrogenation of alkenes produce alkanes, alkynes to alkenes, esters to secondary alcohols, aldehydes and ketones to alcohols, and amides to amines [25-27].

Hydrogenation reactions without metal catalysts will occur between hydrogen and organic compounds only higher than $480^\circ C$. Catalysts are used for promoting the reaction between the hydrogen and the substrate. Platinum, ruthenium, palladium, and rhodium, catalysts are required, which can operate at lower pressures and temperatures [25, 27].

2.2 Properties of platinum

Platinum (Pt) is a chemical element and atomic number 78. Platinum is in group 10 (VIIIb), period 6 of the periodic table of elements. It is a silverish-white transition metal, precious, dense, ductile, malleable, highly unreactive, good corrosion resistance, and chemical attack. Furthermore, platinum is also capable of absorbing large volumes of hydrogen [28].

For Pt supported catalysts, platinum metal catalysts have many applications in chemical processes such as automotive catalytic converters to strip out pollutants from exhaust gases of motor vehicles, petroleum refining, selective hydrogenation of chemical, gas-phase oxidation, pharmaceutical feedstocks, and fuel cell power generation [28-30].

Platinum forms an important series of compounds with the oxidation states of +2 and +4 are the most stable [29]. Generally, platinum is a mixture of six isotopes: Pt-190 (0.0127 percent), Pt-192 (0.78 percent), Pt-194 (32.9 percent), Pt-195 (33.8 percent), Pt-196 (25.3 percent), and Pt-198 (7.21 percent) [28, 29, 31].

Table 1 Physical properties of Platinum [28]

Physical properties of Platinum	
Atomic number	78
Atomic weight	195.09
Specific gravity	21.45 (20° C)
Melting point	1,769° C (3,216° F)
Boiling point	3,827° C (6,920° F)
Electron configuration	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
Oxidation states	+2, +4

2.3 Titanium dioxide support

Titanium dioxide (TiO_2) or titania is the naturally occurring oxide of titanium with chemical formula TiO_2 . Titanium dioxide is frequently used in the production of paints, plastics, paper, cosmetics, and welding rod-coating material. Moreover, Titanium dioxide is used as semiconductor photocatalysts and catalyst support [19, 20] that showed properties depend on the morphology of nanocrystals, structure, and surface [32].

Titanium dioxide is non-toxicity, long-term photostability, and high effectiveness, which is applied in mineralizing toxic and non-biodegradable environmental contaminants. It has good mechanical resistance and stability in acidic and oxidative environments. These properties are suitable for heterogeneous catalyst support [19].

Titanium dioxide exists in several polymorphs i.e. rutile, anatase, brookite, columbite, baddeleyite, cotunnite, pyrite, and fluorite, etc [33]. Commonly, Titanium dioxide exists in three crystalline forms: anatase (tetragonal) and rutile (tetragonal) are the most common types, and the crystalline size of the rutile is always larger than the anatase phase. The third crystalline form is brookite (orthorhombic), which is rarely applied. The rutile phase is the most thermally stable among the three phases. Commonly, anatase and brookite convert into the rutile phase crystalline is above 600°C [19, 20]. The anatase and rutile structures with tetragonal geometry are highly symmetrical where each Ti atom is surrounded by six oxygen atoms forming a TiO_6 octahedron. The only difference between the two structures is the distortion and linkage between the octahedrally coordinated Ti and O atoms [33]. The anatase phase contains zigzag chains of octahedral molecules linked to each other, while the rutile consists of linear chains of opposite edge-shared octahedral structure [19].

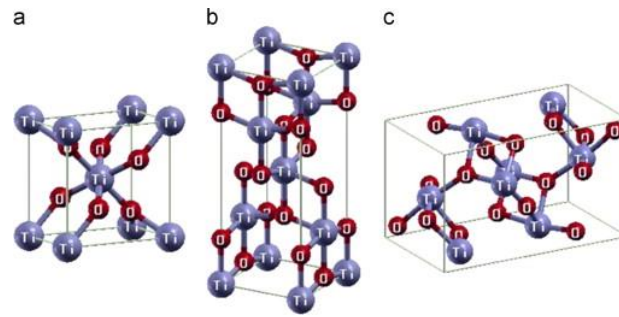


Figure 1 Structure of TiO_2 polymorphs: rutile (a), anatase (b), and brookite (c) [33].

2.4 Magnetron sputtering

Magnetron sputter is a physical vapor deposition (PVD) method of thin film deposited by sputtering. The general sputtering method can be used to prepare a variety of materials such as metals, semiconductors, insulators, etc., and has the advantages of simple equipment, easy control, large coating area, and strong adhesion. Furthermore, the magnetron sputtering method developed in the 1970s achieves high speed, low damage, and low temperature [34].

Magnetron sputtering is a high-rate vacuum coating technique for depositing metals, alloys, and compounds onto a wide range of materials with thickness up to millimeter. It exhibits several significant advantages over other vacuum coating techniques, a property that led to the development of a large number of commercial applications from microelectronic fabrication to simple decorative coatings. The advantages of magnetron sputtering are such as [35]

- high deposition rates
- ease of sputtering any metal, alloy, or compound
- high-purity films
- extremely high adhesion of films
- excellent coverage of steps and small features

- ability to coat heat-sensitive substrates
- excellent uniformity on large-area substrates, for example, architectural glass.

Magnetron sputtering is an important technique to grow thin films because a large number of thin films can be prepared at relatively high purity and low cost. This involves ejecting material from a “sputtering target” or a metal precursor that is a source onto a “substrate”, as shown in **Figure 2** [34, 36].

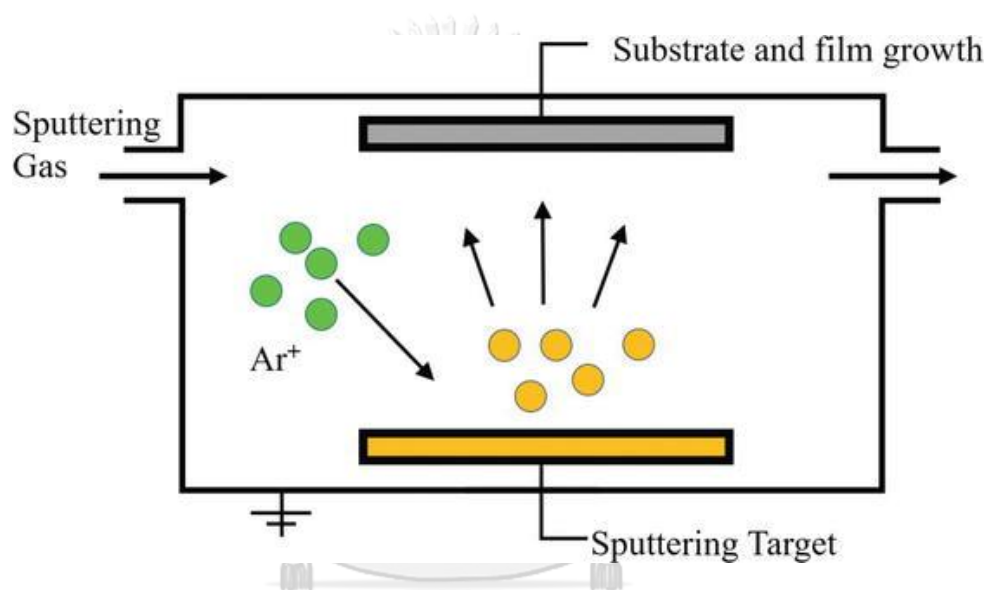


Figure 2 Schematic diagram of magnetron sputtering [34].

Magnetron sputtering is the collision process between active ions of inert gases (e.g., argon or helium) and targets. Seeing that high-speed sputtering is carried out at low pressure, it is necessary to effectively increase the ionization rate of the gas, mostly use argon as the sputtering gas. A target or a metal precursor, that is desired to be deposited, is bombarded with active ions of argon gas. The strong collision of these active ions with the target ejects target metal atoms into space. After that, These metal atoms are then deposited on the substrate material forming a metallic film. Magnetron sputtering increases the plasma density by introducing a

magnetic field on the surface of the target cathode and utilizing the constraints of the magnetic field on the charged particles to increase the sputtering rate [34-36].

Magnetron sputtering includes many types, such as direct current (DC) magnetron sputtering and radio frequency (RF) magnetron sputtering, each has a different working principle and application objects. DC magnetron sputtering uses direct current power to coat the film which is suitable for conductive coatings. And RF magnetron sputtering, using radiofrequency alternating current power to cathode and anode electrodes which is suitable for insulating coatings. [34, 35].

Pulsed direct current magnetron sputtering deposition (PDC-MSD) method is a famous deposition technique applicable to produce thin films layer to packaging coating. This deposition technique has been employed in the industry, due to its easy to scale up, high ability, high stability, controllability, repeatability, uniformity, low environmental effect, and high efficiency in coatings. Nowadays, PDC-MSD method has been applied on the laboratory scale for the deposition of metal nanoparticles on solid and liquid surface supports [22, 23]. Importantly, the PDC-MSD method deposits atoms and atomic clusters from highly pure targets (99.99%) on the substrate [24].



2.5 Hydrogenation of acetophenone (AP)

The selective hydrogenation of aromatic ketones to aromatic alcohols is a significant reaction in the fine chemical industry because of increasing high-value added chemicals [1]. The hydrogenation of acetophenone (AP) has competitive hydrogenation between carbonyl (C=O double bond) and aromatic ring or phenyl groups [3]. As shown in **Figure 3**, the first is the hydrogenation of the carbonyl group of AP, which is converted to 1-phenylethanol (PHE). Second is the hydrogenation of the phenyl group, which is converted to cyclohexylmethylketone (CHMK). After that PHE and CHMK can be hydrogenated to cyclohexylethanol (CHE). The hydrogenolysis

of PHE and CHE can produce ethylbenzene (EB) and ethylcyclohexane (ECH) respectively. Furthermore, EB can be hydrogenated to ECH [1, 5, 10].

PHE is the desired product from the selective hydrogenation of AP. PHE is a high-value chemical and various applications in the fragrance and pharmaceutical industries [2, 3]. In fragrance industries, PHE is extensively used as strawberry fragrance additives in yogurts and chewing gums [2]. In pharmaceutical industries, PHE is an intermediate of analgesic and anti-inflammatory drugs such as Ibuprofen [2, 4] as shown in **Figure 4**.

Considering the selective hydrogenation of AP to PHE in liquid-phase hydrogenation, various pressures, temperatures, and types of solvents have been presented over supported noble metal and non-noble metal catalysts [5]. Noble metal catalysts such as Pt [6-9], Ag [10], Pd [11, 12], Rh [11, 13], Ru [14] and non-noble metals such as Cu [2, 4, 5], Ni [5, 15], Co [1, 3, 5], Zr [16], Fe [4, 17], Cr [17]. Pt-supported catalysts are used in the hydrogenation of AP because of high catalytic activity but Pt-supported catalysts can catalyze hydrogenation of carbonyl (C=O) and phenyl groups of the AP molecule to produce comparable products (PHE and CHMK) It is difficult to obtain high selectivity of PHE products and high activity of AP in a mild condition. So, in mild conditions improving catalytic performance and reducing operating costs are a special challenge such as changing catalyst support and reducing operating conditions.

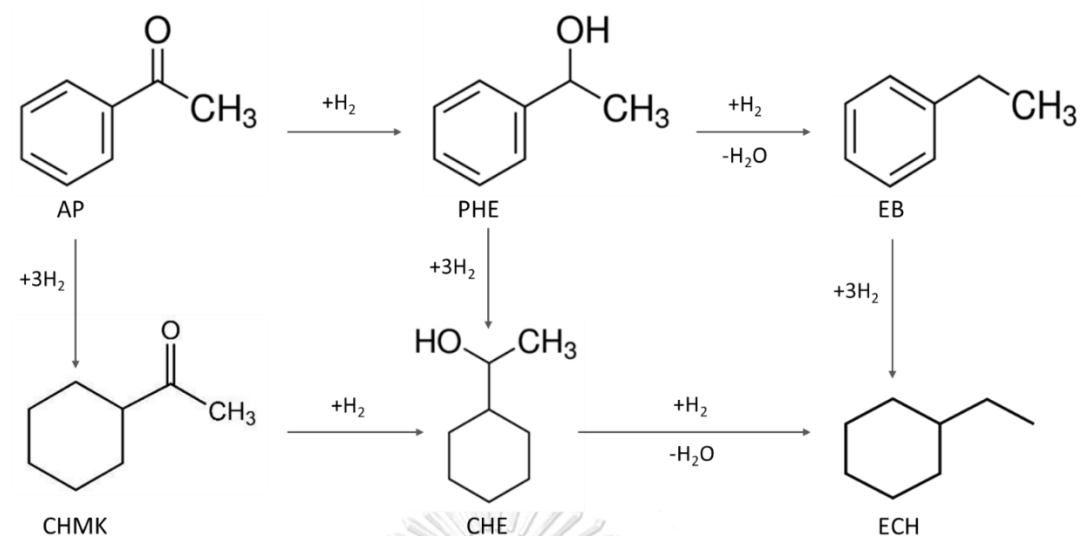


Figure 3 Reaction scheme for the hydrogenation of acetophenone. AP: acetophenone, PHE: 1-phenylethanol, EB: ethylbenzene, CHMK: cyclohexylmethylketone, CHE: cyclohexylethanol, ECH: ethylcyclohexane

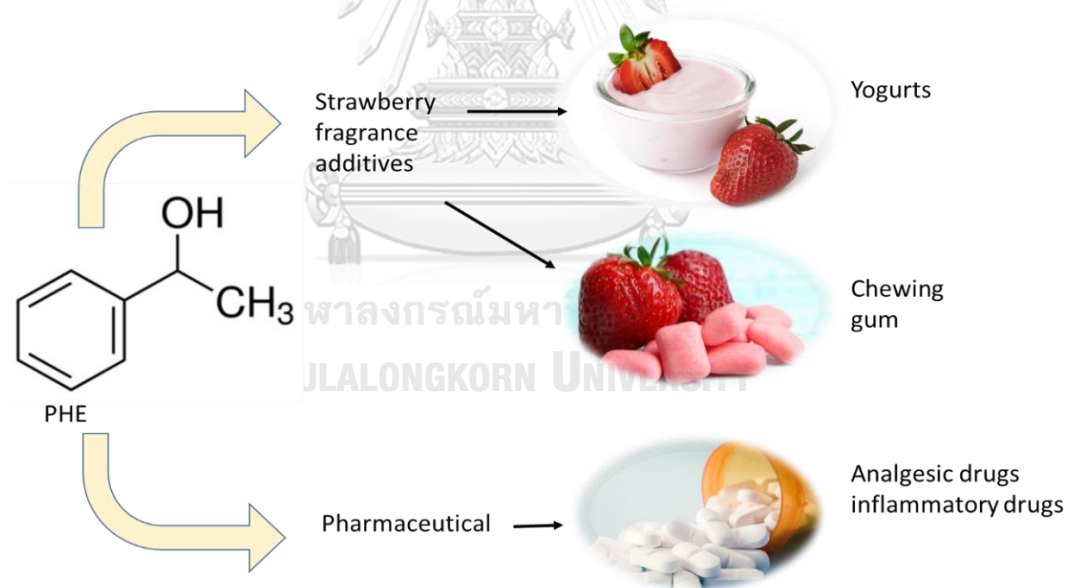


Figure 4 Applications of 1-phenylethanol (PHE)

Previous research of hydrogenation of acetophenone (AP) on various catalysts under different reaction conditions are shown in **Table 2**.

Table 2 Summary of the research of the selective hydrogenation of acetophenone (AP) on various catalysts under different reaction conditions.

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
Alonso, F., et al. (2008). [6]	<ul style="list-style-type: none"> - Studied the effect of reduction temperature over Pt/TiO₂ catalysts for the reduction of AP by hydrogen transfer 	<ul style="list-style-type: none"> - 1.5% Pt/TiO₂ was prepared by the impregnation method. 	<ul style="list-style-type: none"> - T = room temp., 76°C - P_{H₂} = 0 bar - Reaction time = 1, 2, 24 h. - Isopropanol was used as a hydrogen donor or solvent - Add KOH 1 mmol. 	<ul style="list-style-type: none"> - Pt/TiO₂ is suitable for the hydrogen transfer reduction of acetophenone in 2-propanol. - Adding KOH promote yield of PHE up to 84% at reaction times = 2 h. - The Pt/TiO₂ catalyst reduced at 773 K. could be easily reused and maintained good catalytic activity.
Vetere, V., et al. (2015). [7]	<ul style="list-style-type: none"> - Studied the effect of the chemical nature of the substituents groups on the aromatic 	<ul style="list-style-type: none"> - 1% Pt/SiO₂ was prepared by ionic exchange. Pt-Sn/SiO₂ (Sn/Pt atomic ratios 0.2 and 0.8) was prepared by surface 	<ul style="list-style-type: none"> - T = 80°C - P_{H₂} = 1 MPa - Reaction time = 30-400 min. 	<ul style="list-style-type: none"> - At 50% of AP conversion, PtSn0.8/SiO₂ showed the highest selectivity of PHE (84%). - At 400 min, Pt/SiO₂ showed

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
	ketones are adsorbed on the metallic surface.	organometallic chemistry of metals.	- Isopropanol was used as solvent.	50% selectivity of PHE. - The presence of Sn effects encourages the interaction through a carbonyl group (C=O), inhibiting adsorption of the aromatic ring.
Wu, W., et al. (2019).[8]	- Studied the effect of various Pt-Fe morphology in the hydrogenation of AP.	- Pt-Fe nanowires - Pt-Fe nanocubes - Pt-Fe nanoparticles - 5% Pt/C	- T = 70°C - P _{H₂} = 1 bar - Reaction time = 30-450 min. - N-butanol was used as a solvent.	- Pt-Fe nanowires showed the highest conversion of AP (99.3%) and the selectivity of PHE (91.7%) at 200 min. - Pt-Fe nanowires with high-index facets create steric effects which selectively adsorbed the carbonyl group and inhibited the adsorption of aromatic rings.
Liu, H., et al.	- Studied the effects of	- 5% Pt/V-Al ₂ O ₃	- T = 70°C	- The mesoporous Pt/V-Al ₂ O ₃

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
(2009). [9]	<p>Pt/γ-Al₂O₃ catalysts in various preparation methods.</p> <p>- Studied the effects of the amount of chitosan in the hydrogenation of AP.</p>	<p>were prepared by the incipient wetness impregnation method.</p> <p>- 5% Pt/γ-Al₂O₃ was prepared by the “one-step” method (Al₂O₃ was prepared by using chitosan)</p>	<p>- P_{H₂} = 0.6 MPa</p> <p>- Reaction time = 24 h.</p> <p>-Methanol was used as a solvent.</p>	<p>prepared show an excellent catalytic performance (89.1%) and high selectivity to PHE (97.6%), which were much better than the Pt-Al₂O₃ catalyst was synthesized by a “one-step” method and Pt/γ-Al₂O₃ catalyst prepared with commercial γ-Al₂O₃.</p>
Jiang, Y., et al. (2012). [10]	<p>- Studied the effect of the various ratios of bimetallic Pt-Pd/ ZrO₂ catalysts in the hydrogenation of AP without solvent.</p>	<p>- 3% Pt-Pd/ZrO₂ was prepared by the simple flame spray pyrolysis method.</p>	<p>- T = 160°C</p> <p>- P_{H₂} = 60 bar</p> <p>- Reaction time = 3 h.</p> <p>- solvent-free hydrogenation.</p>	<p>- For bimetallic catalysts, Pt sites could promote hydrogenation of the carbonyl group while Pd sites could promote hydrogenation of the phenyl group.</p> <p>- Pt₇₅Pd₂₅/ZrO₂ showed the highest selectivity of PHE (64%).</p>

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
Zhang, X. B., et al. (2019). [3]	<p>- Studied the effect of various solvents (water, ethanol, n-hexane) in the hydrogenation of acetophenone over Co/mordenite.</p> <p>- Studied the effect of the various reaction temperatures (363 K, 373 K, 383 K) in the</p>	<p>- 16.7% Co/mordenite zeolite was prepared by the incipient wetness impregnation method.</p>	<p>- T = 100°C</p> <p>- P_{H₂} = 2 MPa</p> <p>- Reaction time = 6 h.</p> <p>- Water, ethanol, n-hexane were used as a solvent.</p>	<p>- The synthesis of bimetallic Pt-Pd catalysts by flame-spray pyrolysis results in a high dispersion of Pt and Pd and allows easy control of the metal loading on the zirconia surface.</p> <p>- The highest selectivity of PHE was maintained at 100% when the conversion of AP was below 99.9% in a water solvent.</p> <p>- Increasing the reaction temperature would promote the hydrogenolysis of PHE to EB.</p> <p>- Neutral and alkaline conditions are beneficial to the</p>

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
	<p>hydrogenation of AP over Co/mordenite.</p> <p>- Studied the effect of the various additives (KOH, NaOH, CH₃COOH) in the hydrogenation of AP over Co/mordenite.</p>			<p>hydrogenation of AP to PHE.</p> <p>The acid additives in the solvent were not favorable to the hydrogenation of AP.</p>
Trasarti, A. F., et al. (2014). [5]	<p>- Studied the effect of various solvents (2-propanol, cyclohexane, toluene, benzene) and metal nature on the liquid-phase hydrogenation of AP over Ni/SiO₂, Co/SiO₂, and Cu/SiO₂.</p>	<p>- 8 wt% Ni/SiO₂, Co/SiO₂, and Cu/SiO₂ were prepared by the incipient wetness impregnation method.</p>	<p>- T = 90°C</p> <p>- P_{H₂} = 10 bar</p> <p>- 2-propanol, cyclohexane, toluene, benzene were used as a solvent.</p>	<p>- The maximum yield in PHE follows the pattern: Cu/SiO₂ > Ni/SiO₂ > Co/SiO₂.</p> <p>- The initial hydrogenation rate of acetophenone depends on the solvent as follows: 2-propanol > cyclohexane > toluene > benzene.</p> <p>- 2-propanol increases the hydrogenation rate of AP</p>

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
Raj, K. J. A., et al. (2012). [16]	<ul style="list-style-type: none"> - Studied the catalytic activity of Ni impregnated on various phases of titania (anatase, rutile, and high surface area) - Studied the catalytic activity of various % Ni loadings impregnated on titania in the hydrogenation of AP. 	<ul style="list-style-type: none"> - 15 wt% Ni catalysts supported on various phases of titania (anatase, rutile, and high surface area). - 2.5, 5.0, 7.5, 10.0, and 12.5 wt% Ni/TiO₂ were prepared by an incipient wetness impregnation method. 	<ul style="list-style-type: none"> - T = 120-140°C - P_{H₂} = 10-40 kg/cm² - Reaction time = 1-14 h. - Methanol was used as a solvent. 	<p>through hydrogen transfer.</p> <ul style="list-style-type: none"> - 15 wt% Ni catalysts under hydrogen pressure of 40 kg cm² and 140 °C were found to be optimum reaction conditions to achieve a good activity of AP. - The catalytic activity order is Ni/rutile > Ni/anatase > Ni/TiO₂. - The electronic interaction between Ni and rutile improves the adsorption of H₂ molecules and formation of electron-enriched Ni-H species which interact with the carbonyl (C=O) group of AP.
Wang, B., et al.	<ul style="list-style-type: none"> - Studied the catalytic 	<ul style="list-style-type: none"> - 25 wt% Cu/SiO₂ was 	<ul style="list-style-type: none"> - T = 80-150°C 	<ul style="list-style-type: none"> - 25% Cu/SiO₂ exhibited 99.8%

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
(2019). [4]	performances of 25% Cu/SiO ₂ on various conditions in the hydrogenation of AP.	prepared by urea homogeneous precipitation method.	- P _{H₂} = 1-3 MPa - LHSV = 0.6-1.2 h ⁻¹ .	conversion of AP and 99.08% selectivity of PHE under the optimum reaction conditions (Temperature: 353 K; Pressure: 2.0 MPa, LHSV: 1.0 h ⁻¹ and the molar ratio of H ₂ /AP=15). - The presence of copper phyllosilicate improved the ratio of Cu ⁺ / (Cu ⁺ +Cu ⁰) promoted the activity and stability of the Cu/SiO ₂ catalyst.
Fujita, S.-i., et al. (2016). [12]	- Studied the effect of various solvents (water, methanol, n-hexane) with commercial 5 wt% Rh/C, Rh/Al ₂ O ₃ , 5% Pd/Al ₂ O ₃ , and 5% Pd/C	- 5 wt% Rh/C, Rh/Al ₂ O ₃ , Pd/C, and Pd/Al ₂ O ₃	- T = 80°C - P _{H₂} = 2 MPa for Rh catalysts, 4 MPa for Pd catalysts - Reaction time = 60-360 min.	- The Rh/Al ₂ O ₃ showed the highest conversion of AP (78%) and the selectivity of PHE (85%) in water - The effect of solvents depends on the support

Researchers	Studies	Catalyst and preparation method	Reaction conditions	Results
	<p>catalysts</p> <p>- Studied the influence of CO₂ pressurization as a reaction promoter in heterogeneous AP hydrogenation reactions with supported Pd and Rh catalysts in different solvents.</p>		<p>- Water, methanol, and n-hexane were used as a solvent.</p> <p>- P_{CO₂} = 2 MPa (for reaction in the CO₂-dissolved solvents)</p>	<p>materials (Al₂O₃, C) but not depends on the metal species (Pd, Rh).</p> <p>- The pressurization with CO₂ (1 MPa) improves the conversion of AP hydrogenation with Pd/Al₂O₃ in methanol, due to the action of H⁺ species formed.</p>

Alonso, F., et al. (2008). [6] studied the effect of reduction temperature (473 or 773 K) over 1.5 wt% Pt/TiO₂ catalysts, which was prepared by the impregnation method in the reduction of AP by hydrogen transfer. In the results, it was found that Pt/TiO₂ is suitable for the hydrogen transfer reduction of acetophenone in isopropanol as the hydrogen donor. Adding KOH promoted yield of PHE up to 84% at 2 hours reaction times. Furthermore, The Pt/TiO₂ catalyst reduced at 773 K could be easily reused and maintained good catalytic activity over four repeated cycles while the Pt/TiO₂ catalyst reduced at 473 K could not be reused in three cycles because the yield of PHE decreased significantly.

Vetere, V., et al. (2015). [7] studied the effect of the chemical nature of the substituents groups on the aromatic ketones which were absorbed on the metallic surface over Pt catalyst. As follows, 1% Pt/SiO₂ was prepared by ionic exchange. Pt-Sn/SiO₂ (Sn/Pt atomic ratios 0.2 and 0.8) was prepared by surface organometallic chemistry of metals. In the results, it was found that at 50% of AP conversion, PtSn0.8/SiO₂ showed the highest selectivity of PHE (84%). At 400 min, Pt/SiO₂ showed 50% selectivity of PHE. Furthermore, the presence of Sn effects encourages the interaction through a carbonyl group (C=O) and inhibiting adsorption of the aromatic ring for these reasons, increasing the initial hydrogenation rate of AP.

Wu, W., et al. (2019). [8] studied the effect of various Pt-Fe morphology in the hydrogenation of AP. Pt-Fe nanowires, Pt-Fe nanocubes, Pt-Fe nanoparticles, and 5% Pt/C were used as catalysts. In the results, it was found that Pt-Fe nanowires showed the highest conversion of AP (99.3%) and the selectivity of PHE (91.7%) at 200 min. Pt-Fe nanowires with abundant high-index facets create steric effects that selectively adsorbed the carbonyl group and inhibited the adsorption of phenyl group. Moreover, the construction of high-index facets offers a strategy to create steric effects for improved selectivity without occupying or passivating active sites.

Liu, H., et al. (2009). [9] studied the effects various preparation methods of Pt/ γ -Al₂O₃ catalysts. 5% Pt/ γ -Al₂O₃ were prepared by the incipient wetness impregnation method, 5% Pt/ γ -Al₂O₃ was prepared by the “one-step” method including Al₂O₃ support was prepared by using chitosan. Moreover, the effects of the amount of chitosan in the hydrogenation of AP was studied. In the results, it was found that the mesoporous Pt/Al₂O₃ prepared using 1 g of chitosan exhibits an excellent catalytic performance (89.1%) and high selectivity to PHE (97.6%), which were much better than the Pt-Al₂O₃ catalyst was synthesized by a “one-step” method and Pt/ γ -Al₂O₃ catalyst prepared with commercial γ -Al₂O₃ because chitosan encourages shape and surface morphology of Al₂O₃ support of Pt catalyst. Moreover, the calcination temperature of the catalyst influenced the Pt dispersions of Pt/ γ -Al₂O₃ including the activity of the Pt active sites on Pt/ γ -Al₂O₃ catalyst and the size of Pt particles on mesoporous Al₂O₃ were affected by the surface morphology and structure of Al₂O₃.

Jiang, Y., et al. (2012). [10] studied the effect of the various ratios of bimetallic 3% Pt-Pd/ ZrO₂ catalysts with different Pt and Pd atomic ratios. The catalysts were prepared by the simple flame spray pyrolysis method in the solvent-free hydrogenation of AP. In the results, it was found that for bimetallic catalysts, Pt sites seem to favor hydrogenation of the carbonyl group while Pd sites favor the phenyl group. Pt₇₅Pd₂₅/ZrO₂ showed the highest selectivity of PHE (64%). Moreover, the synthesis of bimetallic Pt-Pd catalysts by flame-spray pyrolysis results in a high dispersion of Pt and Pd and allows easy control of the metal loading on the zirconia surface. Although the electronic properties of bimetallic catalysts are changed compared to their monometallic counterparts, the Pd and Pt active sites still kept their specific properties of product selectivity. The catalysts could be reused because activity and selectivity decreased slightly after suitable treatment.

Zhang, X. B., et al. (2019). [3] studied the effect of various solvents (water, ethanol, n-hexane), reaction temperatures (363 K, 373 K, 383 K), and additives (KOH,

NaOH, CH₃COOH) in the hydrogenation of acetophenone over Co/mordenite catalysts, in which 16.7% Co/mordenite zeolite was prepared by the incipient wetness impregnation method. In the results, it was found that the highest PHE selectivity was maintained at 100% when the conversion of AP was below 99.9% in a water solvent. The highest PHE yield was found in water solvent. Increasing the reaction temperature would promote the hydrogenolysis of PHE to EB. The reaction rate without significant loss when the AP concentration and catalyst loading increased to three times. The conversion of AP was 98.6% and 99.6% when KOH and NaOH were added in water, respectively, although the conversion of AP decreased to 62.6% after CH₃COOH was added. Therefore, The alkaline and neutral conditions have promoted the hydrogenation of AP to PHE but the acid additives in the solvent were not favorable to the hydrogenation of AP. Moreover, the conversion of AP and the reaction selectivity to PHE decreased slightly after four cycles of solvent water when compared with fresh solvent water.

Trasarti, A. F., et al. (2014). [5] studied the effect of various solvents (2-propanol, cyclohexane, toluene, benzene) and metal nature on the liquid-phase hydrogenation of AP over Ni/SiO₂, Co/SiO₂, and Cu/SiO₂ catalysts, in which 8 wt% of these catalysts were prepared by the incipient wetness impregnation method. In the results, it was found that the catalytic activity follows the pattern: Ni/SiO₂ > Co/SiO₂ > Cu/SiO₂ while, the initial selectivity to PHE follows the pattern: Cu/SiO₂ \cong Co/SiO₂ > Ni/SiO₂. So, the maximum yield in PHE follows the pattern: Cu/SiO₂ > Ni/SiO₂ > Co/SiO₂. For the reasons, in lack of solvent-catalyst interactions, various catalytic activity depends on the capability of each metal for dissociative hydrogen chemisorption. The initial hydrogenation rate of acetophenone depends on the solvent follows the pattern: 2-propanol > cyclohexane > toluene > benzene. For the reasons, the effect of the solvent depends on metal nature. Moreover, Isopropanol could increase the hydrogen transfer hydrogenation rate of AP.

Raj, K. J. A., et al. (2012). [16] studied the catalytic activity of Ni impregnated on various phases of titania and studied the catalytic activity of various % Ni loadings impregnated on titania in the hydrogenation of AP. 15 wt% Ni catalysts supported on various phases of titania (anatase, rutile, and high surface area) including, 2.5, 5.0, 7.5, 10.0, and 12.5 wt% Ni/TiO₂ were prepared by an incipient wetness impregnation method. In the results, it was found that 15 wt% Ni catalysts under hydrogen pressures of 40 kg cm² and 140 °C were found to be optimum reaction conditions to achieve a good activity of AP. For, the catalytic activity follows the pattern: Ni/rutile > Ni/anatase > Ni/TiO₂ because of the high concentration of Ni on the surface of rutile and SMSI between rutile and Ni more than that between Ni and anatase or TiO₂. The catalyst samples calcined at 900°C showed sintering of Ni follows the pattern: Ni/TiO₂ > Ni/anatase > Ni/rutile, which caused their catalytic activity to decrease. Moreover, the electronic interaction between Ni and rutile improves the adsorption of H₂ molecules and the formation of electron-enhanced Ni-H species which interact with the carbonyl (C=O) group of AP.

Wang, B., et al. (2019). [4] studied the catalytic performances of 25% Cu/SiO₂ on various conditions in the hydrogenation of AP, in which 25 wt% Cu/SiO₂ was prepared by urea homogeneous precipitation method. In the results, it was found that 25% Cu/SiO₂ showed 99.8% conversion of AP and 99.08% selectivity of PHE under temperature: 353 K, hydrogen pressure of 2.0 MPa, LHSV: 1.0 h⁻¹, and the molar ratio of H₂/AP=15. Moreover, the presence of copper phyllosilicate improved the ratio of Cu⁺/ (Cu⁺+Cu⁰) promoted the activity and stability of the Cu/SiO₂ catalyst that operates consistently for 500 h without observable change.

Fujita, S.-i., et al. (2016). [12] studied the effect of various solvents (water, methanol, n-hexane) with commercial 5 wt% Rh/C, Rh/Al₂O₃, 5% Pd/Al₂O₃, and 5% Pd/C catalysts and studied the influence of CO₂ pressurization as a reaction promoter in heterogeneous hydrogenation of AP with supported Pd and Rh catalysts in different solvents. In the results, it was found that the Rh/Al₂O₃ showed the highest

conversion of AP (78%) and the selectivity of PHE (85%) when using water as a solvent because its large polarity/polarizability index might lead to the high selectivity to the formation of PHE. For, the effect of solvents depends on the support materials (Al_2O_3 , C) but not depends on the metal species (Pd, Rh). Moreover, the pressurization with 1 MPa of CO_2 can improve the conversion of AP hydrogenation with Pd/ Al_2O_3 in methanol due to the action of H^+ species formed. The Rh/ Al_2O_3 catalyst deactivates through poisoning with CO formed from H_2 and CO_2 . Therefore, the nature of supported metal catalysts is important for the occurrence of positive and negative effects of CO_2 pressurization in the hydrogenation of AP.

From the literature review, the selective hydrogenation of AP to PHE was carried out at 70-180°C, 1-60 bar of H_2 , and 1-24 h reaction time in 2-propanol, methanol, n-butanol, ethanol, n-hexane, cyclohexane, benzene, toluene. It was found that the 2-propanol solvent showed the highest AP conversion, the highest selectivity, and the highest yield of PHE. Moreover, Pt-supported catalysts could be operated at low-pressure conditions (1 bar) and showed high catalytic activity.



CHAPTER III

MATERIAL AND METHODS

3.1 Catalyst preparation

3.1.1 Preparation of Pt/TiO₂ catalysts by PDC-MSD method

Surface Engineering and Advanced Materials Group, Manchester Metropolitan University has prepared Pt/TiO₂ catalysts by the pulsed direct current magnetron sputtering deposition (PDC-MSD) method, using the type of commercial TiO₂ support as PC500 (pure anatase) and P25 (mixed anatase/rutile phase) in which each type of support has adjusted the Pt coating time on the supports equal to 3, 6, 9 minutes respectively. The Pt/TiO₂ catalysts prepared by the PDC-MSD method are denoted as MSD-Pt-P25-3, MSD-Pt-P25-6, MSD-Pt-P25-9 for the type of TiO₂ support as P25, MSD-Pt-PC500-3, MSD-Pt-PC500-6, and MSD-Pt-PC500-9 for the type of TiO₂ support as PC500.

A Schematic of Pt/TiO₂ catalysts preparation by PDC-MSD method is shown in **Figure 5**. The PDC-MSD system was applied in a sputter-down configuration, through a single 7.5 cm diameter type II unbalanced planar magnetron as the magnetron sputtering source installed on the chamber roof, with the Pt target together. The TiO₂ powder holder was placed below the magnetron and installed on a shaker mechanism, which allowed continuous powder mixing during the PDC-MSD process. The distance between the substrate and the Pt target was fixed at 5 cm. The magnetron sputtering source was powered by an Advanced Energy Pinnacle Plus power supply. The Pt target was sputtered at 250W and 350 kHz with a 50% duty cycle (corresponding to 1.4 μ s pulse-off period). Sputtering took place under an Ar atmosphere at a working pressure of about 2.6 Pa. For each time, 2 g of commercial TiO₂ PC500 and P25 powder was placed in the substrate holder and treated for various sputtering times [22, 23].

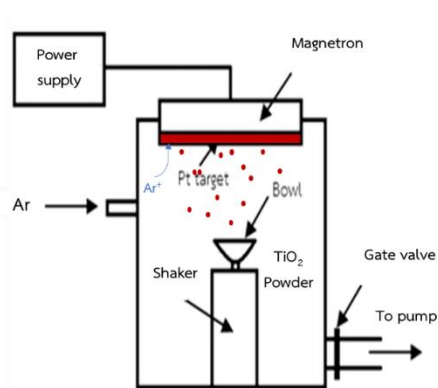


Figure 5 Schematic of Pt/TiO₂ catalysts preparation by PDC-MSD method

3.1.2 Preparation of Pt/TiO₂ catalysts by incipient wetness impregnation method

The 1.4 wt% Pt/TiO₂ catalysts were prepared by incipient wetness impregnation method using various TiO₂ polymorphs as PC500 and P25 as supports. Platinum(II) acetylacetonate was used as the Pt precursor. The desired amount of Pt precursor was dissolved in xylene and slowly dropped on various TiO₂ supports. After that, the catalysts were left at room temperature for 6 h and dried in an oven overnight at 110 °C. Finally, the catalysts were calcined in air at 400 °C for 4 h, as shown in **Figure 6**. The Pt/TiO₂ catalysts prepared by the incipient wetness impregnation method are denoted as IMP-Pt-P25, and IMP-Pt-PC500 for the type of TiO₂ support as P25 and PC500, respectively.

Table 3 Supports used for Pt/TiO₂ catalysts preparation

Chemicals	Formula	Suppliers
PC500 (pure anatase)	TiO ₂	Sigma-Aldrich
P25 (mixed anatase and rutile)	TiO ₂	Sigma-Aldrich

Table 4 Chemicals used for Pt/TiO₂ catalysts preparation by incipient wetness impregnation method

Chemicals	Formula	Suppliers
Platinum (II) acetylacetonate 99.99%	Pt(C ₅ H ₇ O ₂) ₂	Aldrich
Xylene 99.8%	C ₈ H ₁₀	Merck

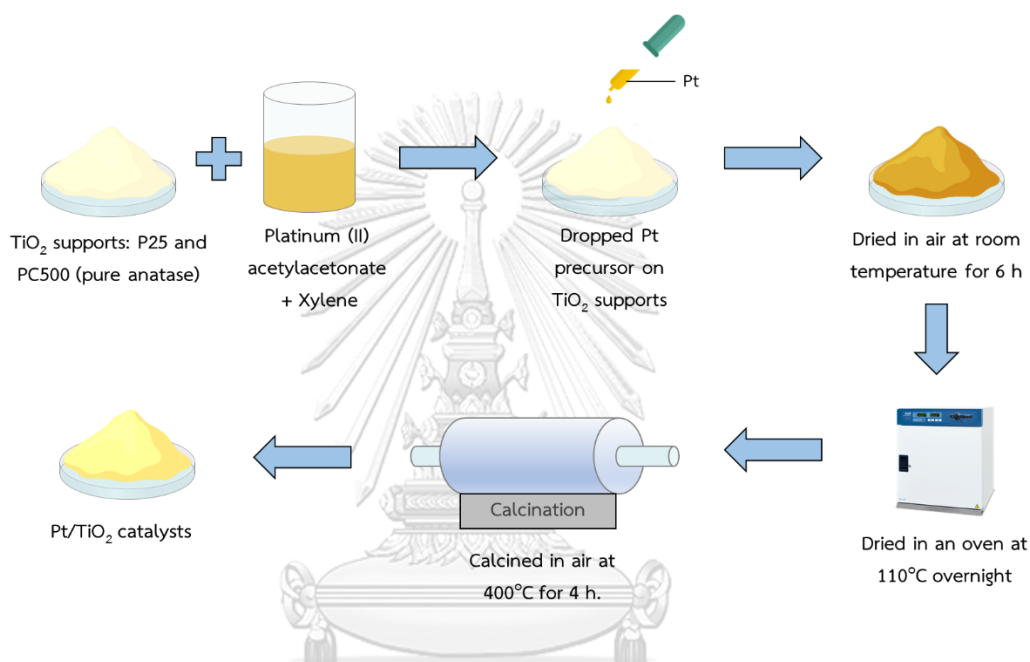


Figure 6 Diagram of Pt/TiO₂ catalysts preparation by incipient wetness impregnation method.

3.2 Catalyst Characterization

3.2.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were analyzed by a SIEMENS XRD D5000 X-ray diffractometer with CuK α radiation in a scanning range from 20° to 80° of 2 θ . The average crystallite size (d_{XRD}) of TiO₂ was calculated using Scherrer's equation. This technique was employed to identify and quantify the crystalline phases.

3.2.2 N₂ – physisorption

The BET specific surface area, pore volumes, average pore size diameters, and N₂ adsorption-desorption isotherms of catalysts were analyzed by using N₂ - physisorption technique on a Micromeritics ASAP 2020 automated system.

3.2.3 X-ray photoelectron spectroscopy (XPS)

The XPS spectra, the binding energy, and the surface composition of catalysts were analyzed by using the Kratos AMICUS X-ray photoelectron spectroscopy. This experiment was operated with MgK α X-ray source at 20 mA and 12 kV (240 W) as a primary excitation. The KRATOS VISION II software was performed in computer-controlled. The C 1s line was referenced at a binding energy of 285.0 eV as the internal standard.

3.2.4 Inductively coupled plasma optical emission spectrometer (ICP-OES)

The actual Pt loading of the catalysts after deposition and impregnation on various TiO₂ supports were analyzed by using inductively coupled plasma optical emission spectrometer (ICP-OES).

3.2.5 Transmission electron spectroscopy (TEM)

The morphology and metal sizes of catalysts were analyzed by using HT7700 transmission electron microscope operated at 200 kV.

3.2.6 CO-pulse chemisorption

The amounts of Pt active sites, percentages of Pt dispersion, and average Pt particle size on catalysts were analyzed by using the CO-pulse chemisorption technique on a Micromeritics Chemisorb 2750 with ChemiSoftTPx software. The catalyst samples were performed in a glass U-tube reactor and pretreated under He flow (25 cm³/min) and then the catalyst was reduced under H₂ flow (25 cm³/min) at 500°C for 2 h with a heating rate of 10 °C/min and cooled down to 40°C under He flow. After that, CO gas was injected into the sample cell to adsorb on the Pt active

sites whereas unadsorbed CO was detected by the thermal conductivity (TCD). Pulsing was performed until not longer adsorbed CO is detected.

3.2.7 H₂ temperature-programmed reduction (H₂-TPR)

The reducibility of the catalysts and the interaction of metal and support were analyzed by H₂ temperature-programmed reduction (H₂-TPR) using a Micromeritics Chemisorb 2750 with ChemiSoftTPx software. The catalyst samples were performed in a quartz U-tube reactor and pretreated under N₂ flow (25 cm³/min) at 300 °C for 1 h to remove water. Then, cooling down to room temperature under N₂ flow. After that, a gas mixture of 10% H₂ in Ar (25 cm³/min) was passed through the quartz U-tube reactor to the catalyst sample with a temperature ramp at a heating rate of 10 °C/min from room temperature to 800 °C.

3.3 Catalytic test in the selective hydrogenation of acetophenone

For the catalyst prepared by the incipient wetness impregnation method, the catalysts were reduced with H₂ (30 cm³/min) at 500 °C for 2 h before the reaction test.

The selective hydrogenation of acetophenone (AP) to 1-phenylethanol (PHE) was tested in the liquid phase by using the various catalysts in a 100 mL stainless steel autoclave reactor (JASCO, Tokyo, Japan). Approximately 100 mg of the catalysts, 292 μL of AP (2.5 mmol), and 10 ml of 2-propanol were placed into an autoclave reactor supplied with a hot plate and magnetic stirrer. Then, heating the oil bath set about 80 °C after that purged the autoclave reactor with H₂ up to 5 bars three times. The selective hydrogenation of AP was carried out at 80 °C, 1 bar of H₂ for 2 h while stirring the reaction mixture with a magnetic stirrer at 450 rpm. After each reaction, the autoclave reactor was cooled down quickly to 5 °C with ice and carefully depressurized. The reaction mixture was centrifuged and separated from

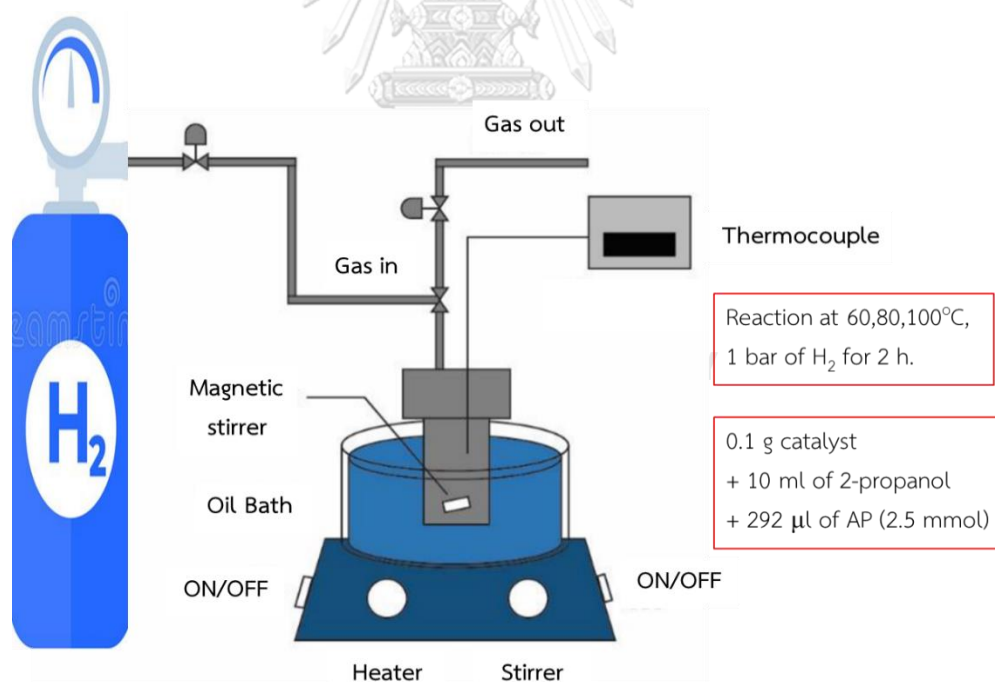
the catalyst. The liquid product was analyzed by a Gas Chromatograph-Mass Spectrometer (GC-MS) equipped with a DB-5 capillary column.

Table 5 Chemicals used in the liquid-phase hydrogenation of acetophenone

Chemicals	Formula	Suppliers	Molecular weight (g/mol)	Density
Acetophenone 99%	C ₈ H ₈ O	Sigma-Aldrich	120.15	1.030 g/ml at 25°C (lit.)
1-Phenylethanol 98%	C ₈ H ₁₀ O	Sigma-Aldrich	122.16	1.012 g/ml at 25°C (lit.)
Ethylbenzene 99.8%	C ₈ H ₁₀	Sigma-Aldrich	106.17	0.867 g/ml at 25°C (lit.)
Ethylcyclohexane >99%	C ₈ H ₁₆	Sigma-Aldrich	112.21	0.788 g/ml at 25°C (lit.)
Cyclohexyl methyl ketone 95%	C ₈ H ₁₄ O	Alfa Aesar	126.20	0.917 g/ml at 25°C (lit.)
1-Cyclohexylethanol 97%	C ₈ H ₁₆ O	Sigma-Aldrich	128.21	1.012 g/ml at 25°C (lit.)
2-Propanol >99.8	C ₃ H ₈ O	Supeico	60.10	0.785 g/ml at 25°C (lit.)
Hydrogen gas (UHP; 99.9% vol)	H ₂	linde	2	0.08988 at STP

Table 6 Gas-chromatography-Mass spectroscopy (GC-MS) operating conditions

Gas Chromatograph-Mass Spectrometer	Shimadzu GCMS-QP2010
Capillary column	DB-5 (30m x 0.25 mm x 0.25 μ m)
Carrier gas	Helium (99.99 vol%)
Make-up gas	Air (99.9 vol%)
Injection volume	1 μ L
Initial column oven temperature	60 $^{\circ}$ C
Injection temperature	300 $^{\circ}$ C
Detector temperature	300 $^{\circ}$ C
Injection mode	Split
Total flow rate	50 ml/min
Time analysis	63.87 min

**Figure 7** Schematic of the liquid-phase hydrogenation of acetophenone

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the investigation of the catalyst characterizations and the catalytic properties in the liquid phase selective hydrogenation of acetophenone (AP) to 1-phenylethanol (PHE) over the Pt/TiO₂ prepared by pulsed direct current magnetron sputtering deposition (PDC-MSD) and incipient wetness impregnation method were discussed. The results and discussion are divided into two parts.

In the first part, the investigation of Pt-based catalysts prepared on TiO₂ supports by PDC-MSD compared to the incipient wetness impregnation method were reported. In the PDC-MSD method, Pt-based catalysts on various TiO₂ polymorphs such as PC500 (pure anatase) and P25 (mixed anatase and rutile phase). For each type of support, the deposition time spent on Pt coating was varied at 3, 6, and 9 minutes. For comparison purposes, Pt/TiO₂ catalysts were also prepared by the incipient wetness impregnation method with similar amount of Pt loadings (1.4 wt.%). The catalyst samples in the liquid phase selective hydrogenation of AP were analyzed by X-ray diffraction (XRD), N₂ – physisorption, X-ray photoelectron spectroscopy (XPS), Inductively coupled plasma optical emission spectrometer (ICP-OES), transmission electron spectroscopy (TEM), CO-pulse chemisorption, and H₂ temperature-programmed reduction (H₂-TPR)

In the second part, the effect of reaction temperature of the selective hydrogenation of AP to PHE over Pt/TiO₂ catalysts prepared by the PDC-MSD method on various TiO₂ polymorphs with similar Pt loadings (3 wt.%) were reported.

Part I The investigation of Pt-based catalysts prepared on TiO₂ supports by PDC-MSD compared to the incipient wetness impregnation method

4.1 Characterizations of Pt/TiO₂ catalysts

4.1.1 X-ray diffraction (XRD)

The XRD patterns of all the catalyst samples prepared by the PDC-MSD method and the incipient wetness impregnation method at diffraction angles (2θ) between 20° and 80° are shown in **Figure 8**. All the catalyst samples showed the anatase phase of TiO₂ diffraction peak at $2\theta = 25.2^\circ$ (major), 36.9°, 37.7°, 48°, 53.9°, 55°, 62.7°, 68.9°, 70.3°, and 75.1°. The rutile phase of TiO₂ diffraction peak was detected at $2\theta = 27.4^\circ$ (major), 36°, 41.3°, 48°, 54.3°, and 56.6°. Moreover, for the catalyst samples prepared by the PDC-MSD method, additional diffraction peaks corresponding to Pt appeared at $2\theta = 39.8^\circ$ (major), 46.2°, 67°, and 82°.

The average crystallite sizes of anatase TiO₂ were calculated by Scherrer equation from the XRD diffraction peak at $2\theta = 25.2^\circ$ and the results are shown in **Table 7**. The crystallite size of anatase TiO₂ of Pt catalyst supported on P25 and PC500 were similar at 22.6-25 nm and 6.8-7.6 nm, respectively. It was found that the catalysts prepared on P25 supports had larger crystallite sizes of anatase phase of TiO₂ than those prepared on PC500 supports for the same deposition time.

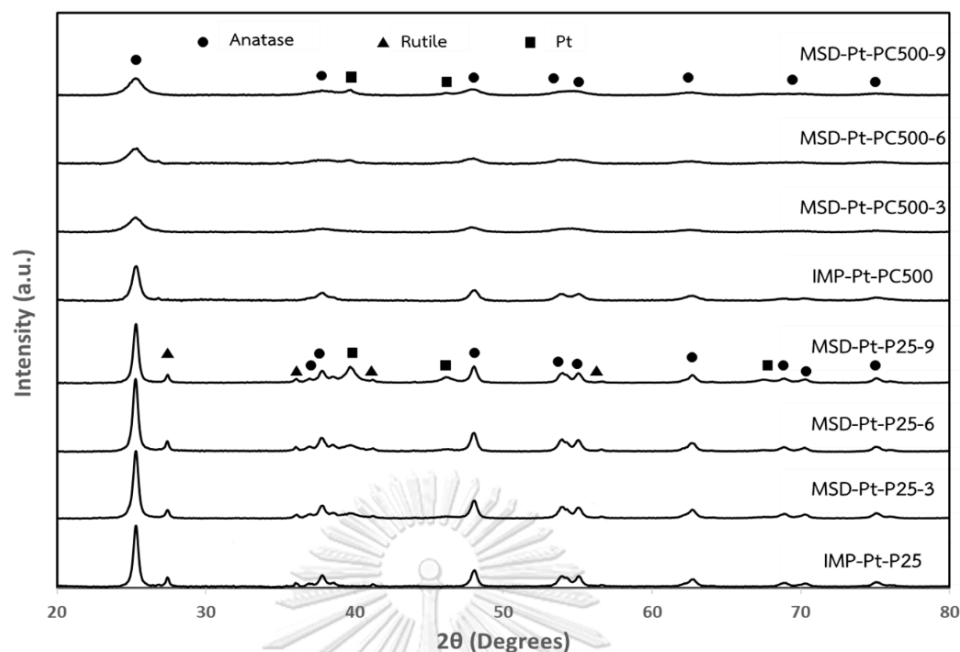


Figure 8 The XRD patterns of Pt/TiO₂ catalysts

4.1.2 N₂ – physisorption

The BET surface area, pore size, and pore volume of all catalyst samples are shown in **Table 7**. The pore size and the pore volume were determined from the Barret-Joyner-Halenda (BJH) desorption method. The BET surface area, pore size, and pore volume of Pt catalyst supported on P25 were similar at 47.8-59.6 m²/g, 11-12.1 nm, and 0.16-0.28 cm³/g respectively. The BET surface area, pore size, and pore volume of Pt catalyst supported on PC500 were 167.3-244.9 m²/g, 3.9 nm, and 0.23-0.3 cm³/g respectively. It was found that all the Pt catalysts supported on PC500 had greater surface area and pore volume but smaller pore size than the Pt catalyst supported on P25 for the same deposition time. Similar results have been reported by Rui, Z. et al. [37] that Pt catalyst supported on TiO₂ pure anatase phase had greater surface area and pore volume but smaller pore size than Pt catalyst supported on TiO₂ pure rutile phase. The BET surface area, pore size, and pore volume of commercial P25 TiO₂ support were 65.3 m²/g, 12.1 nm, and 0.17 cm³/g respectively. Bettini, L. et al. [38] reported that The BET surface area, pore size, and

pore volume of TiO₂ support (mixed anatase and rutile same ratio as P25) prepared by flame spray pyrolysis in xylene solvent were 113 m²/g, 12 nm, and 0.2 cm³/g respectively.

The N₂ adsorption-desorption isotherms of all the catalyst samples prepared by the PDC-MSD method and the incipient wetness impregnation method are shown in **Figure 9**. From Brunauer-Deming-Teller (BDTT), All the Pt/TiO₂ catalyst samples exhibited type-IV isotherm with its hysteresis loop indicated that capillary condensation taking place in mesopores. The shape of the hysteresis loop for all catalysts prepared on P25 supports and IMP-Pt-PC500 was typed H3 hysteresis loop. The type H3 hysteresis can be observed with aggregates of plate-like particles giving rise to slit-shaped pores. For the catalysts prepared on PC500 supports except IMP-Pt-PC500, The shape of the hysteresis loop was type H4, which indicating the narrow slit-shaped pore and containing both micropores and mesopores [39].

Table 7 Physical properties of Pt/TiO₂ catalysts

Catalyst	Crystallite size of anatase TiO ₂ (nm)	BET Surface Area (m ² /g)	Pore size (nm)	Pore Volume (cm ³ /g)
MSD-Pt-P25-3	22.6	47.8	11.0	0.16
MSD-Pt-P25-6	23.7	57.4	11.3	0.19
MSD-Pt-P25-9	24.1	53.1	15.0	0.25
IMP-Pt-P25	25.0	59.6	12.1	0.28
MSD-Pt-PC500-3	7.6	189.5	3.9	0.23
MSD-Pt-PC500-6	7.5	244.9	3.9	0.30
MSD-Pt-PC500-9	7.7	234.6	3.9	0.28
IMP-Pt-PC500	15.2	167.3	3.9	0.25

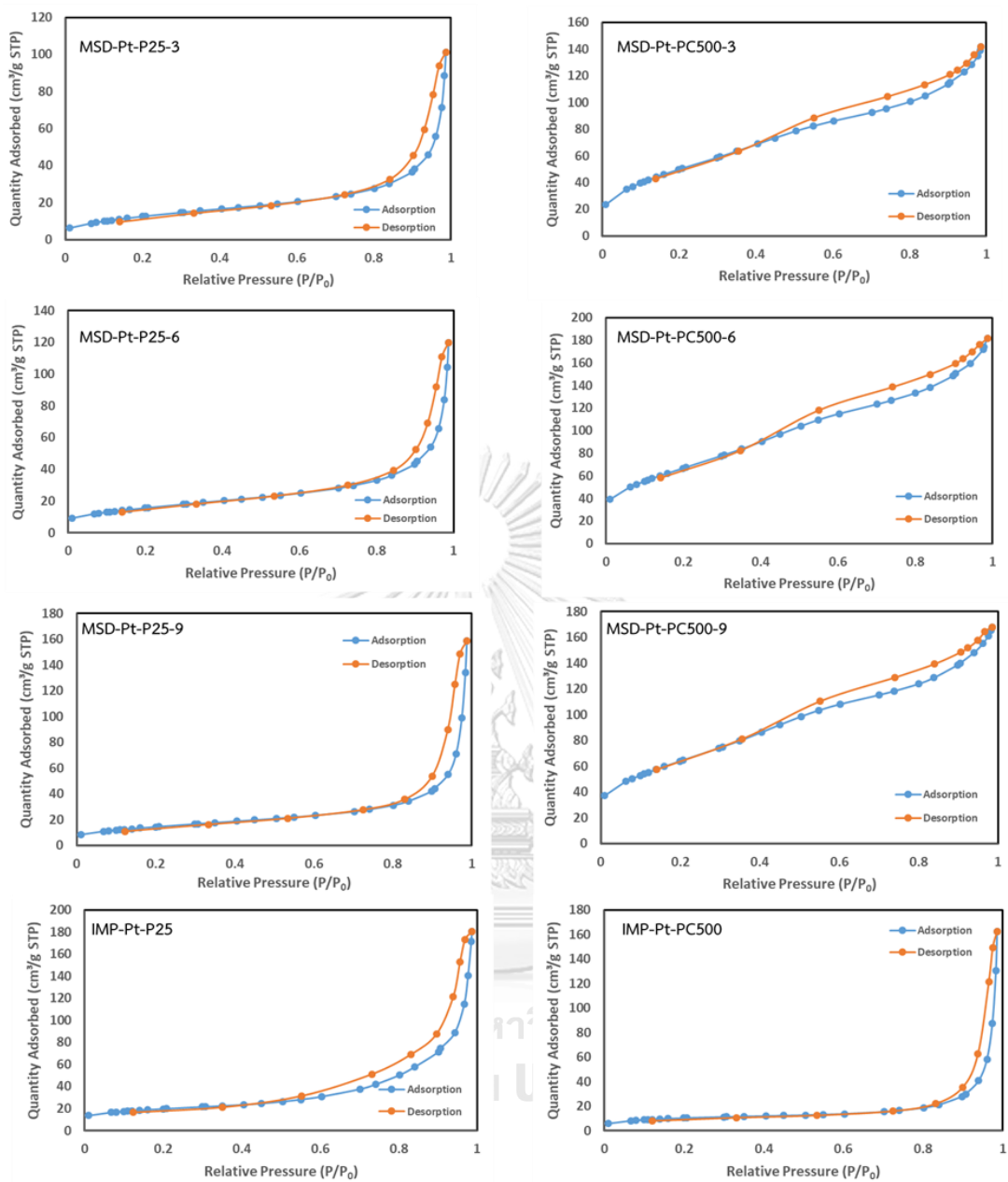


Figure 9 N_2 adsorption-desorption isotherms of Pt/TiO₂ catalysts

4.1.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a technique to determine the surface composition of catalysts. The XPS Pt 4f spectra of all the catalyst samples are shown in **Figure 10**. The binding energy spectra of Pt 4f had 4 peaks at approximately 75.6, 74.1, 72.3, 70.9 eV with indicated Pt-O 4f_{5/2}, Pt⁰ 4f_{5/2}, Pt-O 4f_{7/2}, Pt⁰ 4f_{7/2}, respectively [22, 37, 40]. Pt⁰ 4f_{5/2} and Pt⁰ 4f_{7/2} were major peaks of Pt metal form. Pt-O 4f_{5/2}, Pt-O 4f_{7/2} were peaks of Pt oxide form. Considering the MSD-Pt-P25-9 catalyst, the metallic Pt⁰ 4f_{7/2} shifted toward lower binding energy. Pongthawornsakun, B et al. [22] reported that the shifting of Pt 4f to lower binding energy because of synergistic contributions between the final state effect and the interaction between Pt and TiO₂ in which the charges transferred from the TiO₂ to the metallic Pt that effect to the larger size of Pt nanoparticles and/or cluster formed and high coordinated surface Pt atoms during PDC-MSD method. So, the MSD-Pt-P25-9 catalyst showed high coordinated surface Pt atoms which attributed to a larger size of Pt nanoparticles as compared to other Pt/TiO₂ catalysts. However, the Pt 4f peaks of Pt/TiO₂ prepared by the incipient wetness impregnation method did not appear probably because of the low amount of Pt presented on the catalyst surface.

The atomic ratios of Pt/Ti and Pt species on the surface of Pt/TiO₂ catalysts from the XPS results are shown in **Table 8**. It was found that the greater deposition time, the higher atomic ratio of Pt/Ti on the catalyst surface. For the same deposition time, the PC500 support had higher atomic ratio Pt/Ti at catalyst surfaces than the P25 support although the PC500 support had less Pt metal (%) than the P25 support. Moreover, the atomic ratio Pt/Ti on the catalyst surfaces of all Pt/TiO₂ catalysts prepared by PDC-MSD were higher than Pt/TiO₂ catalysts prepared by the incipient wetness impregnation method.

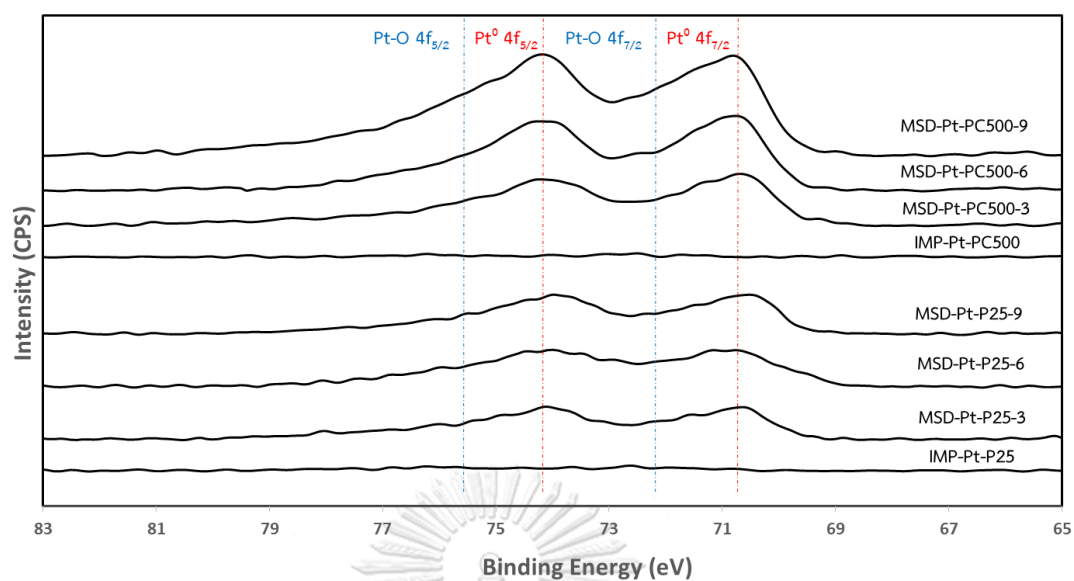


Figure 10 The XPS Pt 4f patterns of Pt/TiO₂ catalysts

Table 8 XPS results: Atomic ratio of Pt/Ti and Pt species composition of Pt/TiO₂ catalyst surfaces

Catalyst	Atomic ratio		Pt species	
	Pt/Ti	Pt metal (%)	Pt metal (%)	Pt oxide (%)
MSD-Pt-P25-3	0.07	70.70	70.70	29.30
MSD-Pt-P25-6	0.08	70.48	70.48	29.52
MSD-Pt-P25-9	0.08	68.78	68.78	31.22
IMP-Pt-P25	0.02	0	0	100
MSD-Pt-PC500-3	0.12	53.45	53.45	46.55
MSD-Pt-PC500-6	0.20	56.27	56.27	43.73
MSD-Pt-PC500-9	0.36	63.64	63.64	36.36
IMP-Pt-PC500	0.01	0	0	100

4.1.4 Inductively coupled plasma optical emission spectrometer (ICP-OES)

The actual Pt metal content or Pt loading (%) of all catalysts samples were determined by the ICP-OES and the results are shown in **Table 9**. The Pt loading (%) on MSD-Pt-P25-9 was highest at platinum content 7.1% while the Pt loading (%) of PC500-3 was lowest at platinum content 1.4%. Moreover, increasing deposition time to prepare the catalyst resulted in increasing Pt loading (%) coated on TiO₂ supports. The Pt catalyst supported on P25 had greater Pt loading (%) than the Pt catalyst supported on PC500 for the same deposition time.

Table 9 Deposition time and Pt loading of Pt/TiO₂ catalysts

Catalyst	Type of TiO ₂ support	Deposition time [min]	Pt loading (%)
MSD-Pt-P25-3	Anatase, Rutile	3	3.0
MSD-Pt-P25-6	Anatase, Rutile	6	4.0
MSD-Pt-P25-9	Anatase, Rutile	9	7.1
IMP-Pt-P25	Anatase, Rutile	-	1.4
MSD-Pt-PC500-3	Anatase	3	1.4
MSD-Pt-PC500-6	Anatase	6	3.1
MSD-Pt-PC500-9	Anatase	9	4.3
IMP-Pt-PC500	Anatase	-	1.4

4.1.5 Transmission electron spectroscopy (TEM)

The morphology of Pt/TiO₂ catalysts is shown in **Figure 11**. Pt clusters were found on the TiO₂ supports. The average particle size of MSD-Pt-P25-3 and MSD-Pt-P25-9 were 22.8 and 25.2 nm respectively, Therefore, the average particle size of P25 was larger than PC500 which corresponded well to the XRD results. Moreover, The average Pt particle size of MSD-Pt-P25-9 was the largest because Pt particles could be found obviously which corresponded well to the XPS results.

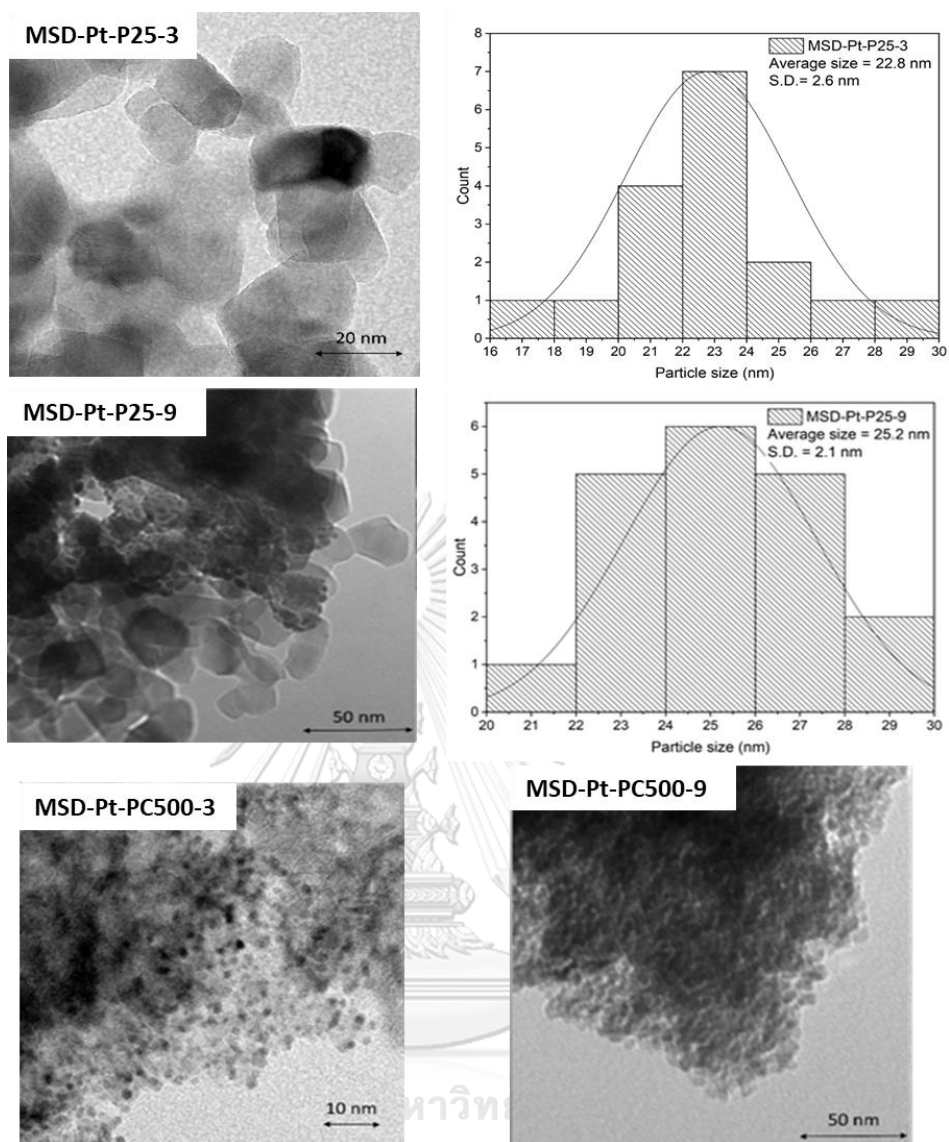


Figure 11 TEM images and particle size distribution of Pt/TiO₂ catalysts

4.1.6 CO-pulse chemisorption

The amounts of Pt active sites, Pt dispersion (%), and average Pt particle size on Pt/TiO₂ catalysts were determined by the CO chemisorption results based on the assumption that one CO molecule was adsorbed on one Pt site as shown in Appendix C. The amounts of Pt active sites and Pt dispersion (%) of Pt/TiO₂ catalysts are shown in **Table 10**. For the same deposition time, the amounts of CO chemisorption on Pt catalysts supported on PC500 TiO₂ support were much higher, suggesting higher amount of Pt active sites and Pt dispersion (%) than the P25 TiO₂

support although the PC500 TiO₂ support had less Pt loading (%) than the P25 TiO₂ support. However, MSD-Pt-P25-9 exhibited the lowest Pt dispersion (7.7%), and the highest average Pt particle size (14.03 nm) although it had the highest Pt actual loading (7.1%) based on the ICP-OES technique.

Table 10 CO chemisorption and Pt loading results of Pt/TiO₂ catalysts

Catalyst	Pt loading (%) (ICP)	Amount of Pt active sites (molecule CO X 10 ¹⁹ /g cat.)	Pt dispersion (%)	Average Pt particle size (nm)
MSD-Pt-P25-3	3.0	0.70	7.9	13.67
MSD-Pt-P25-6	4.0	1.00	8.3	13.01
MSD-Pt-P25-9	7.1	1.70	7.7	14.03
IMP-Pt-P25	1.4	1.76	40.9	2.64
MSD-Pt-PC500-3	1.4	1.87	43.3	2.49
MSD-Pt-PC500-6	3.1	2.85	29.7	3.64
MSD-Pt-PC500-9	4.3	3.00	22.6	4.78
IMP-Pt-PC500	1.4	2.02	46.8	2.31

4.1.7 H₂ temperature-programmed reduction (H₂-TPR)

The H₂ temperature-programmed reduction (H₂-TPR) technique was carried out to study the reduction behaviors and metal and support interaction. The reduction performances of Pt catalysts supported on P25 and PC500 TiO₂ are shown in **Figure 12** and **Figure 13** respectively. The Pt/TiO₂ catalysts prepared by the incipient wetness impregnation method (IMP-Pt-P25 and IMP-Pt-PC500) exhibited three reduction peaks. The first peak at below 100 °C was associated with the reduction of Pt oxide (PtO_x) to Pt metal [34, 41]. The second peak as a large peak between 250-450 °C was associated with the reduction of Pt species interacting with the TiO₂ support to form Pt-TiO_x interface sites [22, 34, 42]. The last reduction peak

above 500 °C was attributed to the reduction of surface capping oxygen of TiO₂ support [22, 34].

From the H₂-TPR profiles of Pt catalysts supported on P25 TiO₂ results (**Figure 12**), the Pt catalysts supported on P25 TiO₂ prepared by PDC-MSD method (MSD-Pt-P25-3, MSD-Pt-P25-6, MSD-Pt-P25-9) exhibited two reduction peaks. The first peak with a maximum at 330-345 °C was associated with the reduction of Pt species interacting with the TiO₂ support to form Pt-TiO_x interface sites. The second peak with a maximum at 465-475 °C was associated with the reduction of the surface capping oxygen of TiO₂ support. Meanwhile, the H₂-TPR profiles of Pt catalysts supported on PC500 TiO₂ results (**Figure 13**), the first peak with a maximum at 340-360 °C and the second peak with a maximum at 398-416 °C were associated with the reduction of Pt species interacting with the TiO₂ support and the reduction of the surface capping oxygen of TiO₂ support, respectively. Moreover, it was found that the second reduction peak of Pt catalysts supported on P25 TiO₂ shifted toward higher temperature, compared to the Pt catalysts supported on PC500 TiO₂. It can be evaluated that P25 support had stronger surface capping oxygen of TiO₂ support interaction than PC500 support.

However, the H₂-TPR profiles of Pt/TiO₂ catalysts prepared the PDC-MSD method did not appear any peak at a temperature below 100 °C, which could be associated with the reduction of Pt oxide (PtO_x) to Pt metal because the Pt/TiO₂ catalysts prepared the PDC-MSD method had very little Pt oxide form so the reduction peak was absent.

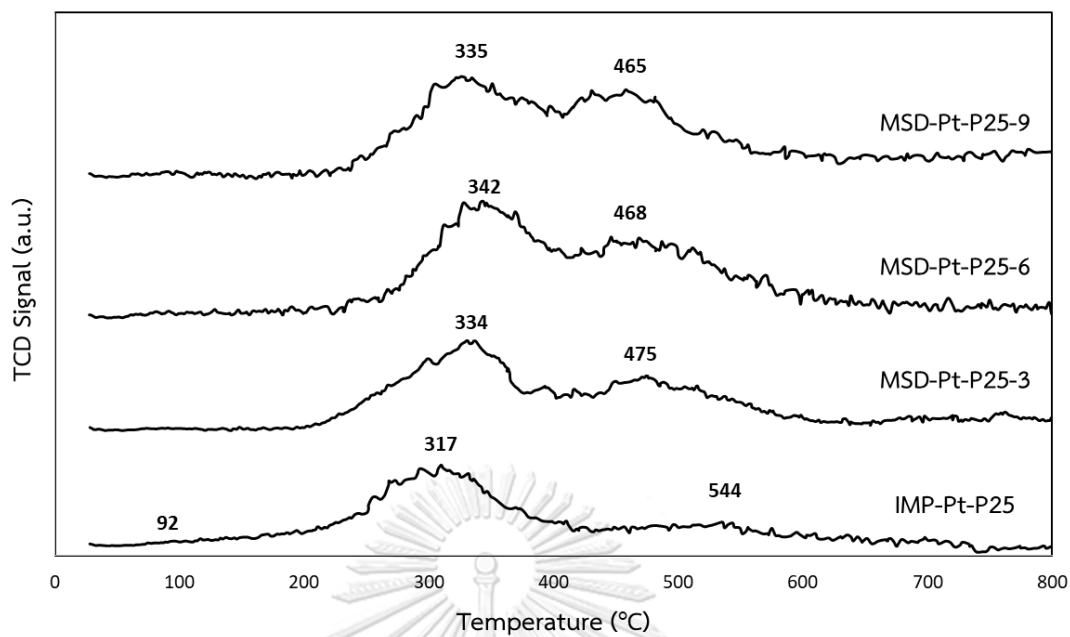


Figure 12 The H₂-TPR profiles of Pt catalysts supported on P25 TiO₂

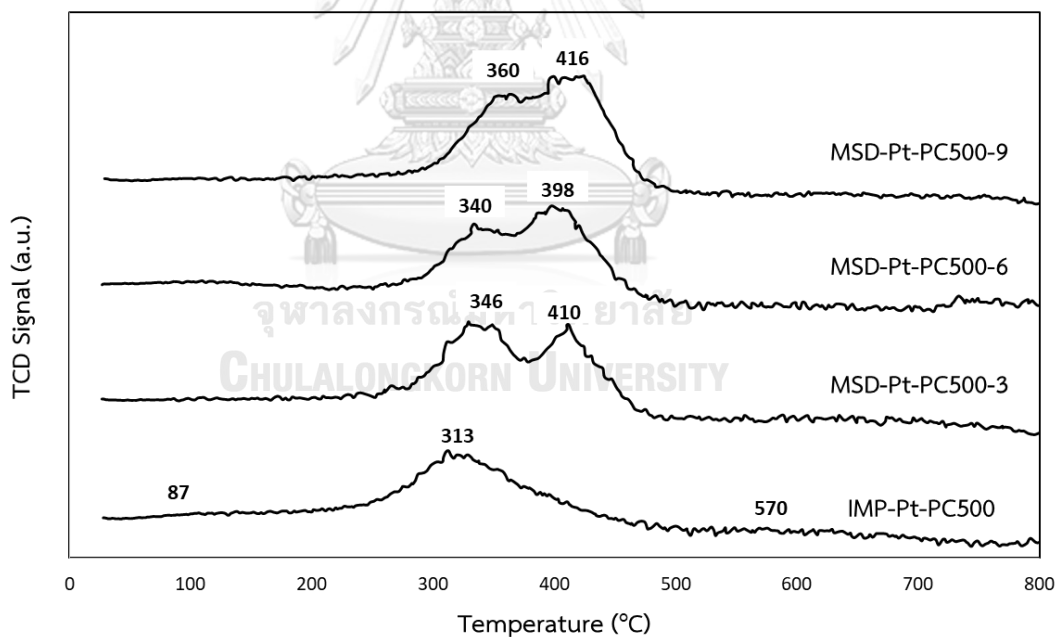


Figure 13 The H₂-TPR profiles of Pt catalysts supported on PC500 TiO₂

4.2 Catalytic reaction study in the liquid phase selective hydrogenation of acetophenone (AP) to 1-phenylethanol (PHE)

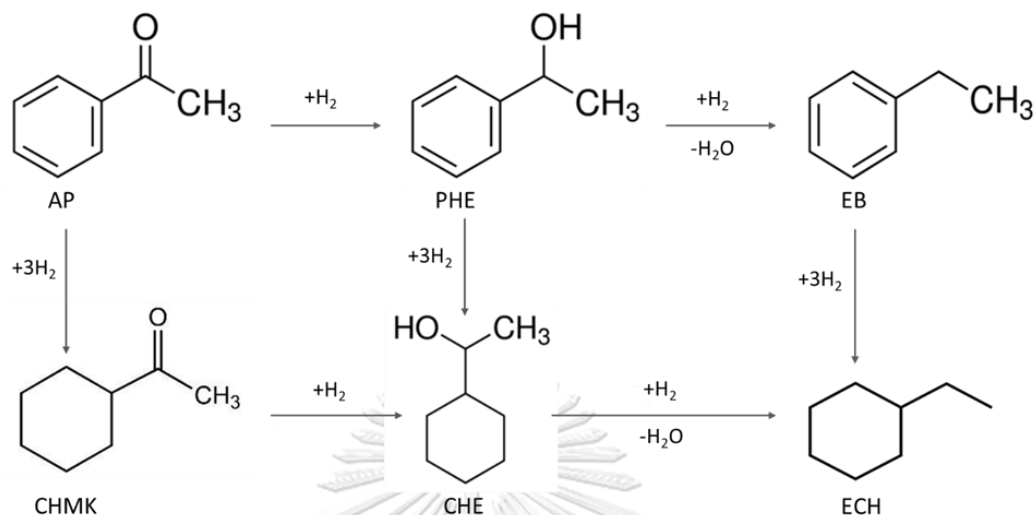


Figure 14 Reaction scheme for the hydrogenation of acetophenone. AP: acetophenone, PHE: 1-phenylethanol, EB: ethylbenzene, CHMK: cyclohexylmethylketone, CHE: cyclohexylethanol, ECH: ethylcyclohexane

The hydrogenation of acetophenone (AP) in 2-propanol over Pt/TiO₂ catalyst has competitive hydrogenation between carbonyl (C=O double bond) and aromatic ring or phenyl groups. As shown in **Figure 14**, the first is the hydrogenation of the carbonyl group of AP, which is converted to 1-phenylethanol (PHE). Second is the hydrogenation of the phenyl group, which is converted to cyclohexylmethylketone (CHMK). After that PHE and CHMK can be hydrogenated to cyclohexylethanol (CHE). The hydrogenolysis of PHE and CHE can produce ethylbenzene (EB) and ethylcyclohexane (ECH) respectively. Furthermore, EB can be hydrogenated to ECH [1, 5, 10].

The catalytic performances of the prepared catalysts in the selective hydrogenation of AP were investigated at 80 °C, 1 bar of H₂ for 2 h reaction time using 2-propanol as the solvent. The results of the selective hydrogenation of AP including the conversion of AP, the selectivity to PHE, and the yield of PHE are summarized in **Table 11**.

From the catalytic performances of Pt/TiO₂ catalysts prepared by the PDC-MSD method, the MSD-Pt-PC500-3 showed the highest yield of PHE (67.1%). The Pt catalysts supported on PC500 had higher selectivity to PHE than P25 supports for the same deposition time. The superior catalytic performances were correlated well to the higher atomic ratio Pt/Ti on the catalyst surfaces and the higher BET surface area of Pt/TiO₂ catalysts on PC500 support as compared to the Pt/TiO₂ catalysts on P25 support. The higher Pt dispersion (%) was beneficial to the selectivity of PHE corresponding to the study by Alonso, F. et al. [6]. However, for the MSD-Pt-P25-9 catalyst, the yield of PHE was the lowest because the size of the Pt was fairly large as confirmed by TEM and XPS results and the catalyst exhibited the lowest Pt dispersion (%) according to the CO-chemisorption results.

Comparing the catalytic performances of Pt/TiO₂ catalysts prepared by the PDC-MSD with the incipient wetness impregnation method on the PC500 support with the equal Pt loading (MSD-Pt-PC500-3 and IMP-Pt-PC500), it was found that the yield of PHE of Pt/TiO₂ catalysts prepared by PDC-MSD was higher than Pt/TiO₂ catalysts prepared by the incipient wetness impregnation method because of higher atomic ratio Pt/Ti on the catalyst surface.

Considering the selective hydrogenation of AP to PHE reaction, it was found that high Pt dispersion (%) could promote the PHE selectivity (%) which avoided the formation of by-product. The low coordination on small Pt size, high atomic ratio Pt/Ti at catalyst surface, high BET surface area, and weak surface capping oxygen of TiO₂ interaction enhanced the selective hydrogenation of AP to PHE reaction. However, increasing Pt loading (%) may also increase the hydrogenolysis of PHE to EB, resulting in lower PHE product. Similar results have been reported by Jiang, Y et al. [10] that when the Pt contents (%) on zirconia support increased, the selectivity of PHE decreased because high Pt loading (%) promoted the hydrogenolysis of PHE to EB.

Table 11 The catalytic performances of the Pt/TiO₂ catalysts in the selective hydrogenation of AP in 2-propanol (AP: acetophenone, PHE: 1-phenylethanol, ECH: ethylcyclohexane, EB: ethylbenzene, CHMK:cyclohexylmethylketone, CHE: cyclohexylethanol)

Catalyst	%Pt (ICP)	Conversion of AP (%)	Selectivity (%)					Yield of PHE (%)
			PHE (product)	ECH	EB	CHMK	CHE	
MSD-Pt-P25-3	3	99	27	6.3	49.1	5.3	12.3	26.7
MSD-Pt-P25-6	4	98.8	32.8	3	60.4	2.4	1.4	32.4
MSD-Pt-P25-9	7.1	100	0	25	71.3	2.6	1.1	0
IMP-Pt-P25	1.4	72.0	71.5	0	0	25.0	3.5	51.5
MSD-Pt-PC500-3	1.4	91.4	73.4	0.7	3.8	12.9	9.2	67.1
MSD-Pt-PC500-6	3.1	98.7	63.3	2.1	14	9.4	11.2	62.5
MSD-Pt-PC500-9	4.3	99	33.3	5.1	25	12.2	24.4	33.0
IMP-Pt-PC500	1.4	37.4	89.4	0	0	10.6	0	33.4

Part II The effect of reaction temperature of the selective hydrogenation of AP to PHE over Pt/TiO₂ catalysts prepared by the PDC-MSD method

4.3 Catalytic reaction study of Pt/TiO₂ catalysts prepared by the PDC-MSD method on the various reaction temperature

The catalytic performances of the prepared catalysts in the selective hydrogenation of AP were investigated at 60,80,100 °C, 1 bar of H₂ for 2 h reaction time using 2-propanol as the solvent. The results of the selective hydrogenation of AP including the conversion of AP, the selectivity to PHE, and the yield of PHE are summarized in **Table 12** and **Figure 15-16**. From the results, at the reaction temperature of 60 °C, MSD-Pt-P25-3 and MSD-Pt-PC500-6 (about 3 wt% Pt) showed the highest conversion of AP (%). As the reaction temperature increased, the conversion tended to decrease insignificantly. However, the selectivity and the yield of PHE ranged in the order of reaction temperature 60 °C < 100 °C < 80 °C and were highest at the reaction temperature of 80 °C. These results suggest that for Pt/TiO₂ catalysts prepared by the PDC-MSD method, at the reaction temperature of 80 °C could enhance the hydrogenation of AP to PHE and inhibit the hydrogenolysis of PHE to EB in 2-propanol solvent which in good agreement with the study by Alonso, F. et al. [6].

Table 12 The catalytic performances of the Pt/TiO₂ catalysts in the selective hydrogenation of AP in 2-propanol with various temperature (AP: acetophenone, PHE: 1-phenylethanol, ECH: ethylcyclohexane, EB: ethylbenzene, CHMK:cyclohexylmethylketone, CHE: cyclohexylethanol)

Catalyst	%Pt (ICP)	Reaction temperature (°C)	Conversion of AP (%)	Selectivity (%)					Yield of PHE (%)
				PHE (product)	ECH	EB	CHMK	CHE	
MSD-Pt-P25-3	3	60	99.8	0.27	22.3	71	2	4.5	0.3
		80	99	27	6.3	49.1	5.3	12.3	26.7
		100	98.7	4.3	16	63	7.1	9.6	4.2
MSD-Pt-PC500-6	3.1	60	99	40	6.2	27	18.8	7.8	39.6
		80	98.7	63.3	2.1	14	9.4	11.2	62.5
		100	98.5	51.2	4.4	21	14.1	9.3	50.4

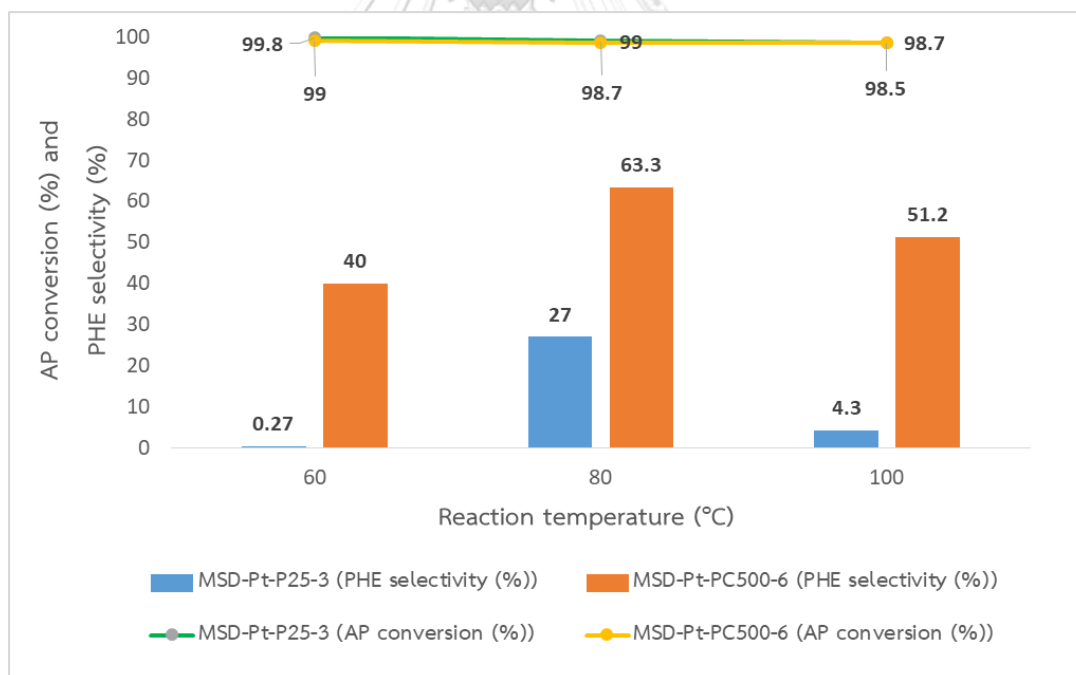


Figure 15 AP conversion (%) and PHE selectivity (%) of MSD-Pt-P25-3 and MSD-Pt-PC500-6

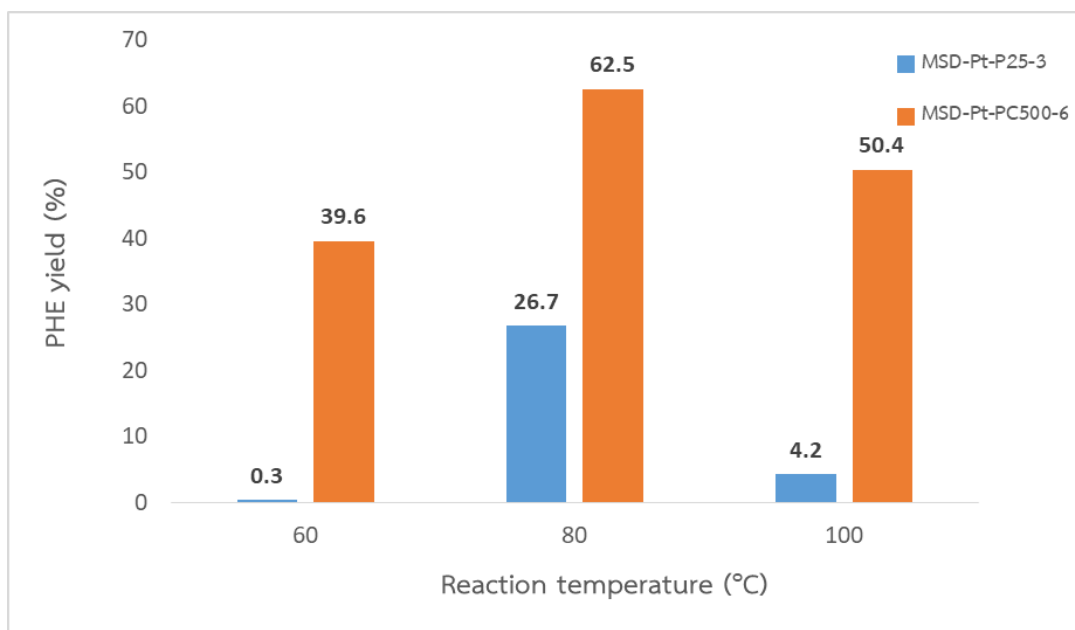


Figure 16 PHE yield (%) of MSD-Pt-P25-3 and MSD-Pt-PC500-6



CHAPTER V

CONCLUSIONS

5.1 Conclusions

In the present work, Pt-based catalysts on TiO₂ supports were prepared by PDC-MSD method on various TiO₂ polymorphs including PC500 and P25 with deposition time spent on Pt coating at 3, 6, and 9 minutes. Increasing deposition time resulted in increasing Pt loading (%) coated on the TiO₂ supports as revealed by the higher atomic ratio of Pt/Ti on the catalyst surfaces from the XPS results. For the equal time spent on the platinum coating on the supports, the PC500 TiO₂ supports had a greater atomic ratio of Pt/Ti on catalyst surfaces, and as a consequence smaller size of Pt, greater Pt dispersion (%), and less surface capping oxygen of TiO₂ support interaction was obtained with lower Pt loading (%) compared to those on P25 TiO₂ supports. The PC500 TiO₂ supported catalysts exhibited higher yield than the P25 supports because of higher atomic ratio of Pt/Ti on the catalyst surfaces, higher BET surface area, and greater Pt dispersion (%). The MSD-Pt-PC500-3 showed the best catalytic performance and the highest yield of PHE (67.1%). Moreover, despite its high Pt loading, the MSD-Pt-P25-9 catalyst exhibited low yield of PHE because the size of Pt was large and low Pt dispersion (%). Increasing Pt dispersion (%) may also enhance the PHE selectivity (%) which avoid the formation of by-product. However, Increasing Pt loading (%) may also increase the hydrogenolysis of PHE to EB, resulting in lower PHE product.

Considering the effect of the reaction temperature in the selective hydrogenation of AP using 2-propanol as the solvent, the reaction temperature of 80 °C could promote the hydrogenation of AP to PHE and inhibit the hydrogenolysis of PHE to EB in 2-propanol solvent for Pt/TiO₂ catalysts prepared by the PDC-MSD method.

5.2 Recommendations

1. The other factors such as type of solvents, type of additives in the solvent, and acetophenone (AP) concentration in the hydrogenation of AP to PHE should be investigated.
2. The stability of the Pt/TiO₂ catalysts prepared by the PDC-MSD and impregnation method for reused should be investigated.



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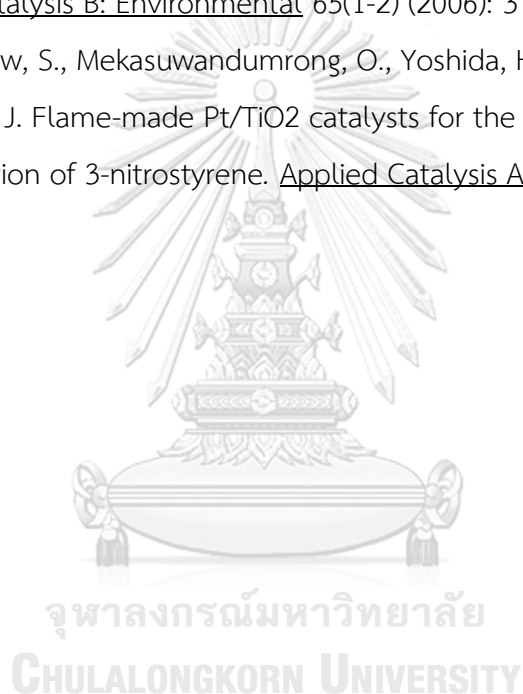
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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
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APPENDIX A

CALCULATION FOR CARALYST PREPARATION

Preparation of 1.4 %Pt/TiO₂ catalysts using various TiO₂ polymorphs as PC500 and P25 as supports by incipient wetness impregnation method were presented below.

Precursor

Platinum(II) acetylacetonate (Pt(C₅H₇O₂)₂) 99.99%, MW.= 393.29 g/mol

Calculation

Based on 1 g of catalysts used, the composition of catalysts will be as follows:

For preparation of 1.4 %Pt/TiO₂ catalysts 1 g

$$\text{Pt required} = 0.014 \text{ g}$$

$$\text{TiO}_2 \text{ required} = 1 - 0.014 = 0.986 \text{ g}$$

Platinum 0.014 g was prepared by using Platinum (II) acetylacetonate 99.99%

$$= \frac{(\text{MW.of platinum (II) acetylacetonate 99.99\%})(\text{weight of Pt required})}{\text{MW.of Pt}}$$

$$= \frac{393.29 \frac{\text{g}}{\text{mol}} \times 0.014 \text{ g}}{195.078 \frac{\text{g}}{\text{mol}}}$$

$$= 0.0282 \text{ g}$$

So, Platinum (II) acetyl acetonate 0.0282 g and TiO₂ support 0.986 g were required.

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the width at half of the height or full width of the diffraction peak of the XRD pattern by the Debye-Scherrer equation.

Debye-Scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where

D = Crystallite size, Å

k = Crystallite-shape factor = 0.9 for

λ = X-ray wavelength, 1.5418 Å for CuK α

β = X-ray diffraction broadening, radian

θ = Observed peak angle, degree

The X-ray diffraction broadening (β) can be obtained by Warren's formula:

$$\beta = \sqrt{\beta_M^2 - \beta_S^2}$$

Where

β_M = Measured peak width at half of peak height

β_S = Corresponding width of the standard material

APPENDIX C

CALCULATION FOR METAL ACTIVE SITES, METAL DISPERSION,
AND AVERAGE METAL PARTICLE SIZE

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

Calculation of Pt active sites

$$\text{Mole of CO injected per loop, } n_{inj} = \frac{PV_{inj}}{RT} = \frac{(1 \text{ atm})(20 \mu\text{L})}{\left(\frac{0.082 \text{ L.atm}}{\text{K.mol}}\right)(313 \text{ K})} = 0.78 \mu\text{mol}$$

$$\text{Mole of CO adsorbed on catalyst, } n_{ads} = \frac{n_{inj}}{m} \times \frac{1}{A_f} \sum_{i=1}^n (A_f - A_i)$$

Where V_{inj} = Volume of CO injected per loop at 313 K = 20 μl

n_{ads} = Mole of CO adsorbed on catalyst per catalyst weight, $\frac{\mu\text{mol of CO}}{\text{g}_{cat}}$

n_{inj} = Mole of CO injected per loop

m = Mass of catalyst used, g

A_i = Area of peak i

A_f = Average area of last 3 peaks where the metal has fully adsorbed carbon

Molecules of CO adsorbed on catalyst = $n_{ads} \times 10^{-6} \times 6.02 \times 10^{23}$ molecules of CO/g_{cat}

So, Pt metal active sites = $n_{ads} \times 6.02 \times 10^{19}$ molecules of CO/g_{cat}

Calculation of Pt metal dispersion (%)

$$\begin{aligned} \text{Metal dispersion (\%)} &= S_f \times n_{ads} \times 10^{-6} \times \frac{MW_{Pt}}{\%Pt_{ICP}} \times 100 \times 100 \\ &= S_f \times n_{ads} \times \frac{MW_{Pt}}{\%Pt_{ICP}} \times 10^{-2} \end{aligned}$$

Where S_f = Stoichiometry factor of CO adsorbed on Pt metal = 1 $\left(\frac{\text{mol Pt}}{\text{mol CO}}\right)$

n_{ads} = Mole of CO adsorbed on catalyst per catalyst weight $\left(\frac{\mu\text{mol of CO}}{g_{cat}}\right)$

MW_{Pt} = Molecular weight of Pt metal = 195 $\left(\frac{g Pt}{mol Pt}\right)$

$\%Pt_{ICP}$ = Pt metal loading (%) based on ICP

Calculation of average Pt particle size (nm) [6]

$$\text{Average Pt particle size (nm)} = \frac{108}{D}$$

Where D = Pt metal dispersion (%)

APPENDIX D

CALCULATION FOR CATALYTIC PERFORMANCE

The catalytic performances for the hydrogenation of AP were evaluated in terms of activity for AP conversion, PHE selectivity, and PHE yield.

The catalytic performances for the hydrogenation of acetophenone (AP) are shown below.

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

$$PHE \text{ selectivity } (\%) = \frac{\text{Mole of } PHE}{\text{Mole of } AP_{in} - \text{Mole of } AP_{out}} \times 100$$

$$PHE \text{ yield } (\%) = \frac{AP \text{ conversion } (\%) \times PHE \text{ selectivity } (\%)}{100}$$

The calibration curve of AP and various products are shown in Figure D.1-D.6.

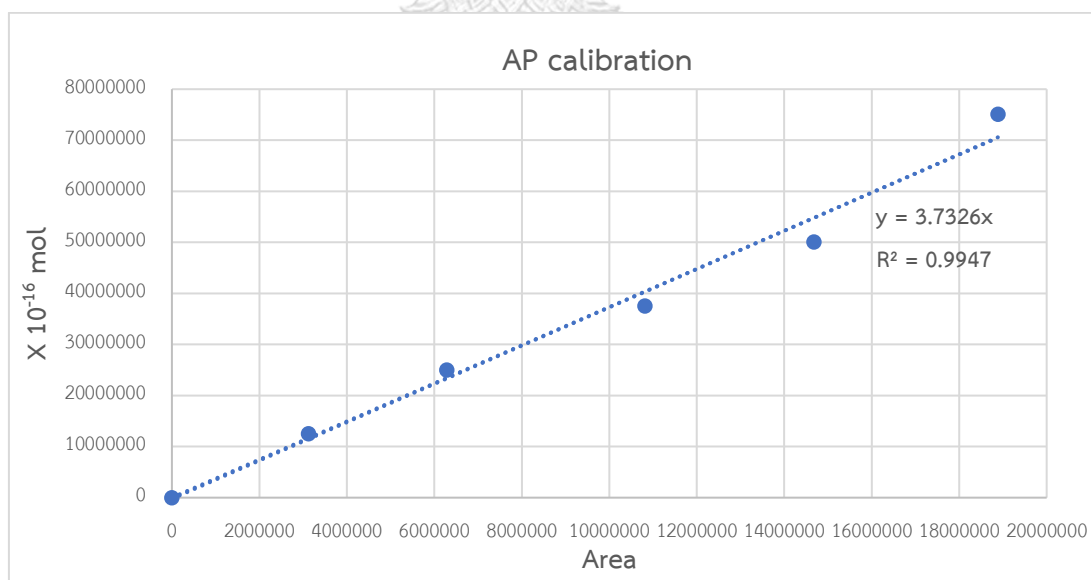


Figure D.1 The calibration curve of acetophenone (AP)

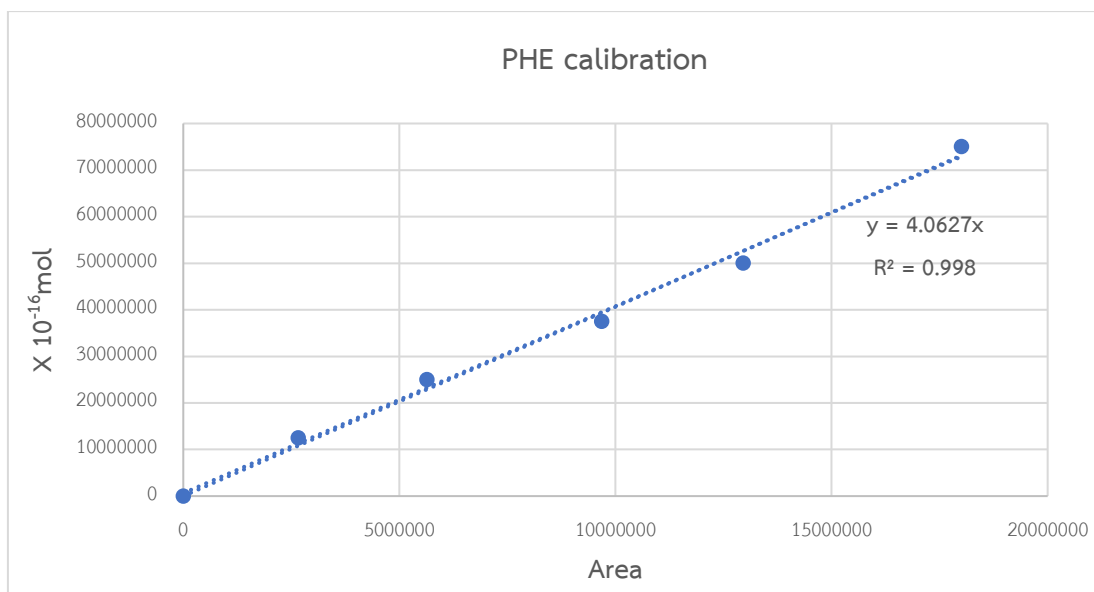


Figure D.2 The calibration curve of 1-phenylethanol (PHE)

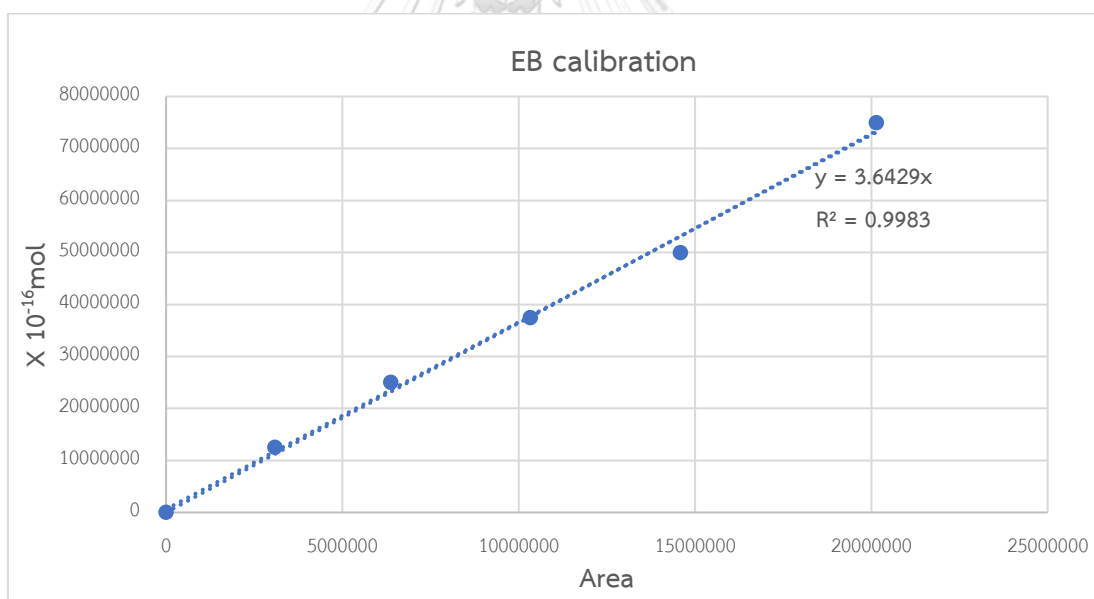


Figure D.3 The calibration curve of ethylbenzene (EB)

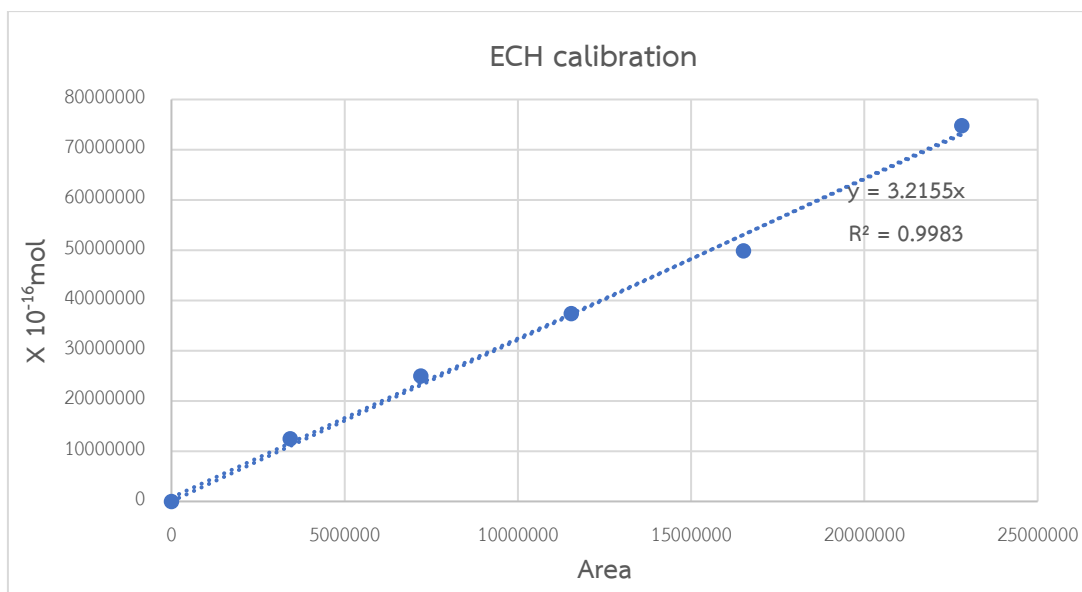


Figure D.4 The calibration curve of ethylcyclohexane (ECH)

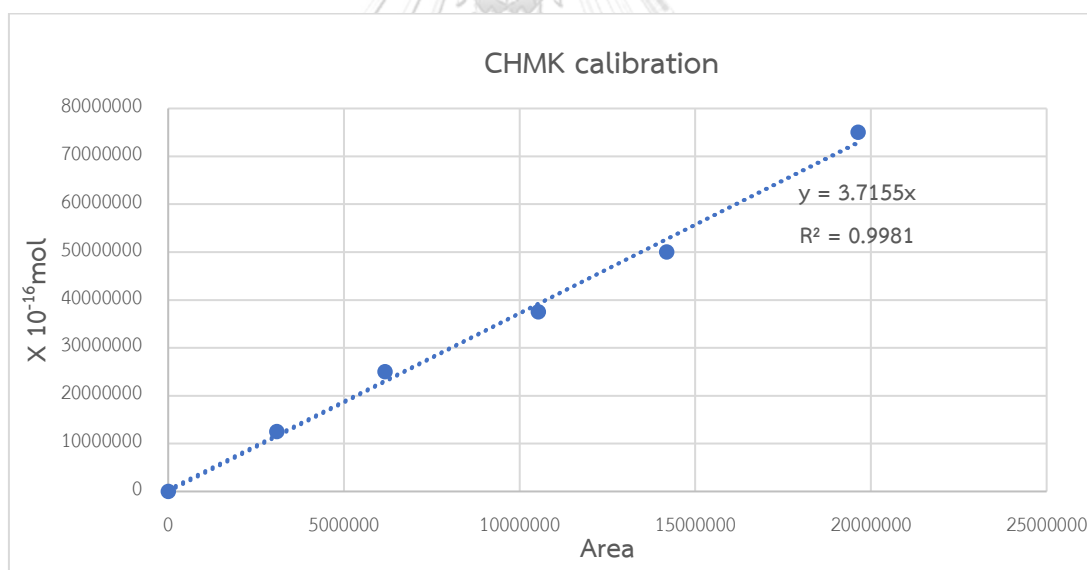


Figure D.5 The calibration curve of cyclohexylmethylketone (CHMK)

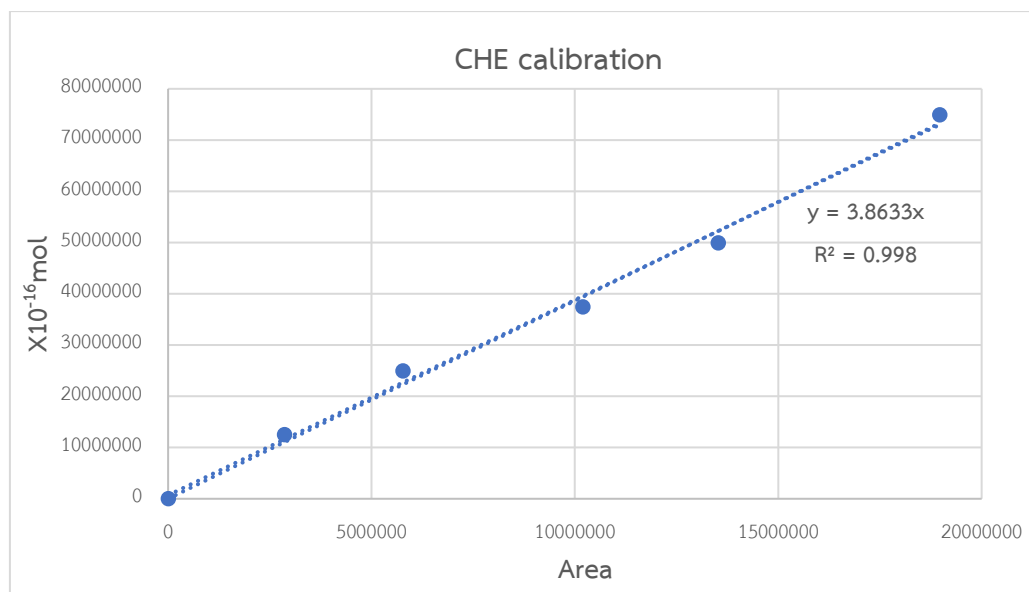


Figure D.6 The calibration curve of cyclohexylethanol (CHE)



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