การเร่งปฏิกิริยาเอทานอลดีไฮเดรชันเป็นไดเอทิลอีเทอร์บนตัวเร่งปฏิกิริยาแกมมาอะลูมินาฟอสฟอรัสที่ปรับปรุงด้วยแพลเลเดียม

นายจักกฤช เค้าชาติชาย

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CATALYTIC ETHANOL DEHYDRATION TO DIETHYL ETHER OVER PALLADIUM-MODIFIED PHOSPHORUS GAMMA ALUMINA CATALYSTS

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A Thesis Submitted in Partial Fulfillment of the Requirements
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จักกฤช เค้าชาติชาย : การเร่งปฏิกิริยาเอทานอลดีไฮเดรชันเป็นไดเอทิลอีเทอร์บนตัวเร่งปฏิกิริยาแกมมาอะลูมินาฟอสฟอรัสที่ปรับปรุงด้วยแพลเลเดียม (CATALYTIC ETHANOL DEHYDRATION TO DIETHYL ETHER OVER PALLADIUM-MODIFIED PHOSPHORUS GAMMA ALUMINA CATALYSTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.บรรเจิด จงสมจิตร, หน้า.

ตัวเร่งปฏิกิริยาแกมมาอะลูมินาได้นำไปปรับปรุงด้วยฟอสฟอรัสโดยวิธีกระตุ้นด้วยกรดและปรับปรุงด้วยแพลเลเดียมโดยวิธีการเคลือบฝังแบบเปียก ตัวเร่งปฏิกิริยาที่ผ่านการปรับปรุงนำมาหาคุณลักษณะด้วยวิธีต่างๆประกอบด้วย การกระเจิงรังสีเอ็กซ์ วิธีอินดัคทีพลีคัพเพิลพลาสมา การส่องกราดด้วยกล้องจุลทรรศน์อิเล็กตรอน และวิธีเอกซเรย์สเปคโตรสโคปีแบบกระจายพลังงาน การดูดซับทางกายภาพด้วยไนโตรเจน การคายซับของแอมโมเนียแบบโปรแกรมอุณหภูมิ การวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยคุณสมบัติทางความร้อน นอกจากนี้ตัวเร่งปฏิกิริยาที่ผ่านการปรับปรุงเหล่านี้นำมาทดสอบด้วยปฏิกิริยาการขจัดน้ำของเอทานอลในเครื่องปฏิกรณ์เคมีแบบเบดนิ่งเพื่อหาค่าร้อยละการเปลี่ยนแปลงสารตั้งต้น และค่าร้อยละการเกิดผลผลิตของผลิตภัณฑ์ที่ความดันบรรยากาศในช่วงอุณหภูมิจาก 200 ถึง 400 องศาเซลเซียส จากผลการทดลองการปรับปรุงด้วยฟอสฟอรัสได้ลดปริมาณกรดปานกลางถึงแก่และเพิ่มปริมาณกรดอ่อน การปรับปรุงตัวเร่งปฏิกิริยาด้วยฟอสฟอรัสแสดงผลผลิตไดเอทิลอีเทอร์สูงที่สุดร้อยละ 38.41 ที่อุณหภูมิ 350 องศาเซลเซียส นอกจากนี้การเติมฟอสฟอรัสบนตัวเร่งปฏิกิริยาช่วยลดปริมาณการเกิดคาร์บอนที่เกาะบนผิวตัวเร่งปฏิกิริยา การปรับปรุงแพลเลเดียมบนตัวเร่งปฏิกิริยามีแนวโน้มทำหน้าที่เป็นตัวสนับสนุนของตัวเร่งปฏิกิริยาส่งผลให้เพิ่มค่าร้อยละการเปลี่ยนแปลงสารตั้งต้นที่อุณหภูมิต่ำ อย่างไรก็ตามการมีแพลเลเดียมอยู่บนตัวเร่งปฏิกิริยาช่วยให้เกิดปฏิกิริยาการขจัดไฮโดรเจนซึ่งได้อะเซทัลดีไฮด์เป็นผลิตภัณฑ์หลักที่อุณหภูมิต่ำประมาณ 200 องศาเซลเซียส

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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CHAKKRIT KHAOCHARTCHAI: CATALYTIC ETHANOL DEHYDRATION TO DIETHYL ETHER OVER PALLADIUM-MODIFIED PHOSPHORUS GAMMA ALUMINA CATALYSTS. ADVISOR: PROF. BUNJERD JONGSOMJIT, Ph.D., pp.

The gamma alumina (γ-Al_2O_3) catalyst was modified with phosphorous (P) by acid activation technique and palladium (Pd) by the incipient wetness impregnation technique. The obtained catalysts were characterized with various techniques including X-ray diffraction (XRD), inductively coupled plasma (ICP), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), N_2 physisorption, ammonia temperature-programmed desorption (NH_3-TPD), and thermogravimetric analysis (TGA). In addition, these modified catalysts were tested in ethanol dehydration reaction in a fixed-bed microreactor to determine ethanol conversion and product yield at the atmospheric pressure with temperatures ranging from 200-400^{o}C. From the results, the phosphorous modification diminished the amount of moderate to strong acid sites leading to increased amount of weak acid sites. The phosphorous modified catalyst exhibited the highest diethyl ether yield of 38.41% at the temperature of 350°C. Furthermore, the phosphorous addition on catalyst significantly decreased the amount of coke deposition on the catalyst surface. The Pd-modified catalyst likely acted as the chemical promoter of catalyst resulting in increased ethanol conversion at low temperature. Nevertheless, the presence of Pd on catalysts enhanced the dehydrogenation reaction to produce acetaldehyde as a major product at low temperature ca. 200°C.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER 1
INTRODUCTION

1.1 General introduction

Biomass is promising resource to replace by non-renewable sources, such as minerals, coal, gas and the petroleum. In the chemical industry, the main use of biomass is ethanol production [1]. Feedstocks for ethanol production in Thailand are sugarcane, molasses (by-products from cane sugar processing), and cassava roots. In the case of Thailand, bioethanol is produced domestically for mostly blending with fuel oil to produce gasohol. The development of competitors to traditional ICE vehicles, including hybrids and electrical vehicles has been considered. These vehicles have a significant impact on demand for ethanol. Thus, the ethanol production exceeds its consumption. It should potentially produce the value-added chemicals from ethanol [2, 3].

The catalytic dehydration of ethanol mainly carries on the production of ethylene, diethyl ether and small amount of acetaldehyde. The selective production of diethyl ether has further attention in present. Diethyl ether is a valuable chemical participated in product of the fuel and chemical industry. It is mostly used as solvent in fine chemistry, fragrance, pharmaceutical chemical processes, some processes involved in explosives synthesis and improving additive ignition in both diesel and gasoline engines to alleviate NO_x emission [4]. Consequently, in this research, we preferred to focus in transformation of ethanol to diethyl ether from dehydration reaction.

Solid catalysts with acid property were considered to have high activity for ethanol dehydration. Particularly, gamma alumina (γ-Al_2O_3) is the most important material used as catalyst and catalyst carrier for metal catalysts due to its distinctive chemical, mechanical and thermal properties [5]. Chen, G et al. [6] investigated the catalytic dehydration of bioethanol to ethylene over TiO_2/γ-Al_2O_3 catalysts. The experimental compared with the undoped TiO_2 exhibited that the doped 10 wt% TiO_2 on catalysts was achieved high ethanol conversion, ethylene selectivity and yield, 99.96%, 99.4% and 72.7%, respectively. Liu, D. et al. [7] reported the catalytic dehydration of methanol to dimethyl ether over modified γ-Al_2O_3 catalyst. The Nb_2O_5

modification on γ-Al_2O_3 improved methanol conversion and increased the number of acid sites but reduced the strength of acid sites on catalyst. Ramesh, K. et al. [8] investigated the effect of phosphorus (P) modification on H-ZSM-5 for the selective dehydration of ethanol to ethylene. The phosphorous modification improved coke resistance properties of catalysts via mainly generating weak acid sites instead of strong acid sites on H-ZSM-5 catalyst resulting in very high ethanol conversion, ethylene selectivity and catalyst stability. Kamsuwan, T. et al. [9] determined the different Si- and Al-based catalysts including HBZ, γ-Al_2O_3, χ-γ-Al_2O_3 and SSP with Pd modification for catalytic ethanol dehydration. The modification of Pd on solid catalysts increased the catalytic activity. The Pd-HBZ catalyst exhibited the highest diethyl ether yield of 48% at 250°C. In addition, γ-Al_2O_3 and χ-γ-Al_2O_3 catalysts with Pd modification tended to increase acetaldehyde yield at low temperature.

The previous studies observed that the low temperature of ethanol dehydration reaction obtained low ethanol conversion and diethyl ether yield. Therefore, noble metal addition on catalysts is used to increase catalytic activity. For noble metal species, palladium (Pd) was suitable to add into catalysts to improve the catalytic performance for diethyl ether production. As mentioned above, the purpose of this study is to investigate the catalyst characteristic and catalytic performance of Pd-modified over Al_2O_3-P catalyst by using incipient wetness impregnation technique. In the experiments, dehydration of ethanol reaction will be carried on using via using a fixed-bed flow microreactor to determine the ethanol conversion and product distribution.

1.2 Research objectives

1) To investigate the characteristics of Al_2O_3-P catalyst with Pd addition of 0.05, 0.1, 0.3 and 0.5 wt% in ethanol dehydration.

2) To determine effect of Al_2O_3-P catalyst with Pd addition of 0.05, 0.1, 0.3 and 0.5 wt% in ethanol dehydration.

3) To compare the characteristics and catalytic performance between the chosen Pd modified Al_2O_3 catalyst and the chosen Pd modified Al_2O_3-P catalyst.

1.3 Research scopes

1) Synthesis of the phosphorous-modified Al_2O_3 catalysts with 5 wt% phosphorous loading using acid activation technique.

2) Modification of the Al_2O_3-P catalysts by varying Pd loading at 0.05-0.5 wt% using incipient wetness impregnation technique.

3) Verification of characteristic of the Al_2O_3-P catalysts by varying Pd loading at 0.05-0.5 wt% by using method as following;

- X-ray diffraction (XRD)
- Inductively coupled plasma (ICP)
- Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)
- N_2 physisorption
- Ammonia temperature-programmed desorption (NH_3-TPD)
- Thermo gravimetric analysis (TGA).

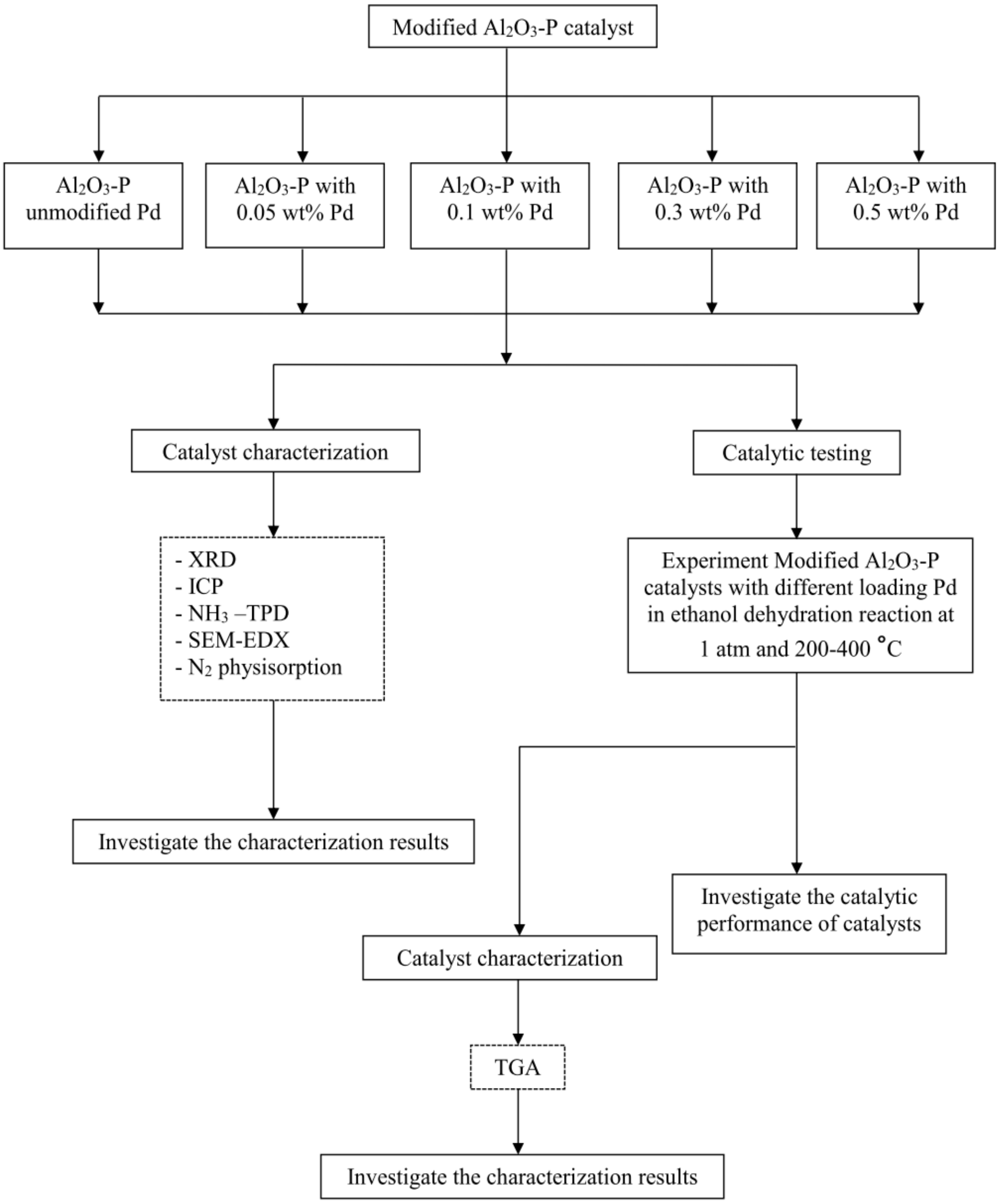
4) Investigating reaction of Pd loading 0.05, 0.1, 0.3 and 0.5 wt% with Al_2O_3-P catalysts in ethanol dehydration reaction, which is carried out in a fixed-bed reactor under atmospheric pressure and temperature range of 200-400°C.

5) Determining the suitable of Pd loading 0.05, 0.1, 0.3 and 0.5 wt% with Al_2O_3-P catalysts and reaction condition, which achieve the highest diethyl ether yield.

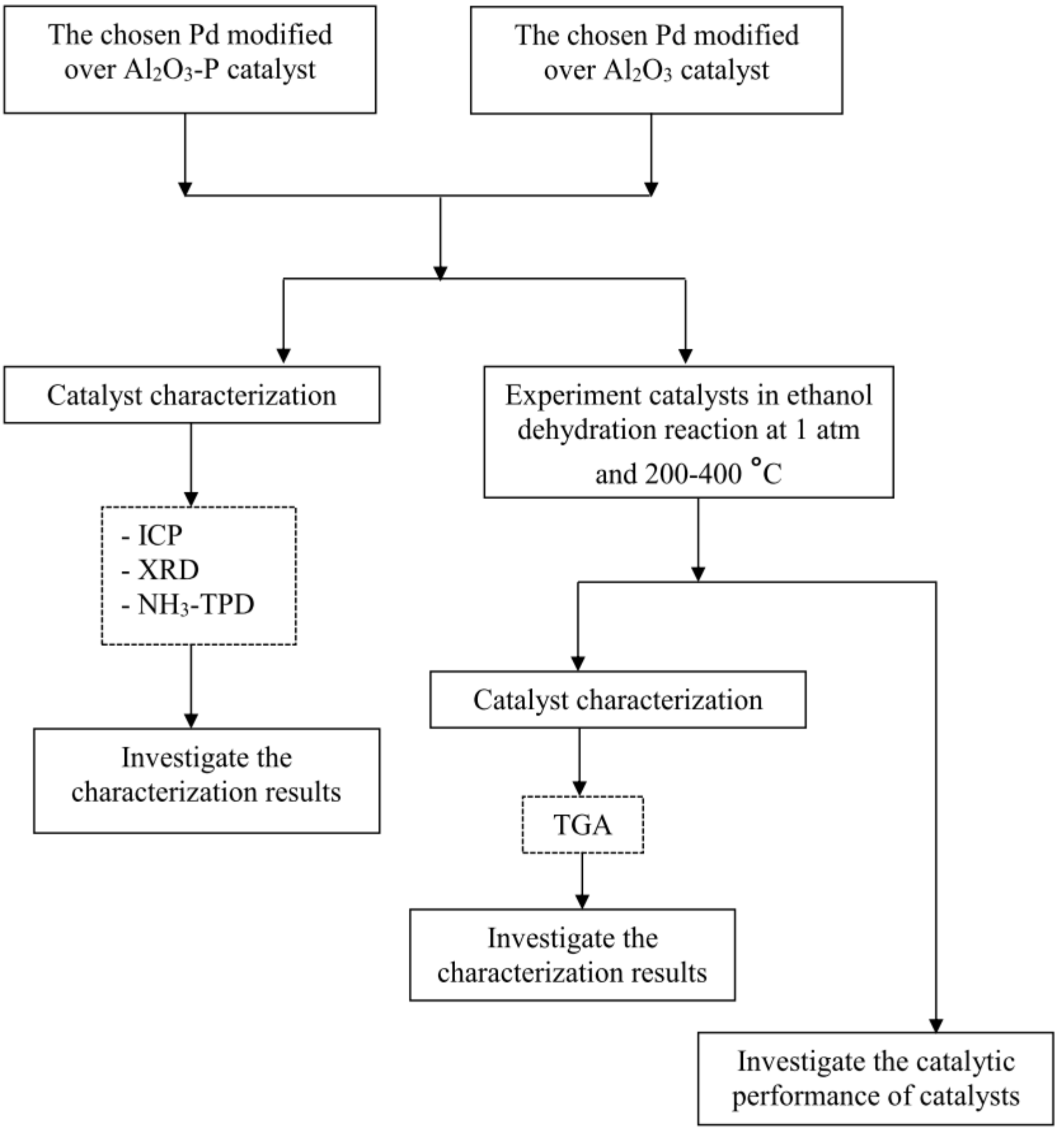
6) Comparison of the catalytic performance between the chosen Pd modified Al_2O_3 catalyst and the chosen Pd modified Al_2O_3-P catalyst, which is carried out in a fixed-bed reactor under atmospheric pressure and temperature range of 200-400°C.

1.4 Research methodology

Part I: The comparison of catalytic activities and catalyst characteristic of the Al_2O_3-P catalysts with different Pd loadings.



Part II: The comparison of catalytic activities and catalyst characteristic between the chosen Pd modified over Al_2O_3 catalyst and the chosen Pd modified over Al_2O_3-P catalyst.



CHAPTER 2
THEORIES

This chapter describes concerning theories consist of the properties of alumina, phosphorous and palladium, the ethanol dehydration mechanism and the literature reviews for catalytic ethanol dehydration.

2.1 Alumina

Alumina, Al_2O_3, is an important catalyst and support catalyst, which alumina could be used for the alcohol dehydration reaction and also used in many other chemical reactions such as isomerization, alkylation, and catalytic cracking, etc. Alumina is a solid inorganic chemical compound formed as shown in **Table 2.1**. The characterization of alumina has been performed high compression strength, high abrasion resistance, high chemical resistance, high thermal shock resistance, high degree of refractoriness, and high dielectric strength [10].

Table 2.1 Alumina properties

Properties	Specification
Molar mass	101.96 g.mol^{-1}
State	Solid
Structure	Octahedral
Density	3.95–4.1 g·cm^{-3}
Melting point	2072°C
Boiling point	2977°C

Alumina can be produced several metastable crystalline structures consisting of η-, γ-, δ-, θ-, β-, κ-, χ-, and α-alumina formed through thermal dehydration as shown in **Fig.2.1**. The type or structure of each alumina undergoes phase transformation with increasing calcination temperature of precursor hydroxide; they are different for gibbsite, bayerite, nordstrandite, boehmite or diaspore [11, 12].

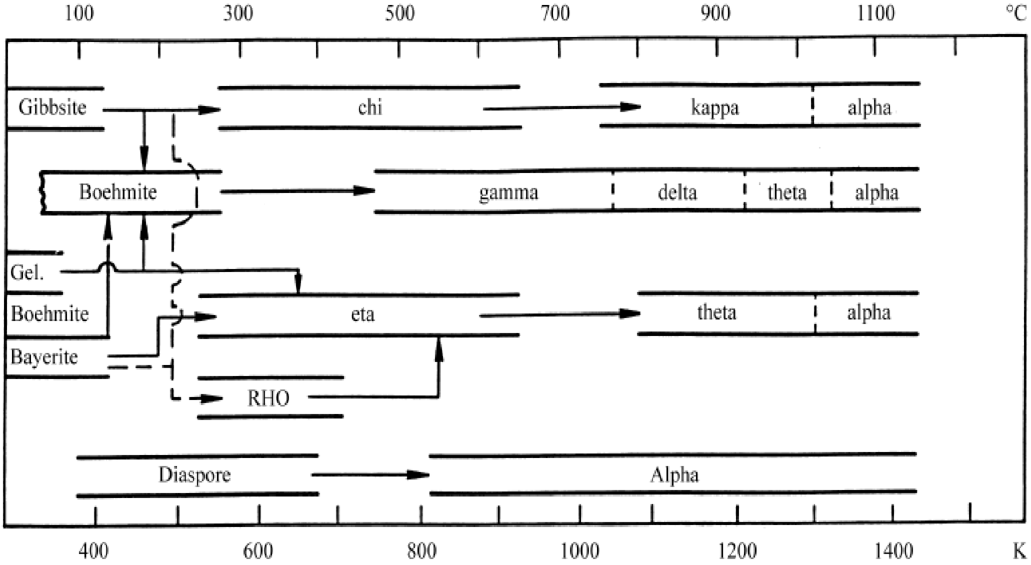


Figure 2.1 Phase transformation of the crystalline alumina.

In addition, alumina surface contains several hydroxyl groups: the linear ones are Lewis acid, and the bridged ones are Brønsted acids [13]. The calcinations temperature of alumina has been influenced on the acid-base properties of alumina surface. Besides, the existence of basic sites on alumina surface has indicated that the basic properties of alumina arise when alumina surface comes into contact with a sufficient quantity of water result in Lewis acid sites are transformed into Brønsted acid sites as shown in **Fig.2.2** [14, 15].

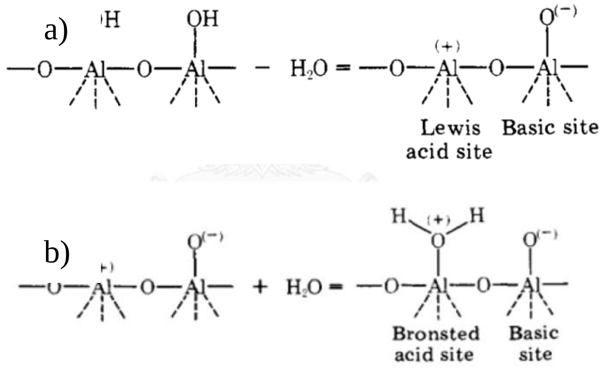


Figure 2.2 Lewis acid formed of alumina (a) Brønsted acid formed of alumina (b).

2.2 Phosphorus

Phosphorus (P) is extensively found in compounds in mineral, which the physical properties of phosphorus are shown in **Table 2.2** [16]. Generally, the two main forms of phosphorus are white phosphorus and red phosphorus. The white phosphorous is a poisonous waxy solid, glow in the dark and is spontaneously flammable when exposed to air, which exhibit the most activity to produce phosphoric acid. The red phosphorous is an amorphous non-toxic solid, which can alter in colour from orange to purple due to slight variations in its chemical structure and more passive in chemical reactions [17]. In this study, phosphorus as phosphoric acid form is modified on catalysts in order to increase catalytic activity and catalyst stability.

Table 2.2 Phosphorus properties

Properties	Specification
Relative atomic mass	30.974
Atomic Radius	110 pm
Group, Block	Group 15 (pnictogens), p-block
State	Solid
Density	1.823 g·cm^{-3}
Melting point	44.15°C
Boiling point	280.5°C

2.3 Palladium

Palladium (Pd) is a soft and lustrous silver-white metal, which the physical properties of phosphorus are shown in **Table 2.3** [18]. Palladium is always found alongside other platinum group metals (PGMs). PGMs, including palladium, platinum, ruthenium, rhodium, iridium and osmium, naturally occur in placer deposits found in rocks such as dunite, chromite, and norite. Palladium, much like platinum, is very resistant to oxidation, corrosion and has excellent catalytic properties. In petrochemical, palladium form is a good catalyst and is used to catalyze for hydrogenation and dehydrogenation reactions [19]. In this study, small amount of palladium compound is used for promoter substance to add in solid catalyst in order to increasing the catalyst activity by facilitating the desired process and escalating the catalyst selectivity by suppressing the undesired reactions.

Table 2.3 Palladium properties.

Properties	Specification
Relative atomic mass	106.42
Atomic Radius	116.42 pm
Group, Block	Group 10, d-block
State	Solid
Density	12.023 g·cm^{-3}
Melting point	1554.9°C
Boiling point	2963°C

2.4 Ethanol dehydration reaction

The ethanol dehydration reaction is mainly produced ethylene and by-product of diethyl ether under the condition of appropriate temperature 180°C to 500 °C. However, the reaction of ethanol dehydration can generate other by-products, such as acetaldehyde, hydrocarbons (methane, ethane, propylene, butylene) and light base-groups (CO_2, CO, H_2) [20].

Based on mainly ethanol dehydration reaction consists of two reactions ways occur to ethylene and diethyl ether. as follows;

$C_2H_5OH = C_2H_4 + H_2O$.......................ΔH + 44.9 kJ/mol (1)

$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O$.........ΔH- 25.1 kJ/mol (2)

$C_2H_5OH = CH_3CHO + H_2$...................ΔH+82.5 kJ/mol (3)

The reaction (1) is dehydration of ethanol to ethylene (endothermic reaction favored thermodynamically at high temperatures), whereas the reaction (2) is dehydration of ethanol to diethyl ether (exothermic reaction favored at low or moderate temperature) [21, 22]. In addition, acetaldehyde can be obtained by dehydrogenation reaction as shown in the third reaction [23].

The mechanism of ethanol dehydration reaction mainly considers the generation of ethylene and ether, which can be summarized as three kinds of routes: (1) parallel reactions, (2) a series of reactions, and (3) a parallel series reaction depending on the catalysts and reactants used as shown in **Fig. 2.3** [24].

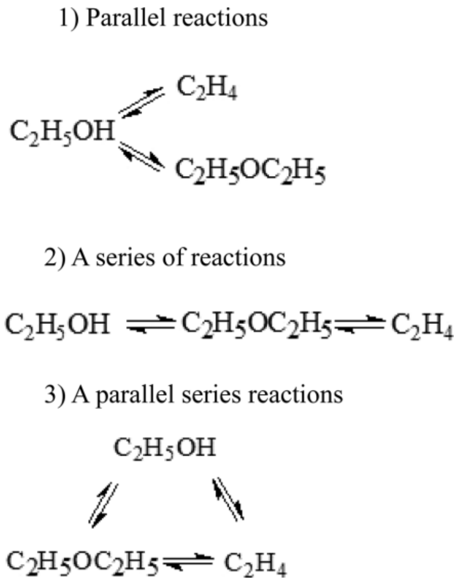


Figure 2.3 Mechanism route of ethanol dehydration reaction[24].

There are mainly three competitive mechanisms of ethanol catalytic dehydration to olefins under different reaction conditions such as E1, E2 and E1cB mechanism is shown in **Fig 2.4**. The reactions of E1, E2, and E1cB are elimination reactions, which A and B are the acidic and basic centers of the catalyst, respectively [24].

The E1 reaction is a single-molecule elimination reaction, normally mechanism proceeds via a carbocation intermediate on acidic catalysts, in which protonation of alcoholic oxygen is followed by the C-O cleavage to form water and a carbocation intermediate. Then, deprotonation of the adjacent C of the carbocation intermediate on the base leads to the formation of ethylene [25, 26].

The E2 reaction is a bimolecular elimination reaction, which mechanism involves the concerted cleavage of C–O and C–H bonds in alcohol using a pair of acid and base catalyst sites to produce the ethylene [24].

The E1cB reaction is a single-molecule conjugate base elimination reaction, mechanism proceeds via a carbanion intermediate on base catalysts, on which C-H bond cleavage takes place first to form carbanion or alkoxy intermediates. This is followed by the elimination of the hydroxyl group on the acid to produce the ethylene [25].

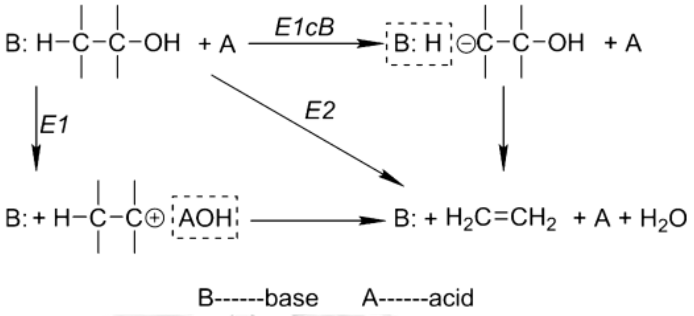


Figure 2.4 Ethanol intramolecule dehydration to ethylene[24].

The mechanism of dehydration reaction of ethanol to diethyl ether, represented by two different pathways termed the associative pathway and the dissociative pathway as shown in **Fig 2.5**. Both pathways occurred at Brønsted acid sites. The associative pathway relates adsorption of two alcohol molecules, which react and form the ether directly. The dissociative pathway relates initial alcohol adsorption, and followed by water elimination, which leading to adsorbed alkyl group and water. The alkyl group reacts with a second alcohol molecule to form the ether [22].

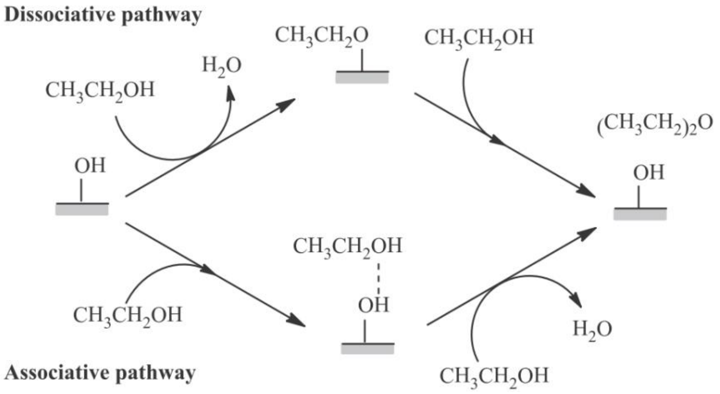


Figure 2.5 Ethanol intermolecule dehydration to diethyl ether[22].

CHAPTER 3
LITERATURE REVIEWS

This chapter describes concerning theories consist of the properties of alumina, phosphorous and palladium, the ethanol dehydration mechanism and the literature reviews for catalytic ethanol dehydration.

3.1 Alcohol dehydration reaction over solid catalysts

The literature reviews of alcohol dehydration reaction over solid catalyst were sequenced from publication years as shown following;

Xu, M. et al. (1997) [27] studied the catalytic dehydration of methanol to dimethyl ether (DME) over 10 wt% Pd/Cab-O-Sil catalysts. As the reaction temperature was increased from 225°C to 280°C, methanol conversion increased from 38% to 77%, while DME selectivity decreased from 78% to 47%. In addition, the effects of hydrogen on the catalytic activity and selectivity in the catalytic system were found that the presence of hydrogen inhibited the catalytic activity via reducing the rate of surface carbonaceous species formation but increased the stability of the catalyst.

Takahara, I. et al. (2005) [28] reported the dehydration of ethanol into ethylene over solid acid catalysts. The solid acid catalysts H-mordenites (HM20 and HM90), H-ZSM5 zeolites (ZSM5-25 and ZSM5-90), H-beta-zeolite (HB25), H-Y zeolite (HY5.5) and silica–alumina (SA) were produced via diethyl ether at temperatures ranging from 453 to 573 K under atmospheric pressure. The results found that the catalyst activity decreases in the following order: HM20>HM90>ZSM5-25>HB25>ZSM5-90>HY5.5>SA. The percentage of Brønsted acid sites on HM20, HM90, ZSM5-25, ZSM5-90, HB25, HY5.5 and SA were estimated to be 83%, 95%, 94%, 92%, 33%, 83%, and 50%, respectively. There are concluded that H-mordenites were the most active for the dehydration and the catalyst activity during the dehydration could be correlated with the number of strong Brønsted acid sites.

Li, Y. et al. (2007) [7] reported the influence of varying the reaction temperature, feed flow rate, and concentration of ethanol in catalytic dehydration of ethanol to ethylene over γ-Al_2O_3 catalyst. In the reaction temperature range 410°C to 440°C described that the selectivity of the γ-Al_2O_3 catalyst increases at the initial of reaction, and then remains constant, while the yield of ethylene is not affect the reaction temperature. As the feed flow rate decreases, the selectivity increases to closely 100%, but the conversion decreases. According to the experimental results, the optimum temperature is about 420°C, the optimum feed flow rate is about 1.0 mL/min, and the optimum concentration of ethanol is in the range 50% to 100%.

Varisli, D. et. Al. (2007) [29] determined ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts, namely silicotungstic acid (STA), molybdophosphoric acid (MPA) and tungstophosphoric acid (TPA). The increasing of reaction temperature from 140°C to 250°C caused the significant increase in ethylene yield while at lower temperatures the main product is diethyl-ether. The presence of water vapor in the dehydration reaction resulted in decrease the catalyst activity. The activity trend was obtained as STA > TPA > MPA due to higher number of protons and the higher stability of STA than TPA at temperatures over 200°C.

Zhang, D. et al. (2008) [30] reported the effect of Phosphorus (P) Content on the Catalytic Performance of P-modified HZSM-5 catalysts in dehydration of ethanol to ethylene. The P contents were 1.9, 3.2, 3.4, 3.6 and 5.1 wt%, which correspond to P/Al atomic ratios of 0.5, 0.9, 0.95, 1.0 and 1.5 respectively. In the catalyst containing 3.4 wt% P, the main product is ethylene at 573–713 K, due to the presence of weak acid sites after P modification.

Ramesh, K. et al. (2009) [31] reported structure and reactivity of phosphorous modified H-ZSM-5 catalysts for ethanol dehydration. The influence of H_3PO_4 on the catalytic performance of modified H-ZSM-5 catalysts for the selective dehydration of ethanol were prepared by dry impregnation method with varying H_3PO_4 loadings from 5 to 20 wt%. The modified catalysts were performed highly active and selective towards ethylene during ethanol dehydration at 673 K. The selectivity was depended on the content of H_3PO_4, reaction temperature and WHSV.

Bi, J. et al. (2010) [32] investigated the dehydration of bio-ethanol into ethylene over nanoscale HZSM-5 zeolite catalyst. In a fixed-bed reactor at 240°C, the experiment compared with microscale HZSM-5 zeolite catalyst, nanoscale HZSM-5 zeolite catalyst exhibits good stability and coke resistance.

Ramesh, K. et al. (2010) [8] investigated the influence of Phosphorus (P) modification on H-ZSM-5 for the selective dehydration of ethanol to ethylene. The P-modified H-ZSM-5 catalysts were varying P loadings from 0 to 7.43 wt% with wet impregnation method. The experiments were found that 7.43P-ZSM-5 catalyst exhibited very high ethanol conversion, ethylene selectivity and catalyst stability compare to bulk H-ZSM-5 catalysts due to P-modified improved coke resistance properties of catalysts. The total acidity of the catalyst was decreased with P content due to the addition P-modified on H-ZSM-5 resulted in the strong acid sites was suppressed by generating mainly weak acid sites.

Han, Y. et al. (2011) [33] investigated the effect of calcination temperature on the catalytic performance of the dehydration of aqueous ethanol on Mo/HZSM-5. Base on calcined temperature at 450, 500, 550, 600 and 700°C, the results found that 5 wt% Mo/HZSM-5 catalyst calcined at 500°C exhibited the highest weak and medium acidity and excellent catalytic performance in ethanol dehydration reaction compared with the original HZSM-5.

Rahmanian, A. and H.S. Ghaziaskar (2013) [34] reported the aluminium phosphate –hydroxyapatite catalyst for continuous dehydration of ethanol to diethyl ether (DEE) under sub and supercritical condition. The experiments were exhibited that the $AlPO_4$/HAP is more active than HAP for dehydration of ethanol to diethyl ether in both sub and supercritical conditions. Consequently, $AlPO_4$/HAP catalysts in supercritical conditions were optimized the reaction temperature, pressure, and flow rate to execute the highest diethyl ether yield, selectivity, and liquid selectivity. As mentioned, the optimum conditions of 340°C, 200 bar and 0.17 mL min^{-1} of ethanol flow rate were achieved conversion of ethanol to diethyl ether, diethyl ether yield, selectivity and liquid selectivity of 78%, 75%, 96% and 97%, respectively.

Krutpijit, C. (2016) [35] reported the catalytic ethanol dehydration to ethylene over montmorillonite clays (MMT) with mineral acid activation including H_2SO_4 (SA-MMT), HCl (HA-MMT) and HNO_3 (NA-MMT). The compared acid-activated results performed that HCl activation, HA-MMT exhibited the highest activity with conversion of ethanol and ethylene yield of 82% and 78% at reaction temperature of 400°C. The apparent HCl activation was increased weak acid sites and acid density relate to enhanced Brønsted acid site of catalyst. Moreover, the MMT and HA-MMT exhibited slight deactivation due to carbon deposition for the stability experiment.

Chanchuey, T and Autthanit C. (2016) [36] investigated the effect of mesoporous Al-SSP and Mo-doped Al-SSP catalysts for the catalytic dehydration of ethanol to ethylene. The influence of mesoporous Al-SSP, 1% Mo/Al-SSP and 5% Mo/Al-SSP catalysts revealed that acidity was the key factor effect to catalytic activity correlate with the amount of Mo loading and concentration of Al on surface catalyst. Increasing of Mo loading in Al-SSP resulted in enhanced weak acids sites. In contrast to the excessive amount of Mo doping (5% Mo/Al-SSP) apparently resulted in decreased amount of Al at catalyst surface leading to low ethanol conversion. The compared of modified Al-SSP catalysts, 1% Mo/Al-SSP catalyst exhibited the highest ethanol conversion and ethylene yield of 90% at reaction temperature of 300°C with slight amounts of diethyl ether (DEE) and acetaldehyde.

Kamsuwan, T. (2017) [37] investigate the characteristics and catalytic properties of H-beta zeolite (HBZ) catalyst with ruthenium (Ru-HBZ) and platinum (Pt-HBZ) modification for diethyl ether production during catalytic dehydration of ethanol. The compared diethyl ether yield of modified catalysts found that the Ru-HBZ catalyst exhibited the highest diethyl ether yield of 47% at 250°C. The Ru-HBZ and Pt-HBZ modification were displayed high dispersed forms and well distributed in the catalyst granule, which facilitated to contacting reactants for catalytic reaction. Moreover, the existing noble metal precursor on catalysts was facilitated to decrease weak acid sites leading to increased diethyl ether yields and intrinsic activity of the catalysts.

3.2 Modified Alumina as solid catalysts for alcohol dehydration

Chen, G et al. (2007) [6] investigated the catalytic dehydration of bioethanol to ethylene over $TiO_2/\gamma\text{-}Al_2O_3$ catalysts in microchannel reactors. The modified catalysts are compared with the undoped TiO_2 in reaction temperatures of 400–500°C. The experimental results demonstrate that the doped 10 wt% TiO_2 on catalysts with was achieved high ethanol conversion, ethylene selectivity and yield, 99.96%, 99.4% and 72.7%, respectively.

Khom-in, J. et al. (2008) [38] investigated dehydration of methanol to dimethyl ether over nanocrystalline Al_2O_3 with mixed χ- and γ-crystalline phases. The mixed catalysts with various phase composition of 0, 10, 20, 50, 80, 90 and 100% χ-phase were prepared by using solvothermal method for methanol dehydration reaction to dimethyl ether. The comparison of pure $\gamma\text{-}Al_2O_3$, $\chi\text{-}Al_2O_3$ and mixed χ/γ-phase was found that $\gamma\text{-}Al_2O_3$ catalyst containing 20 wt% of χ-phase exhibited the highest yield (86%) with good stability for DME synthesis, which performed higher density and strength of surface acidity than pure $\gamma\text{-}Al_2O_3$, $\chi\text{-}Al_2O_3$.

Liu, D. et al. (2011) [7] reported the catalytic dehydration of methanol to dimethyl ether over modified $\gamma\text{-}Al_2O_3$ catalyst. The $\gamma\text{-}Al_2O_3$ catalyst was modified with metal oxide (Nb_2O_5) to improve catalytic activity and stability for dimethyl ether (DME) from methanol. In various Nb_2O_5 loading as 1, 5 and 10 wt% found that the $\gamma\text{-}Al_2O_3$ catalyst containing 10 wt% of Nb_2O_5 exhibited the highest surface area and catalytic activity compared with untreated $\gamma\text{-}Al_2O_3$ catalyst. The modified Nb_2O_5 was improved methanol conversion and increased the number of acid sites but reduced the strength of acid sites on catalyst.

Valdez, R. et al. (2012) [39] reported the result of the acidity of alumina over Pt- and Pd-based catalysts for 2-propanol dehydration reactions. The Pt-and Pd-based catalysts has been prepared through wet impregnation showed that the basic Pt/Al_2O_3 is performed conversion of 100% and 100% selectivity towards to DIPE at temperature of 523 K. In addition, the weakly acidic $Pt\text{–}Pd/Al_2O_3$ sample also presented a conversion of 100% and 100% selectivity towards to Propene at temperature of 523 K.

Then, the application of Pt and the bimetallic catalysts could be reduced deactivate and extend reaction time.

Janlamool, J. (2015) [40] investigated the oxidative dehydrogenation of ethanol over AgLi–Al_2O_3 catalysts containing different phases of alumina, namely pure gamma (CHI00), pure chi (CHI100) and equally mixed phases (CHI50). The experiment reveals that the mixed phases of chi and gamma alumina in AgLi–CHI50 catalyst exhibit high activity in oxidative dehydrogenation of ethanol. The AgLi–CHI50 catalyst was important increased amounts of weak basic sites, $Ag_n^{\delta+}$ clusters and moderate interaction of $Ag_n^{\delta+}$ with alumina to enhanced the catalytic activity.

Wannaborworn, M. (2015) [41] reported the comparative study of solvothermal and sol-gel-derived nanocrystalline alumina catalysts for ethanol dehydration. The results of different preparation method were described alumina synthesized by solvothermal method exhibited the highest activity due to high surface area, large amount of acid site, and high ratio of weak acid sites to strong acid sites. Furthermore, the Fe loading 10%wt on alumina catalyst was improved the acetaldehyde selectivity due to the ethanol dehydrogenation pathway normally occurred over Fe species.

Kamsuwan, T. (2016) [42] investigated the catalytic dehydration of ethanol over three different Al-based solid acid catalysts including H-beta zeolite (HBZ), modified H-beta zeolite with γ-Al_2O_3 (Al-HBZ) and mixed γ-χ phase of Al_2O_3 (M-Al) catalysts. The compared Al-based solid acid catalysts, HBZ exhibited the highest ethanol conversion to achieve ethylene yield of 99.4% at reaction temperature of 400°C. The H-beta zeolite (HBZ) was exhibited the largest amount of weak acid sites relate to Brønsted acid site of catalysts.

Inmanee, T. and Pinthong, P. (2017) [43] reported the effect of calcination temperatures and Mo modification on Nanocrystalline (γ-χ)-Al_2O_3 catalysts for catalytic ethanol dehydration. The compared mixed phase (γ-χ)-Al_2O_3 at different calcination temperatures including 400°C (M-Al-400), 600°C (M-Al-600), 800°C (M-Al-800), and 1000°C (M-Al-1000) revealed that the calcined catalyst (M-Al-600) exhibited the highest catalytic activity to achieve the highest ethylene yield of 98.75%

at 350°C. The total acidity was significantly decreased with increasing the calcination temperature because the hydroxyl group on catalyst surface was released with increasing the calcination temperature, leading to lower acidity. Furthermore, the Mo modification on mixed phase alumina catalyst was enhanced dehydrogenation reaction pathway to acetaldehyde due to the Mo sites dominantly performed as the active site for dehydrogenation of ethanol to acetaldehyde.

CHAPTER 4
EXPERIMENTAL

This chapter describes the research methodology comprise of catalyst preparation, ethanol dehydration reaction experiment and catalyst characterization techniques including X-ray diffraction (XRD), inductively coupled plasma (ICP), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), N_2 physisorption, ammonia temperature-programmed desorption (NH_3-TPD) and thermo gravimetric analysis (TGA).

4.1 Catalyst Preparation

4.1.1 Materials

Table 4.1 The chemicals used in modified Al_2O_3 catalysts.

Chemicals	Supplier
Commercial gamma alumina (γ-Al_2O_3)	Alfa Aesar
Orthophosphoric acid 85% (H_3PO_4)	Carlo Erba
Tetraamminepalladium (II) nitrate 10% $[Pd(NH_3)_4(NO_3)_2]$	Aldrich

4.1.2 Synthesis of phosphorus over Al_2O_3 catalysts

The phosphorous modified over Al_2O_3 catalysts were prepared by acid activation technique. The amount of 85 wt% phosphoric acid dissolved in deionized water as 100 ml was added in solution and stirred at room temperature for 30 minutes to achieve good homogeneity. Then, the obtained samples were filtered, dried in an oven at 110°C overnight and calcined at 600°C for 6 h to obtain the catalyst powder having 5 wt% of phosphorous on Al_2O_3.

4.1.3 Synthesis of Pd modified Al_2O_3-P catalysts

The Pd modified over Al_2O_3-P catalysts were prepared by the incipient wetness impregnation technique with an aqueous tetraamminepalladium (II) nitrate solution. The procedure of modified catalyst preparation was based on 1 g of catalyst used. At beginning, tetraamminepalladium (II) nitrate was dissolved in deionized water, and then gradually dropped the aqueous solution equal to the pore volume of Al_2O_3-P catalyst with 0.05-0.5 wt% loadings of Pd. After the impregnation, the prepared catalyst was dried at 110°C overnight and calcined at 600°C for 6 h.

4.2 Ethanol dehydration reaction

4.2.1 Chemicals and reagents

Table 4.2 The chemicals used in the reaction.

Chemicals	Supplier
Ethanol (99.99%)	Merck
Ultra high purity nitrogen gas (99.99%)	Linde
Ultra high purity hydrogen gas (99.99%)	Linde
Air zero (Grade balance nitrogen)	Linde

4.2.1 Reaction test

The catalytic dehydration of ethanol reaction was operated in a borosilicate glass fixed-bed reactor with an inside diameter of 0.7 cm. In the experiments, both 0.05 g of catalyst and 0.01 g of quartz wool were packed into the reactor. Then, the catalyst was pre-treated in argon (50 mL/min) at 200°C for 1 h under atmospheric pressure to remove moisture on surface of catalyst. The ethanol dehydration reaction was carried out at temperature ranging from 200°C to 400°C by feeding the vaporized ethanol into the reactor. The products were analyzed by using Shimadzu GC14B gas chromatograph with flame ionization detector (FID), which had the operating conditions as shown in **Table 4.3**.

Table 4.3 The operating conditions of gas chromatograph.

Gas chromatograph	**Shimadzu GC-14B**
Detector	FID
Capillary column	DB-5
Carrier gas	Nitrogen (99.99 vol%) Hydrogen (99.99 vol%)
Column temperature	Initial: 40°C Final: 40°C
Injector temperature	150°C
Detector temperature	150°C
Time analysis	8 min.

4.3 Catalyst characterization

4.3.1 X-ray diffraction (XRD)

The bulk crystalline phase and X-ray diffraction (XRD) patterns of the catalysts were determined by using a SIEMENS D5000 X-ray diffractometer with CuK_α radiation source (λ = 1.54439 Å) and Ni filter in the 2θ range of 10° to 90°.

4.3.2 Inductively coupled plasma (ICP)

The phosphorus and Pd contents in the catalysts were measured by Perkin Elmer OPTIMA 2000 TM instrument. The instrument was used energy from inductive coupled plasma to stimulate the transition of atoms from ground state to excited state and collected the energy released when returning to ground state by DBI-CCD (Dual backside-illuminated charge-coupled device).

4.3.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphologies of the catalysts were determined by JEOL mode JSM-6400 scanning electron microscope and the elemental distribution over the catalysts surface were determined by Link Isis Series 300 program energy dispersive X-ray spectroscopy, respectively.

4.3.4 N_2 physisorption

The surface area (using the stand BET method), average pore volume, average pore size (using the BJH desorption analysis) and hysteresis loop (using the adsorption-desorption isotherms) of the catalysts were investigated using a Micromeritics ASAP 2000 automated system. The samples were thermally treated at 110°C for 24 h before the analysis.

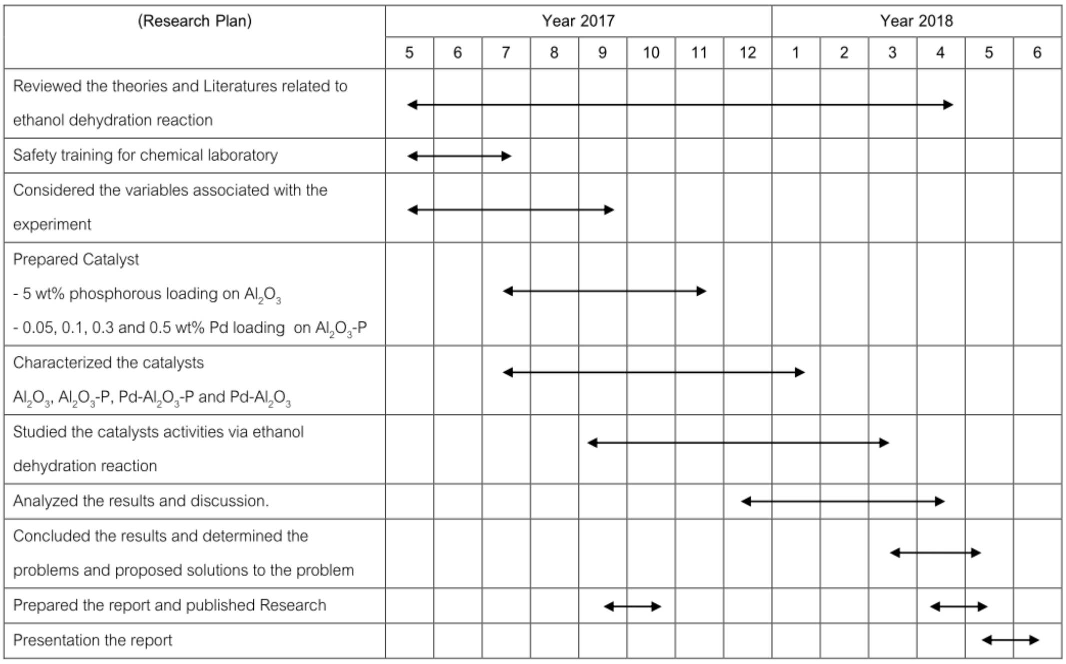
4.3.5 Ammonia temperature-programmed desorption (NH_3-TPD)

The acid properties of the catalysts were determined by using a Micromeritics Chemisorp 2750 Pulse for temperature-programmed desorption of ammonia (NH_3-TPD). In the experiment, a quartz wool and 0.1 g of sample and were loaded in quartz tube and pre-treated at 200°C by using heating rate of 10°C/min. After cooled the temperature down to 40°C, the sample was saturated with 15% NH_3 for 30 minutes and heated up from 40°C to 800°C with heating rate of 10°C/min. The amount of ammonia in effluent was measured by TCD signal as function of temperature.

4.3.6 Thermal gravimetric analysis (TGA)

The spent catalysts were determined coke deposition by Diamond Thermogravimetric and Differential Analyzer, TA Instruments SDT Q600 for Thermal gravimetric analysis in the temperature range of 25°C to 800°C under air atmosphere with heating rate of 10 °C/min.

4.4 Research plan



(Research Plan)	Year 2017								Year 2018					
	5	6	7	8	9	10	11	12	1	2	3	4	5	6
Reviewed the theories and Literatures related to ethanol dehydration reaction	←	—	—	—	—	—	—	—	—	—	—	→		
Safety training for chemical laboratory	←	—	→											
Considered the variables associated with the experiment	←	—	—	—	→									
Prepared Catalyst - 5 wt% phosphorous loading on Al_2O_3 - 0.05, 0.1, 0.3 and 0.5 wt% Pd loading on Al_2O_3-P			←	—	—	—	→							
Characterized the catalysts Al_2O_3, Al_2O_3-P, Pd-Al_2O_3-P and Pd-Al_2O_3			←	—	—	—	—	—	→					
Studied the catalysts activities via ethanol dehydration reaction					←	—	—	—	—	—	→			
Analyzed the results and discussion.								←	—	—	—	→		
Concluded the results and determined the problems and proposed solutions to the problem											←	—	→	
Prepared the report and published Research					←	→						←	→	
Presentation the report													←	→

CHAPTER 5

RESULTS AND DISCUSSION

Part I: The comparison of catalytic activities and catalyst characteristics of the Al_2O_3-P catalysts with different Pd loadings

The studies of P-modified on Al_2O_3 and Pd-modified on Al_2O_3-P catalysts including the characteristic and catalytic activity are presented in **Section 5.1.1** to **Section 5.1.7** as following;

5.1.1 X-ray diffraction (XRD)

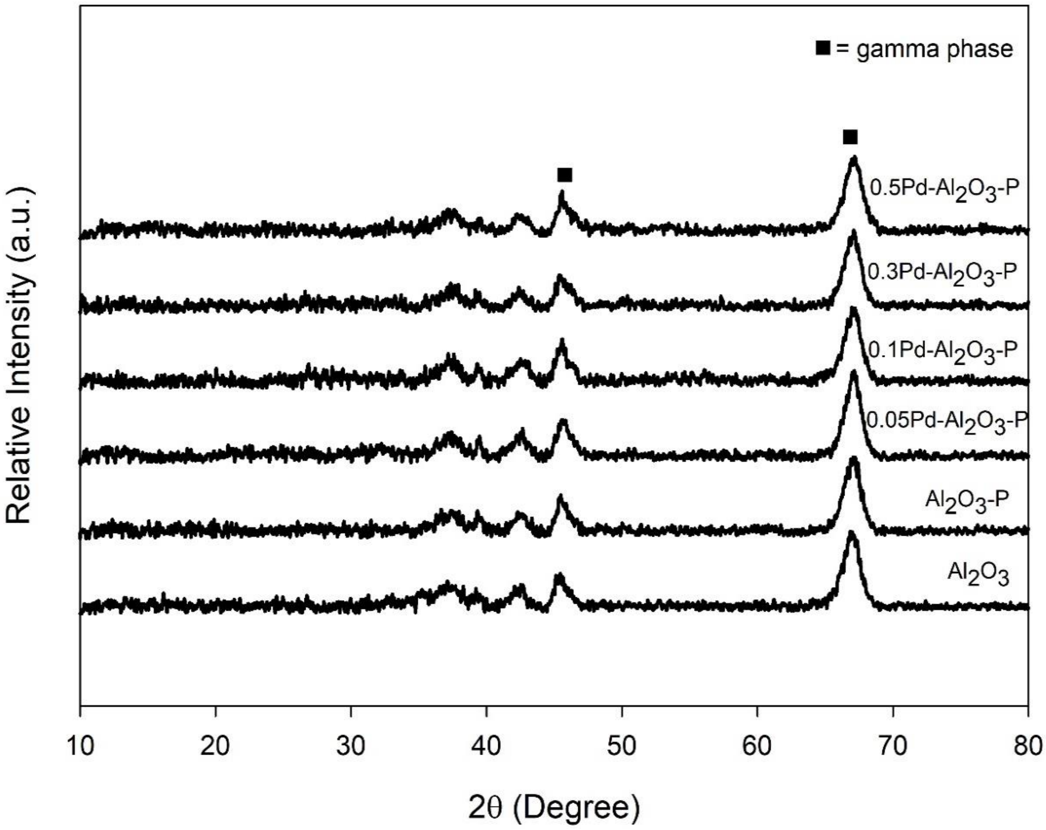


Figure 5.1 XRD patterns of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts

The X-ray diffraction (XRD) patterns of Pd-modified over Al_2O_3-P catalysts are shown in **Figure 5.1**. The characteristic sharp peaks of gamma alumina catalysts (γ-

Al_2O_3), were noticed at 2θ of 46º and 67º [38]. In XRD results, the phosphorous and palladium compound on catalysts presented similar XRD patterns of γ-Al_2O_3. This revealed that the crystalline structure of modified catalysts did not change with modified catalysts. In addition, the phosphorous and Pd loading on catalysts cannot be observed because they were in highly dispersed form on catalysts, which the crystallite size is less than 3-5 nm.

5.1.2 Inductively coupled plasma (ICP)

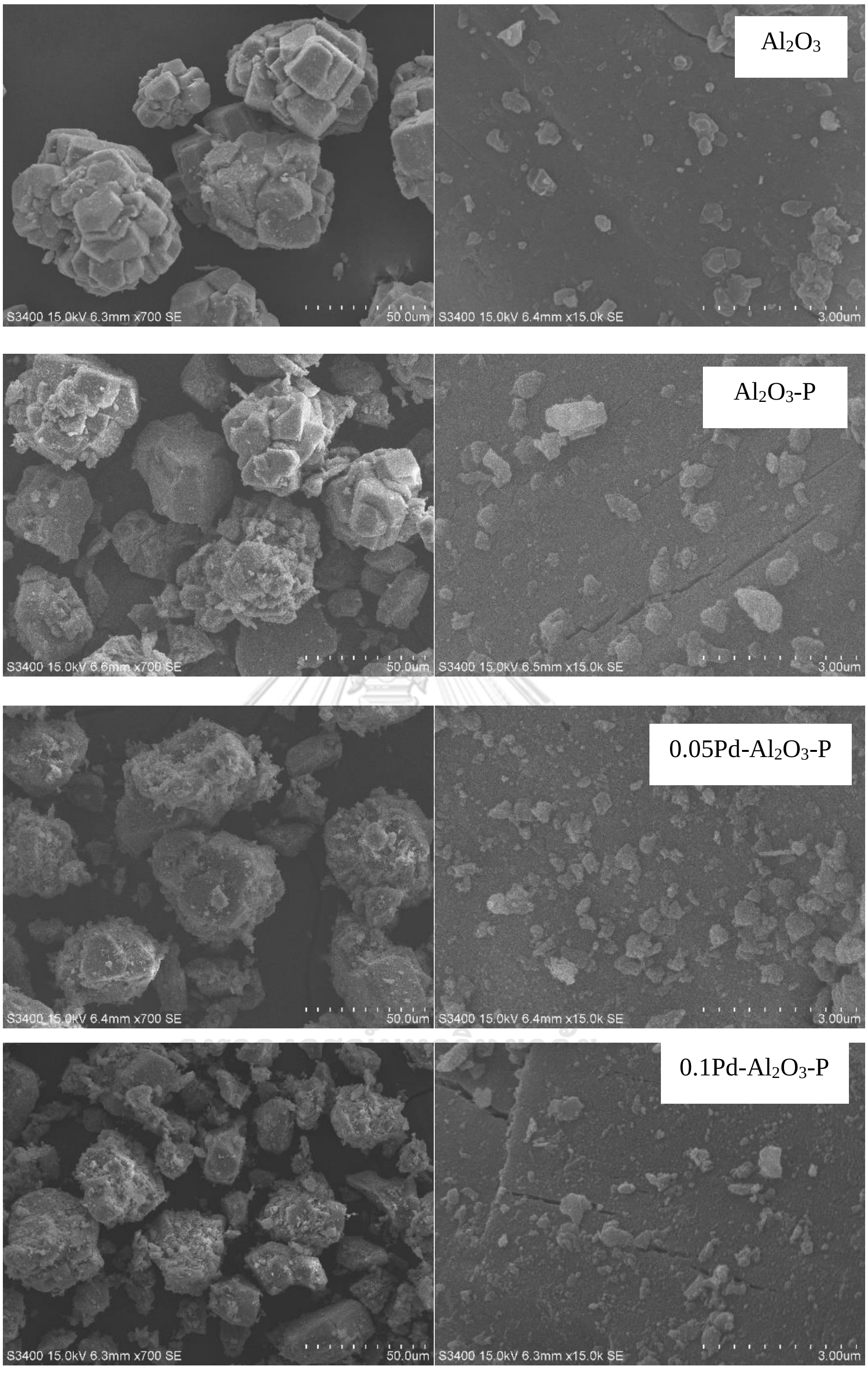
The various Pd contents were doped by the incipient wetness impregnation on Al_2O_3-P catalysts. The amount of Pd composition was determined in the catalyst bulk, which was carried on the contained amount of metal by inductively coupled plasma (ICP) as shown in **Table 5.1**

Table 5.1 The amount of Pd composed in the catalyst bulk.

Catalysts	Amount of Pd in catalyst bulk (wt%)
0.05Pd-Al_2O_3-P	0.08
0.1Pd-Al_2O_3-P	0.13
0.3Pd-Al_2O_3-P	0.35
0.5Pd-Al_2O_3-P	0.55

5.1.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphologies of Pd-modified over Al_2O_3-P catalysts were determined by scanning electron microscope (SEM) as shown in **Figure 5.2**. From SEM results, they were apparently irregular shape of examined catalysts. The amount of phosphorous and palladium doping into catalyst did not affect the morphology of catalysts related to the XRD pattern results as seen on **Section 5.1.1**.


Al2O3
Al2O3-P
0.05Pd-Al2O3-P
0.1Pd-Al2O3-P
S3400 15.0kV 6.3mm x700 SE 50.0um
S3400 15.0kV 6.4mm x15.0k SE 3.00um
S3400 15.0kV 6.6mm x700 SE 50.0um
S3400 15.0kV 6.5mm x15.0k SE 3.00um
S3400 15.0kV 6.4mm x700 SE 50.0um
S3400 15.0kV 6.4mm x15.0k SE 3.00um
S3400 15.0kV 6.3mm x700 SE 50.0um
S3400 15.0kV 6.3mm x15.0k SE 3.00um

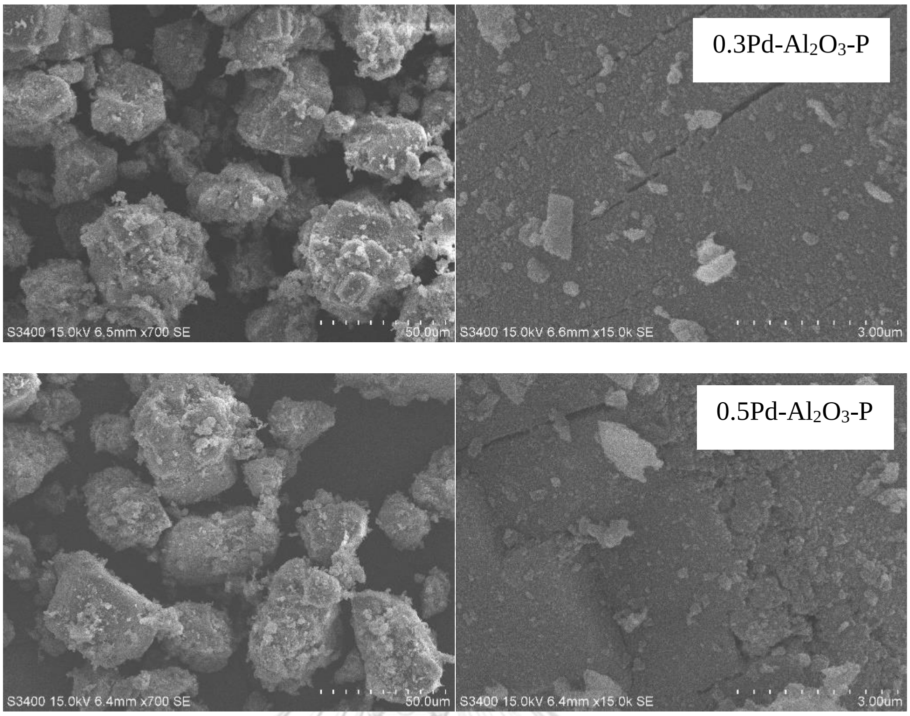


Figure 5.2 SEM micrographs of all catalysts.

The elemental dispersion of Al_2O_3, P-modified Al_2O_3 and Pd-modified Al_2O_3-P catalysts was performed through energy dispersive X-ray spectroscopy (EDX) technique. The elements such that Al, O, P and Pd were displayed in elemental distribution mapping (EDX mapping) of all catalysts. In the figure, dense of dots was related to the amount of existed element. The EDX mappings of each catalyst are shown in **Figure 5.3** to **Figure 5.8**

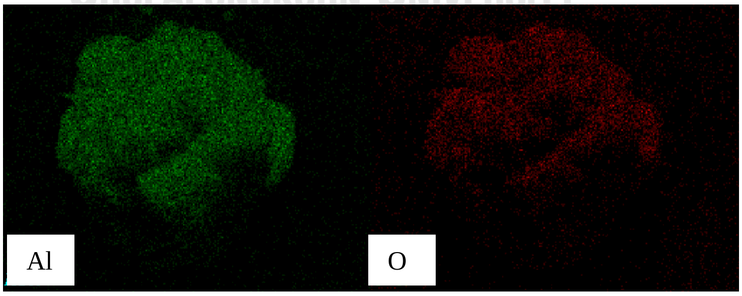


Figure 5.3 EDX mapping of micrographs of Al_2O_3.

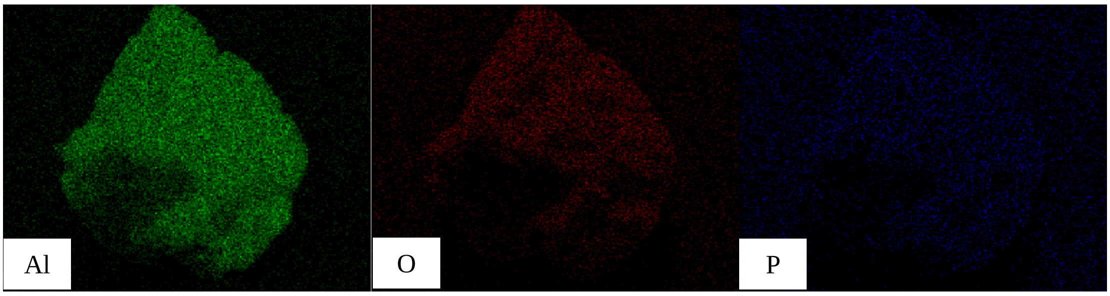


Figure 5.4 EDX mapping of micrographs of Al_2O_3-P.

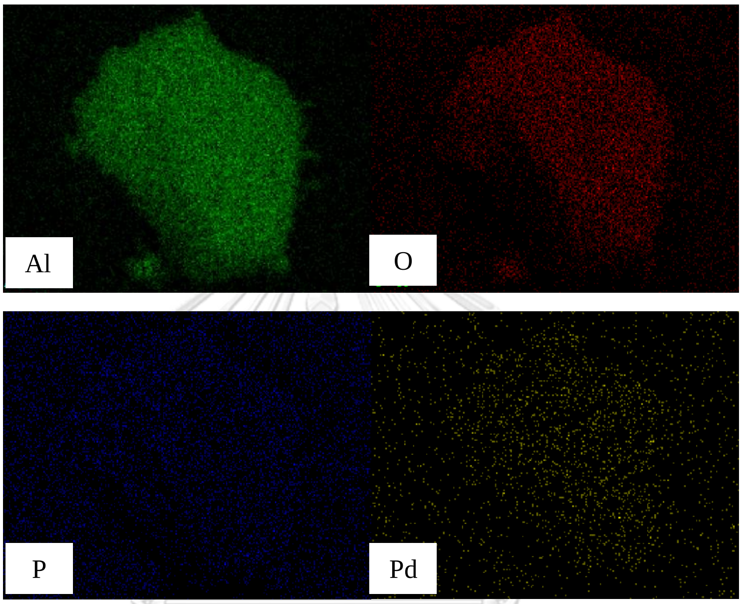


Figure 5.5 EDX mapping of micrographs of 0.05Pd-Al_2O_3-P.

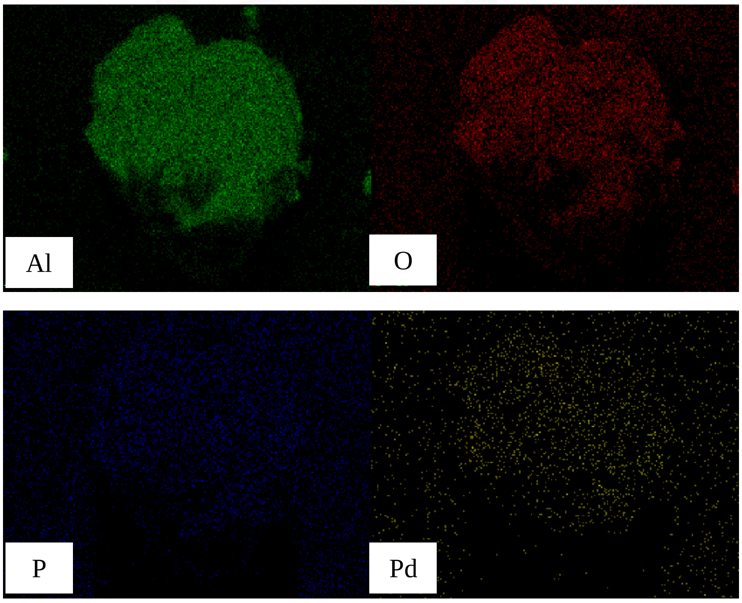


Figure 5.6 EDX mapping of micrographs of 0.1Pd-Al_2O_3-P.

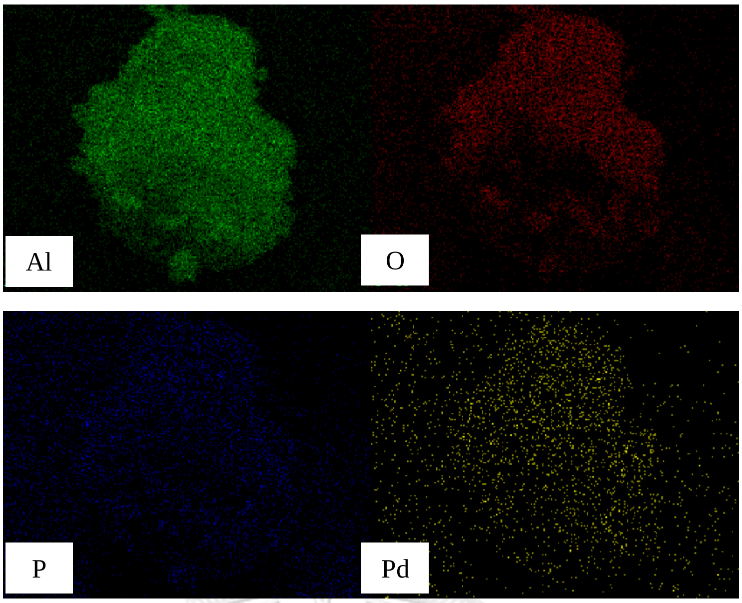


Figure 5.7 EDX mapping of micrographs of 0.3Pd-Al_2O_3-P.

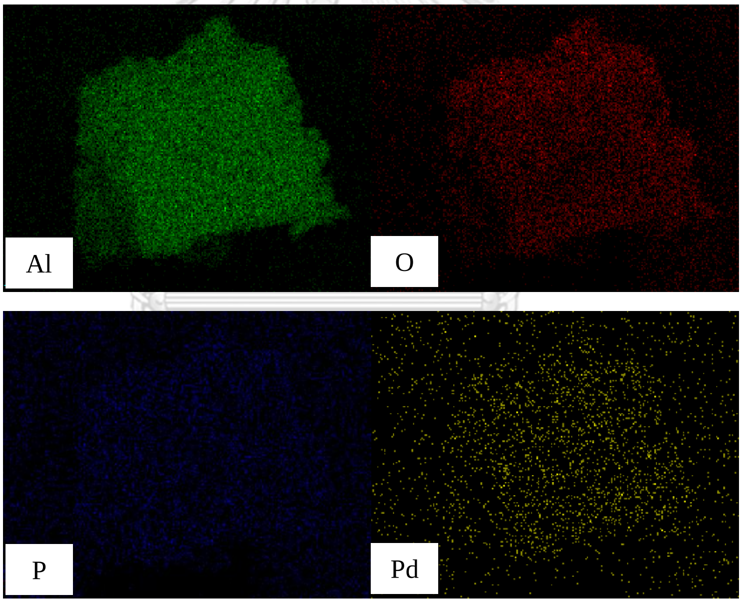


Figure 5.8 EDX mapping of micrographs of 0.5Pd-Al_2O_3-P.

According to EDX mapping, the results were depicted well distribution of phosphorous and palladium on catalysts corresponding with XRD patterns, which cannot detect sharp peak of P and Pd modified on the studied catalysts. The amount of each element was quantitatively summarized in terms of weight percent and atomic percent in **Table 5.2** and **Table 5.3**

Table 5.2 The amount of each element on the surface of catalysts (wt%).

	Amount of element on surface (wt%)				
Catalysts	**Al**	**O**	**P**	**Pd**	**Pd/Al**
Al_2O_3	60.88	39.12	-	-	-
Al_2O_3-P	50.79	37.49	11.71	-	-
0.05Pd-Al_2O_3-P	47.02	37.49	12.66	2.83	0.060
0.1Pd-Al_2O_3-P	48.48	38.53	9.99	2.99	0.062
0.3Pd-Al_2O_3-P	48.53	37.35	10.97	3.16	0.065
0.5Pd-Al_2O_3-P	48.56	36.74	11.2	3.5	0.072

Table 5.3 The amount of each element on the surface of catalysts (at%).

	Amount of element on surface (at%)				
Catalysts	**Al**	**O**	**P**	**Pd**	**Pd/Al**
Al_2O_3	48.6	51.4	-	-	-
Al_2O_3-P	40.89	50.9	8.21	-	-
0.05Pd-Al_2O_3-P	38.55	51.83	9.04	0.59	0.015
0.1Pd-Al_2O_3-P	39.44	52.87	7.08	0.62	0.016
0.3Pd-Al_2O_3-P	39.82	51.68	7.84	0.66	0.017
0.5Pd-Al_2O_3-P	40.08	51.14	8.05	0.73	0.018

Table 5.4 Comparing the amount of Pd loading in the catalyst bulk and catalyst surface.

Catalysts	Amount of Pd in bulk catalyst measured by ICP technique (wt%)	Amount of Pd on catalyst surface measured by EDX technique (wt%)
0.05Pd-Al_2O_3-P	0.08	2.83
0.1Pd-Al_2O_3-P	0.13	2.99
0.3Pd-Al_2O_3-P	0.35	3.16
0.5Pd-Al_2O_3-P	0.55	3.5

The amount of Pd addition was compared to bulk catalysts measured by ICP and catalyst surface measured by EDX. The results in **Table 5.4** presented that Pd contents were located at the catalyst surface due to Pd doping had larger size than pore size of catalysts suggesting the amount of Pd obtained from EDX technique were greater than bulk catalysts measured by ICP technique.

5.1.4 N_2 physisorption

The textural properties such as surface area, pore volume and pore size of Al_2O_3, P-modified Al_2O_3 and Pd-modified Al_2O_3-P catalysts are summarized in **Table 5.5.**

Table 5.5 Textural properties of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

Catalysts	**Surface Area**[a] **(m^2/g)**	**Pore Volume**[b] **(cm^3/g)**	**Pore Size**[b] **(nm)**
γ-Al_2O_3	119	0.267	7.2
Al_2O_3-P	94	0.247	8.4
0.05Pd-Al_2O_3-P	82	0.214	8.5
0.1Pd-Al_2O_3-P	83	0.224	8.0
0.3Pd-Al_2O_3-P	85	0.216	8.5
0.5Pd-Al_2O_3-P	81	0.226	8.3

[a] determined from BET method
[b] determined from BJH adsorption method

According to results of N_2 physisorption presented in **Table 5.5**, BET surface area and pore volume were obviously decreased with loading of phosphorous. These results can be ascribed to blocking of pores by phosphorous species catalyst surface and inside channels. In addition, the Pd loading on catalysts slightly decreased catalyst surface and pore volume occurring Pd clogged up on surface and diffused in the support.

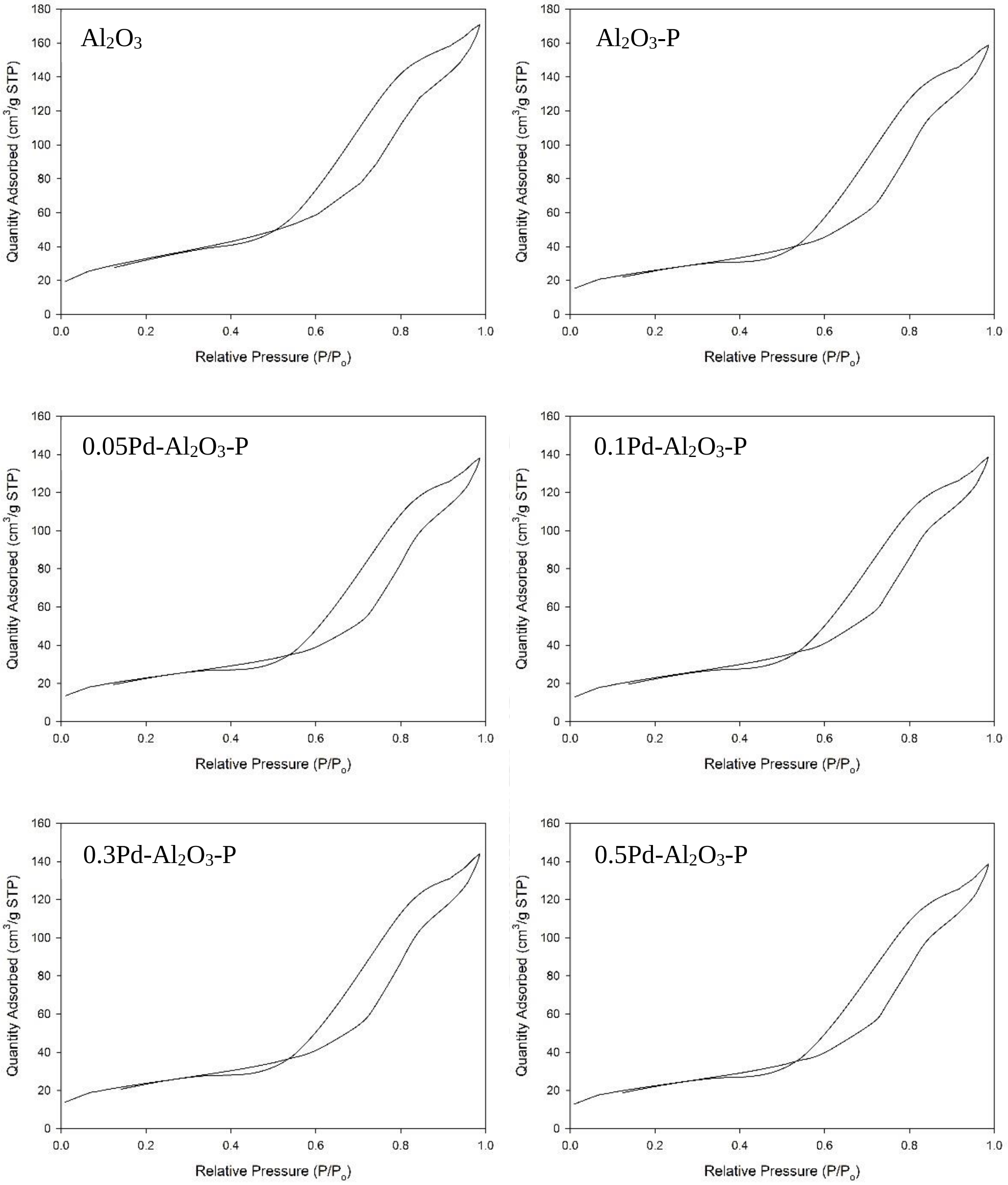


Figure 5.9 The nitrogen adsorption/desorption isotherms of studied catalysts.

The nitrogen adsorption/desorption of studied catalysts is shown in **Figure 5.9**. All samples displayed the hysteresis loop of type H1 occurring at high relative pressure ($P/P_0>0.6$) indicating that they are mesoporous structure corresponding to Type IV as described by IUPAC. The H1 hysteresis indicates larger mesopore and broad pore size distribution with uniform cylindrical shapes [44].

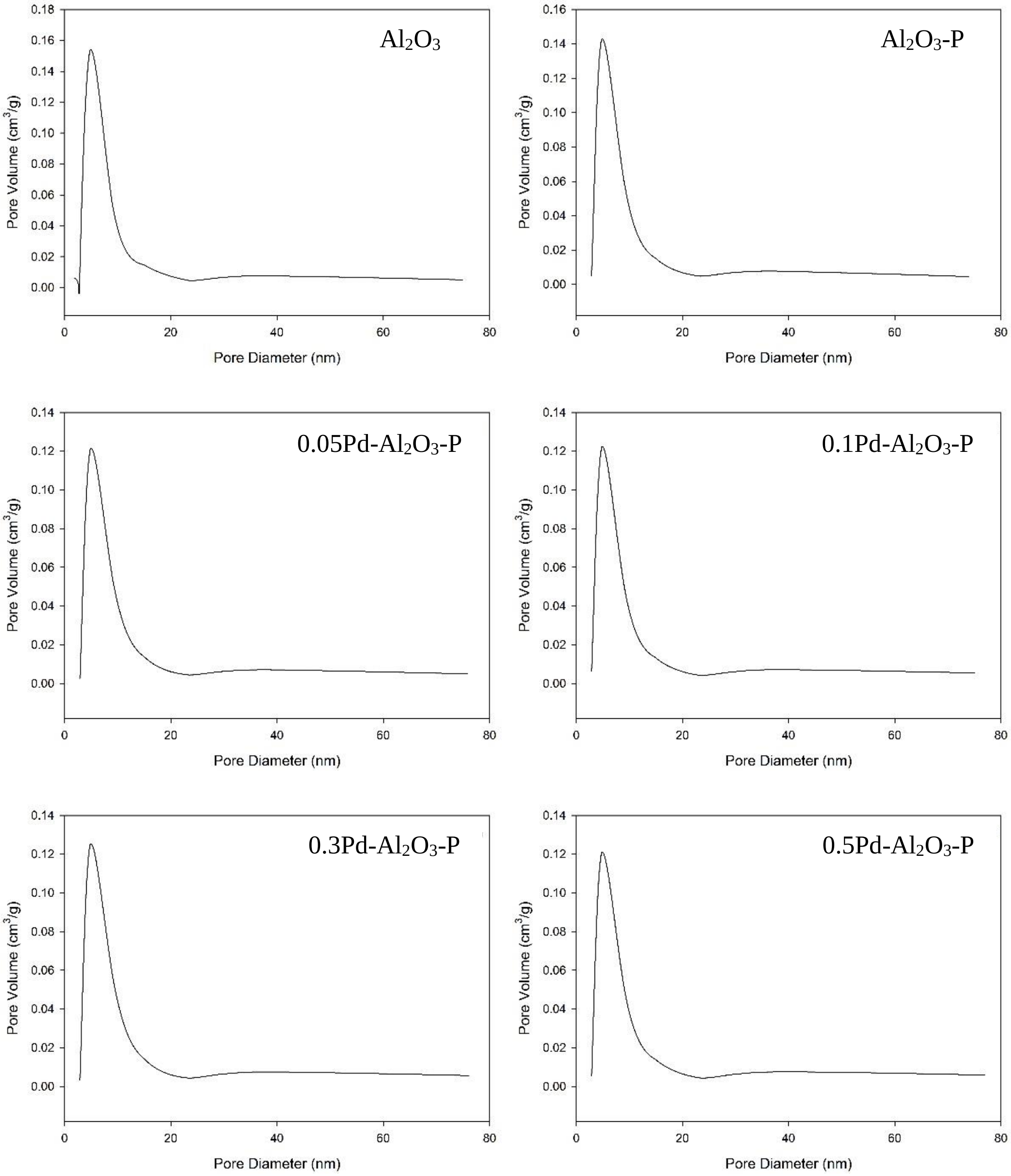


Figure 5.10 The pore size distributions of studied catalysts.

Pore size distribution was calculated by BJH method as shown in **Figure 5.10**. The samples of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts exhibited unimodal pore size distribution that pore diameter was in range of 7-9 nm indicating to mesopore structure related to nitrogen adsorption/desorption results as shown in **Figure 5.9**.

5.1.5 Ammonia temperature-programmed desorption (NH_3-TPD)

The acid properties of catalysts are essential to determine the catalytic activity and product distribution via ethanol dehydration reaction. In **Table 5.6**, the NH_3 temperature programmed desorption (NH_3-TPD) was performed to determine surface acidity of all catalysts.

Table 5.6 The surface acidity of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

Catalysts	Number of acid sites (μmol/g cat.)		
	Weak acid sites	Moderate to strong acid sites	Total acid site
γ-Al_2O_3	245	1042	1287
Al_2O_3-P	274	901	1175
0.05Pd-Al_2O_3-P	232	908	1140
0.1Pd-Al_2O_3-P	217	924	1141
0.3Pd-Al_2O_3-P	210	957	1167
0.5Pd-Al_2O_3-P	201	986	1187

From the results, there are two NH_3 desorption peaks for Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts. The peak at higher temperature above 250°C was due to desorption of ammonia chemisorbed at moderate to strong acid sites, whereas at lower temperature below 250°C was assigned to weak acid sites. The low temperature peak occurred due to the weak acid sites present as surface hydroxy groups and the high temperature peak occurred from structural acidity. The amount of acids sites was determined from NH_3-TPD curve by deconvolution according to the Gauss curve fitting method.

Compare with modified phosphorous and unmodified phosphorous catalysts, the phosphorous addition diminished moderate and strong acid sites to weak acid sites and also total acidity decreased. This is due to introduction of P resulted in modification of surface acidity likely to form P-O-Al.

In addition, increasing Pd loading on catalysts resulted in gradually increased moderate and strong acid sites related to reduction of weak acid sites. The moderate and strong acidity was in the order 0.5Pd-Al_2O_3-P>0.3Pd-Al_2O_3-P>0.1Pd-Al_2O_3-P>0.05Pd-Al_2O_3-P.

5.1.6 Reaction study

The Al_2O_3-P catalysts with different Pd loading of 0.05, 0.1, 0.3 and 0.5 wt% were determined to study the catalytic performance in ethanol dehydration reaction at various reaction temperatures of 200, 250, 300, 350, 400 ^oC at atmospheric pressure. In this reaction study, the catalytic performance terms including ethanol conversion, product selectivity and product yield are presented in **Figure 5.11** to **Figure 5.17**, respectively.

The ethanol conversion of the Al_2O_3-P catalysts with different Pd loading is illustrated in **Figure 5.11** as follows;

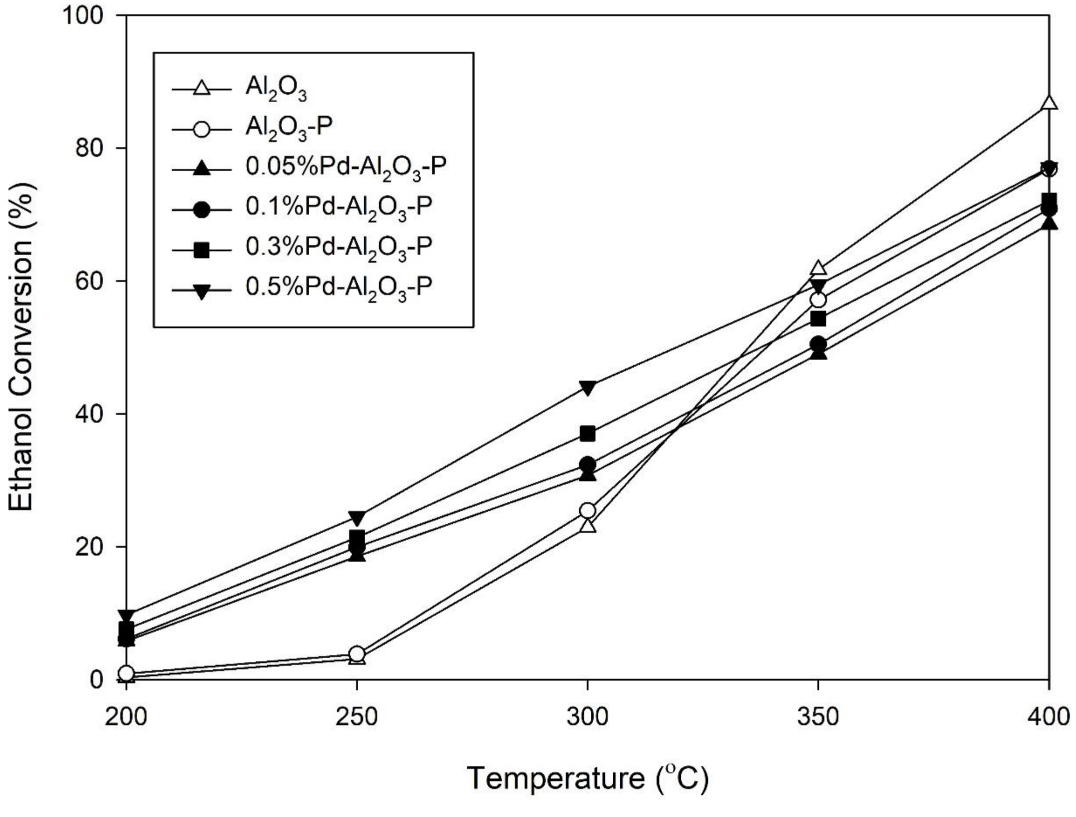


Figure 5.11 Ethanol conversion of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

All catalysts were investigated for ethanol dehydration at reaction temperature from 200 to 400ºC in order to determine influence of Pd loading on Al_2O_3-P catalysts. For all studied catalysts, the ethanol conversion of catalysts increased with raising the reaction temperature.

The results of P-modified catalysts and unmodified catalysts showed that the modified catalysts with P in temperature 200-300°C have slightly increased ethanol conversion compared with unmodified catalysts. After increasing temperature above 300°C, the modified catalysts with P slightly decreased ethanol conversion less than unmodified catalysts. The γ-Al_2O_3 catalysts exhibited the highest ethanol conversion reaching 86.6% at temperature of 400 °C.

In addition, the results of Pd doping on Al_2O_3-P catalysts described in temperature 200°C to 300°C obviously increased ethanol conversion due to Pd precursor likely acted as chemical promoter of catalyst resulting in increased ethanol conversion at low temperature. At temperature over 300°C, it tended to decrease ethanol conversion compared with unmodified catalysts and Pd modification did not affect ethanol conversion at high temperature. The ethanol conversion results can be ordered as follows: 0.5Pd-Al_2O_3-P>0.3Pd-Al_2O_3-P>0.1Pd-Al_2O_3-P>0.05Pd-Al_2O_3-P.

There is summary for the results that Al_2O_3 catalyst presented the highest ethanol conversion at 400°C and 0.5Pd-Al_2O_3-P catalyst exhibited the highest conversion among Pd modified catalysts. The highest conversion of 0.5Pd/Al_2O_3-P catalyst reached 77.0% at temperature of 400°C.

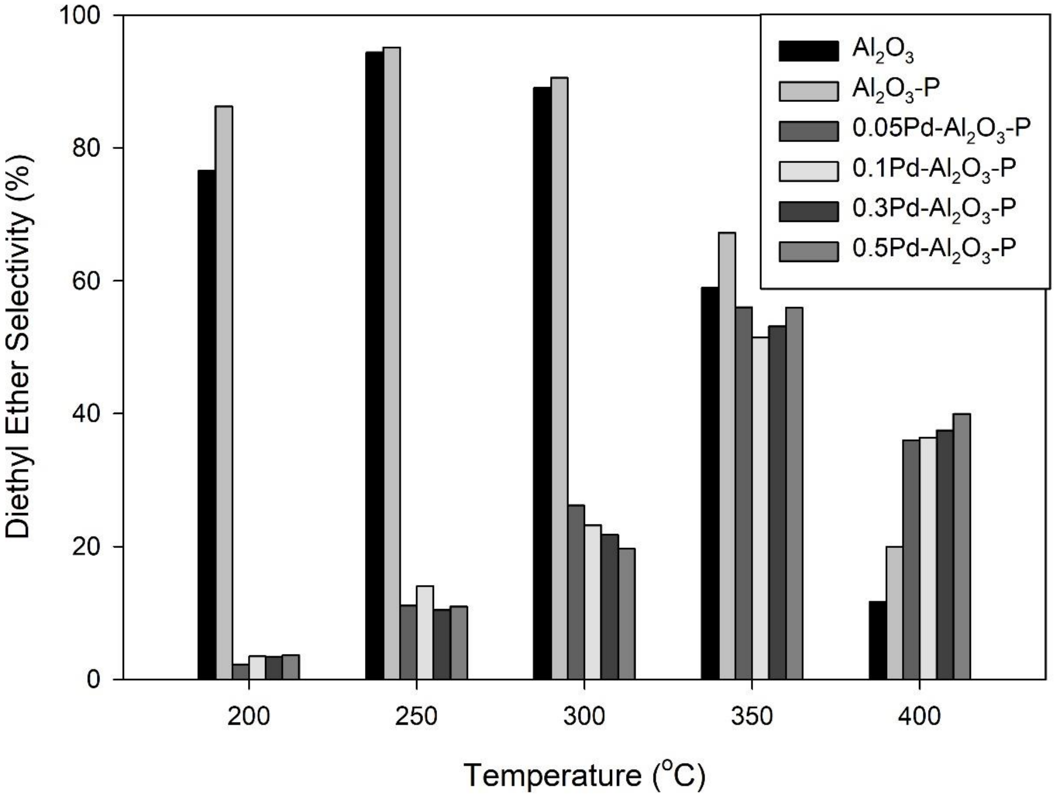


Figure 5.12 Diethyl ether selectivity of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

From **Figure 5.12**, it shows diethyl ether selectivity of all studied catalysts. The diethyl ether selectivity results of P-modified catalysts and Al_2O_3 catalyst increased at temperature from 200°C to 250°C and decreased with raising the reaction temperature above 250°C. The addition of phosphorous in catalysts tended to essentially enhance diethyl ether selectivity, which required only weak acid sites [43].

In addition, the diethyl ether selectivity of Pd modified catalysts enhanced with raising the reaction temperature. All Pd loading in Al_2O_3-P catalysts performed the highest diethyl ether selectivity at temperature of 350°C. On the other hands, the diethyl ether selectivity decreased due to its decompose to ethylene at high temperature of 400°C.

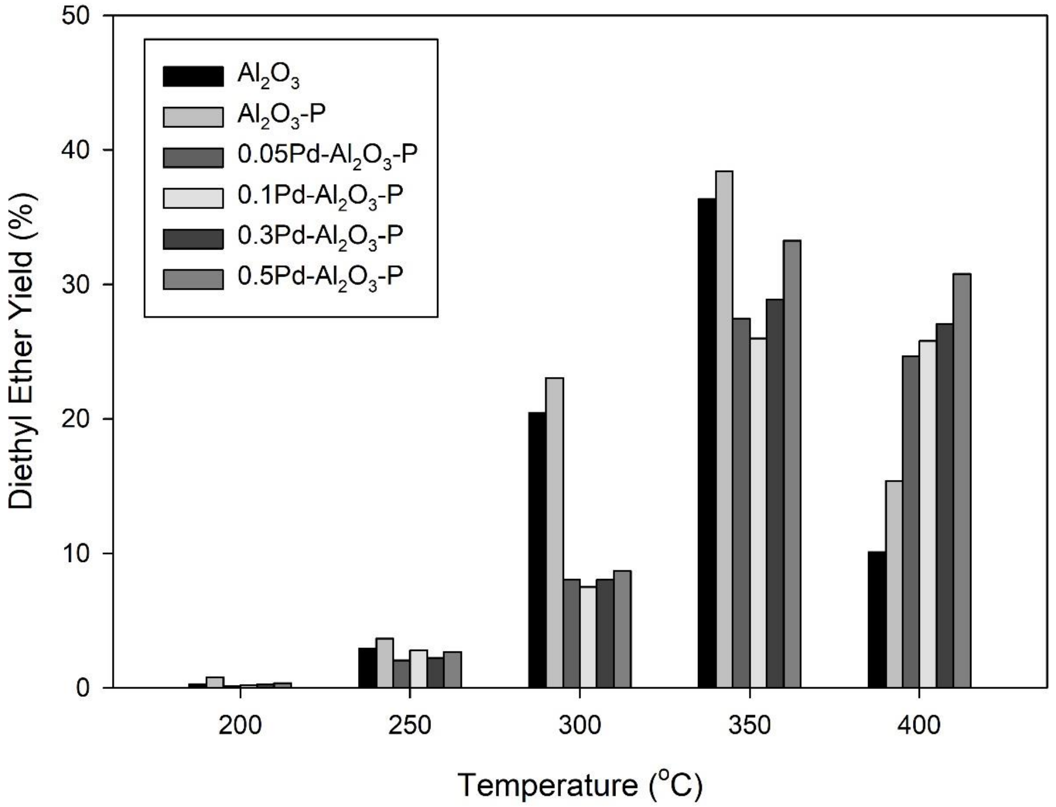


Figure 5.13 Diethyl ether yield of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

Figure 5.13 shows the diethyl ether yield of P-modified Al_2O_3 and Al_2O_3 catalysts. It appeared that at temperature 350°C, it had the highest diethyl ether yield. Although Al_2O_3 and P-modified Al_2O_3 exhibited high diethyl ether selectivity at low temperature 200°C to 300°C as seen in **Figure 5.12**, ethanol conversion at these temperatures range was low resulting in less diethyl ether yield at low temperature 200°C to 300°C. The P-modified catalyst exhibited the highest diethyl ether yield of 38.41% at temperature of 350°C.

Moreover, the diethyl ether yield of Pd modified catalysts escalated with raising the reaction temperature. All Pd loading in Al_2O_3-P catalysts exhibited the highest diethyl ether selectivity at temperature of 350°C. At high temperature 400°C, the diethyl ether selectivity decreased due to its decompose to ethylene at high temperature.

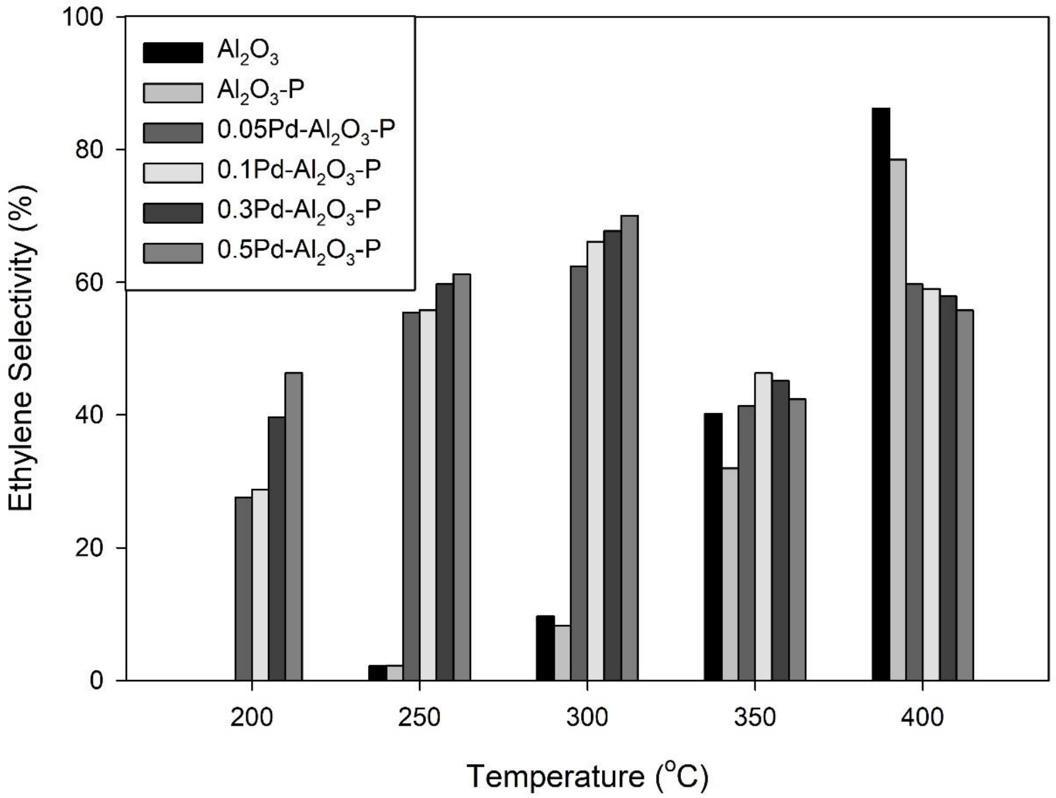


Figure 5.14 Ethylene Selectivity of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

From **Figure 5.14**, it shows ethylene selectivity among all studied catalysts. For ethylene selectivity results, the P-modified catalysts and Al_2O_3 catalyst increased with increasing temperature. The Al_2O_3 catalyst exhibited the highest ethylene selectivity reaching 86.19% at temperature of 400°C due to the ethylene formation was favored by moderate and strong acid sites relate to surface acidity in **Table 5.6** [43].

In addition, Pd modified catalysts remarkably escalated ethylene selectivity with raising the reaction temperature in temperature range between 200°C to 300°C and decreased in temperature of 350°C due to the optimization temperature was produced for diethyl ether as seen in **Figure 5.13**. The increased ethylene selectivity at low temperature 200°C to 300°C was caused by catalytic activity of Pd as chemical promoter, that might completely enhance reaction of ethanol to ethylene. It was related to the ethanol conversion of Pd modified catalysts that increased at low temperature as shown in **Figure 5.11**.

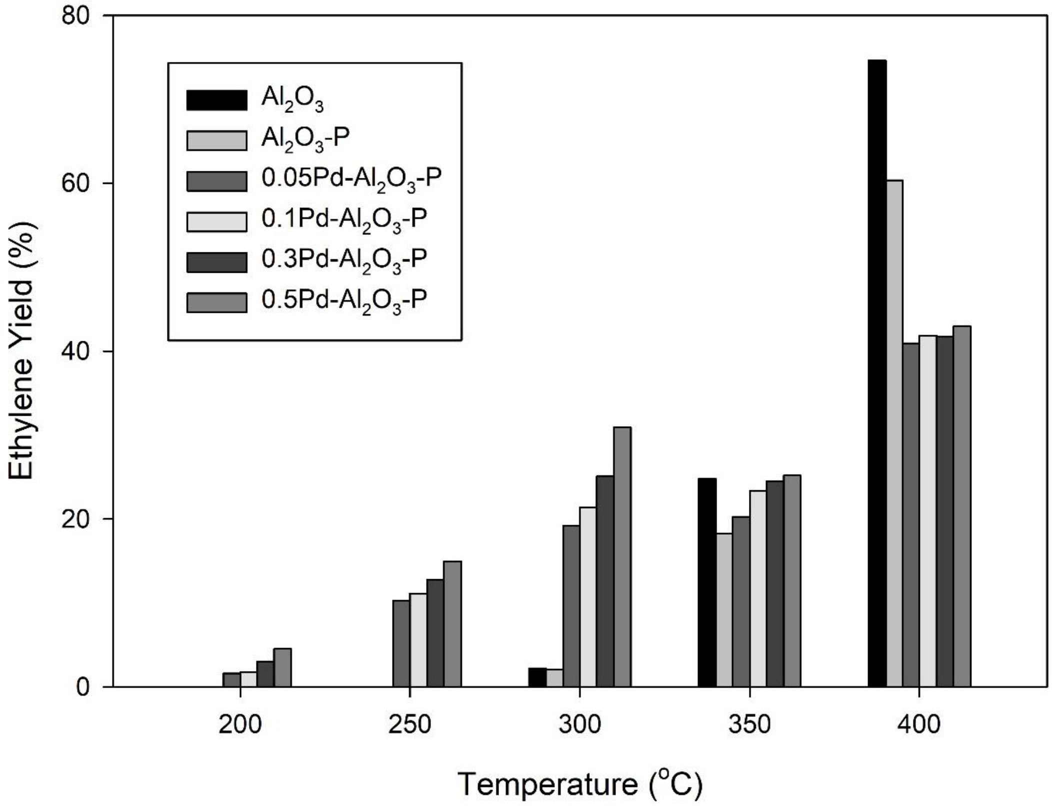


Figure 5. 15 Ethylene yield of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

From the calculation of ethylene yield of P-modified Al_2O_3 and Al_2O_3 catalysts, the results likewise tended to ethylene selectivity that increased with increasing temperature as seen in **Figure 5.14**. The Al_2O_3 catalyst exhibited the highest ethylene yield reaching 74.62% at temperature of 400°C.

The effect of Pd modified catalysts was found to have similar ethylene selectivity as well. At temperature 400°C, the Pd modified catalysts exhibited the highest ethylene yield over 0.5Pd-Al_2O_3-P at 42.96%.

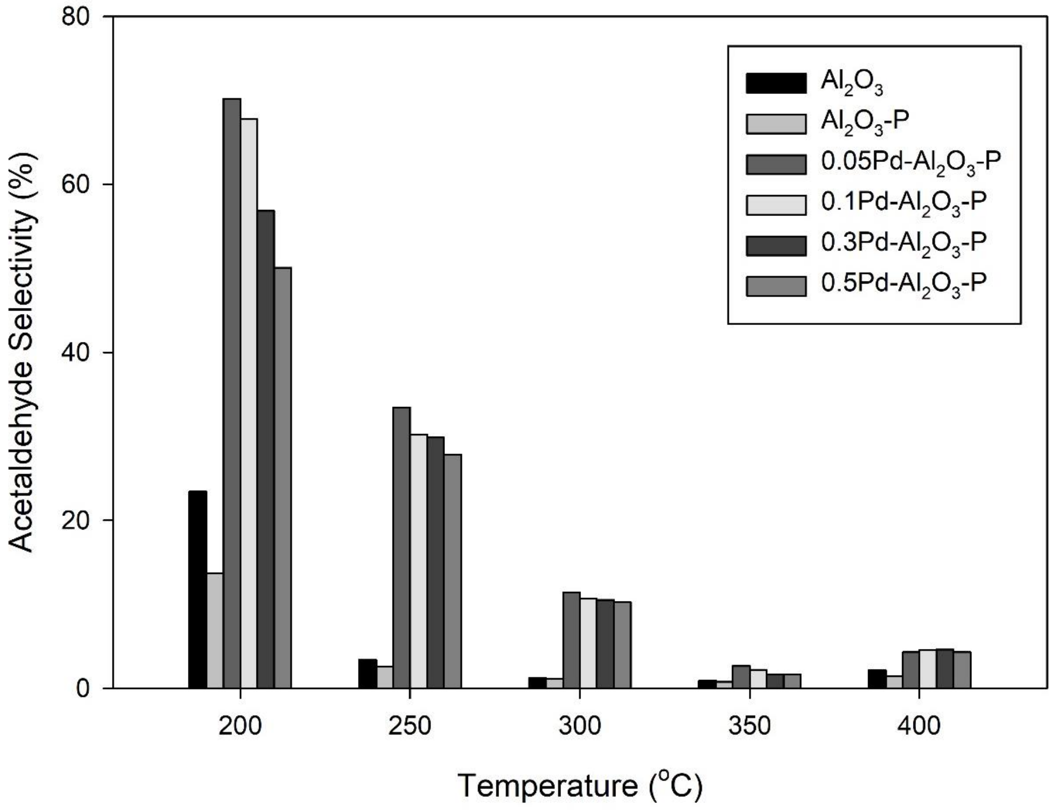


Figure 5.16 Acetaldehyde selectivity of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

Figure 5.16 shows acetaldehyde selectivity among all studied catalysts. The trend of acetaldehyde selectivity of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts were similar where it decreased with increasing temperature. The presence of Pd on catalysts resulted in increased acetaldehyde selectivity at low temperature ranging from 200-250°C by dehydrogenation reaction. The acetaldehyde was main product at low temperature of 200°C.

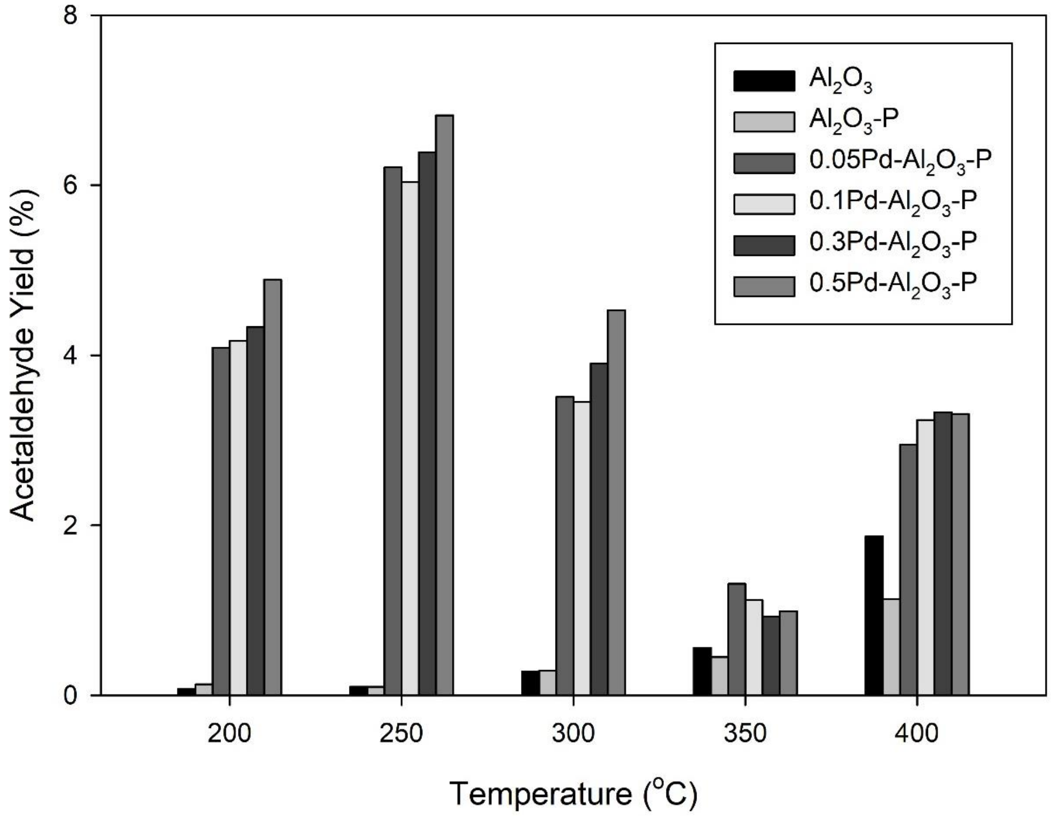


Figure 5.17 Acetaldehyde yield of Al_2O_3, P-modified Al_2O_3 and Pd modified Al_2O_3-P catalysts.

From acetaldehyde yield results, the product yields were calculated from the product of ethanol conversion and acetaldehyde selectivity. For Al_2O_3 catalysts, the acetaldehyde yield increased with increasing temperature. For P-modified Al_2O_3 catalysts, the trend of acetaldehyde yield was similar to Al_2O_3 catalysts. For Pd modified Al_2O_3-P catalysts, Pd modification enhanced acetaldehyde yield at low temperature 200°C to 250°C. The highest acetaldehyde yield occurred by 0.5Pd-Al_2O_3-P catalyst reaching 6.82% at temperature of 250°C.

5.1.7 Thermal gravimetric analysis (TGA)

The Al_2O_3, P-modified Al_2O_3 and Pd-modified Al_2O_3-P catalysts were determined the decomposition of catalysts by increasing the temperature of the samples under air atmosphere. The fresh and spent catalysts after ethanol dehydration examination were tested for the coke deposition as shown in **Figure 5.18** and **Figure 5.19** as follows;

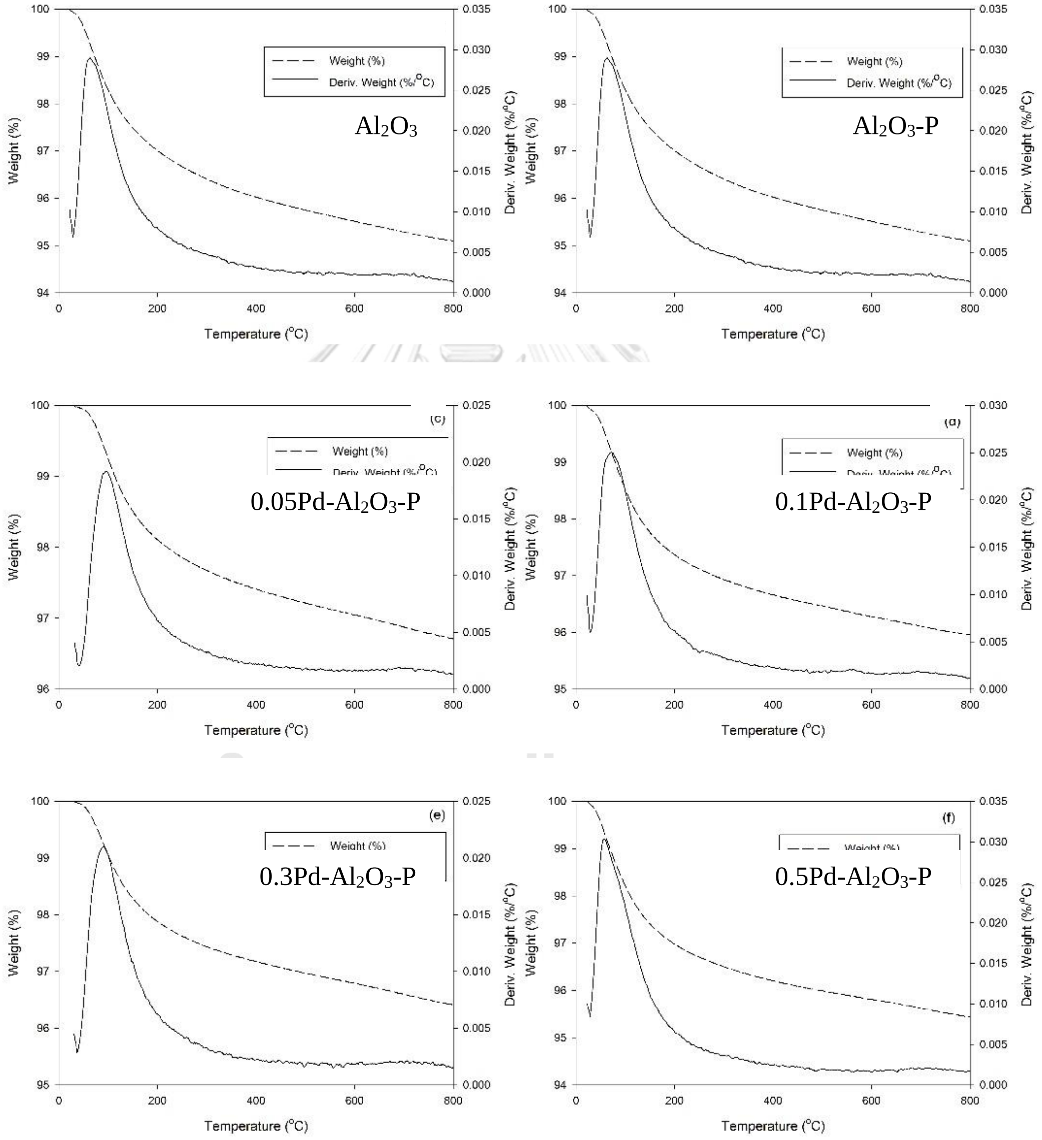


Figure 5.18 TGA/DTA analysis of the fresh catalysts.

The decomposition of all fresh catalysts was depicted in **Figure 5.18**. The studied results were detected similar trend of TGA profiles. The weight loss (%) indicated the divided two stages of losing weight stages of at temperature below 200°C and temperature above 200°C. At the temperature lower than 200°C, it was represented to the removal of physically adsorbed water in the catalyst. While at the temperature above 200°C, it was attributed to decomposition of volatile species in the catalyst.

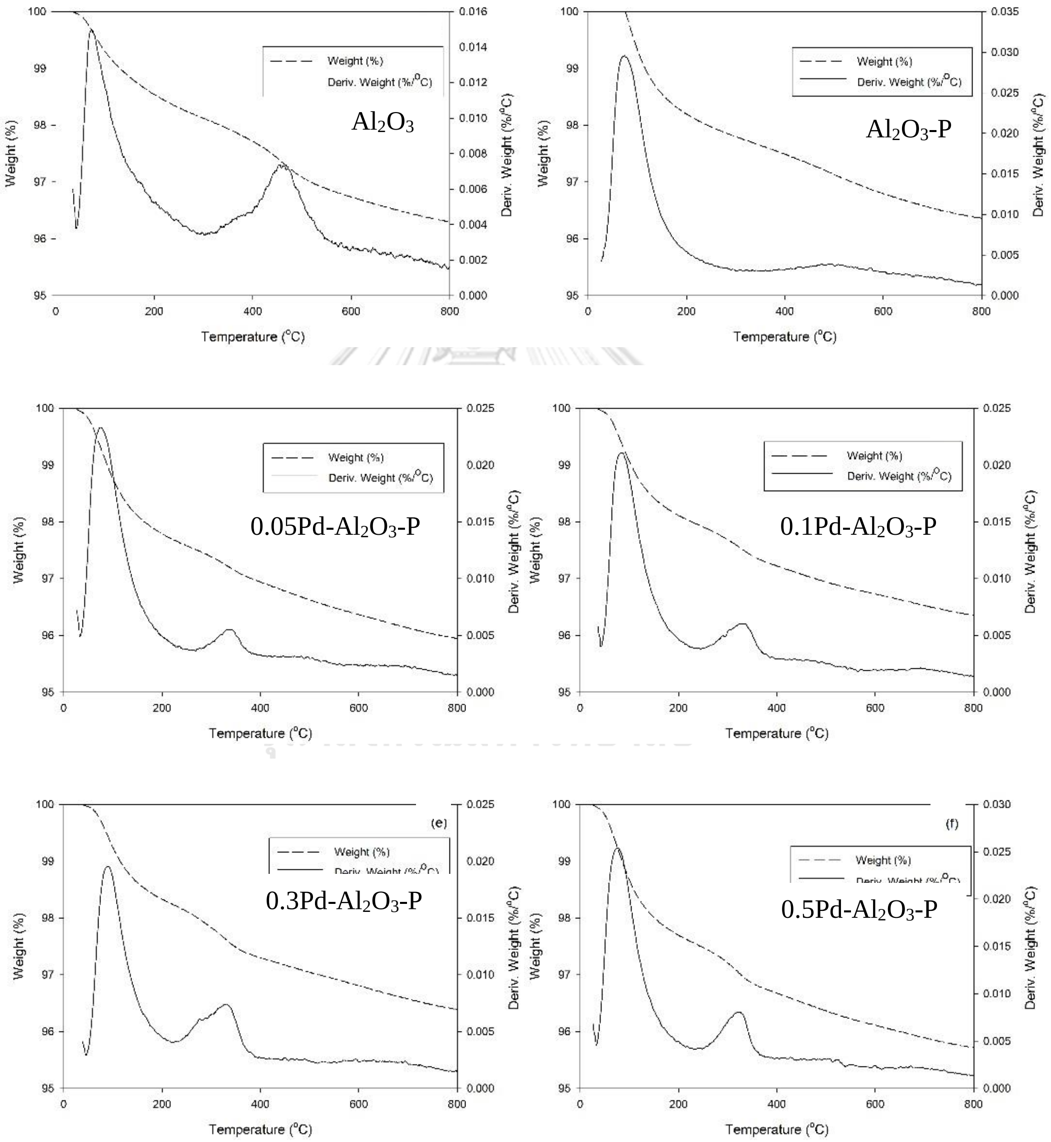


Figure 5.19 TGA/DTA analysis of the spent catalysts.

The examined spent catalysts results were performed as shown in **Figure 5.19**, which was used to measure the amount of coke deposited by thermal decomposition method. The thermal decomposition of spent catalysts was observed in the temperature above 200°C, which indicated the coke formation on the catalyst surface, that could be eliminated in this temperature range. On the other words, the spent catalysts were regenerated with burning of coke deposited in atmospheric air at temperature range higher than 200°C. The evaluated amount of coke formation on the catalysts surface was displayed in **Table 5.7** as follows;

Table 5.7 The amount of coke formation in the spent catalysts.

Catalysts	**Temperature (°C)**	**Weight (%)**	**The amount of coke formation (%wt)**
γ-Al_2O_3	200	98.54	2.24
	800	96.3	
Al_2O_3-P	200	98.2	1.84
	800	96.36	
0.05Pd-Al_2O_3-P	200	97.79	1.84
	800	95.95	
0.1Pd-Al_2O_3-P	200	98.11	1.75
	800	96.36	
0.3Pd-Al_2O_3-P	200	98.33	1.94
	800	96.39	
0.5Pd-Al_2O_3-P	200	97.70	1.98
	900	95.72	

Based on the amount of coke deposition in **Table 5.7**, it noticed that the γ-Al_2O_3 was observed high quantitative of coke formation due to large quantity of strong acid sites corresponding to acidity techniques by NH_3-TPD results. Nevertheless, the phosphorous addition on catalyst significantly decrease the amount of coke deposition on catalyst surface. It can be attributed to the reduction of strong acid sites on catalyst, which possibly improved catalyst stability. In addition, the modification with Pd promoter was slightly different on amount of coke formation.

Part II: The comparison of catalytic activities and catalyst characteristic between the chosen Pd modified over γ-Al_2O_3 catalyst and the chosen Pd modified over Al_2O_3-P catalyst.

From the results in **Part I**, the studies of Pd modified on Al_2O_3-P catalysts enhanced catalytic activity at low temperature. The 0.5Pd-Al_2O_3-P catalyst exhibited the highest ethanol conversion and ethylene selectivity among all of Pd modified catalysts at temperature ranging of 200°C to 300°C. The question is when P is absent what the differences when Pd is solely doped on Al_2O_3. Thus, the experiment in **Part II** was conducted. Consequently, the characteristic and catalytic activity were compared between 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts that described in the **Section 5.2.1** to **Section 5.2.5** as following;

5.2.1 Inductively coupled plasma (ICP)

The amount of Pd composition contained in the catalysts bulk was measured by inductively coupled plasma (ICP) as shown in **Table 5.8**. The sample results indicated amount of Pd composition in catalyst bulk, which nearly examined ICP results in **Part I**.

Table 5 8 The amount of Pd composed in the catalyst bulk

Catalysts	Amount of Pd in catalyst bulk (wt%)
0.5Pd-Al_2O_3	0.54
0.5Pd-Al_2O_3-P	0.55

5.2.2 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts are depicted in **Figure 5.20**. The XRD results revealed the similar XRD patterns as seen in the results from **Part I.** The characteristic sharp peaks of gamma alumina catalysts (γ-Al_2O_3) were indicated at 2θ of 46º and 67º [38]. In addition, Pd loading on catalysts cannot be noticed in XRD results because of its forms in well dispersed form on catalysts.

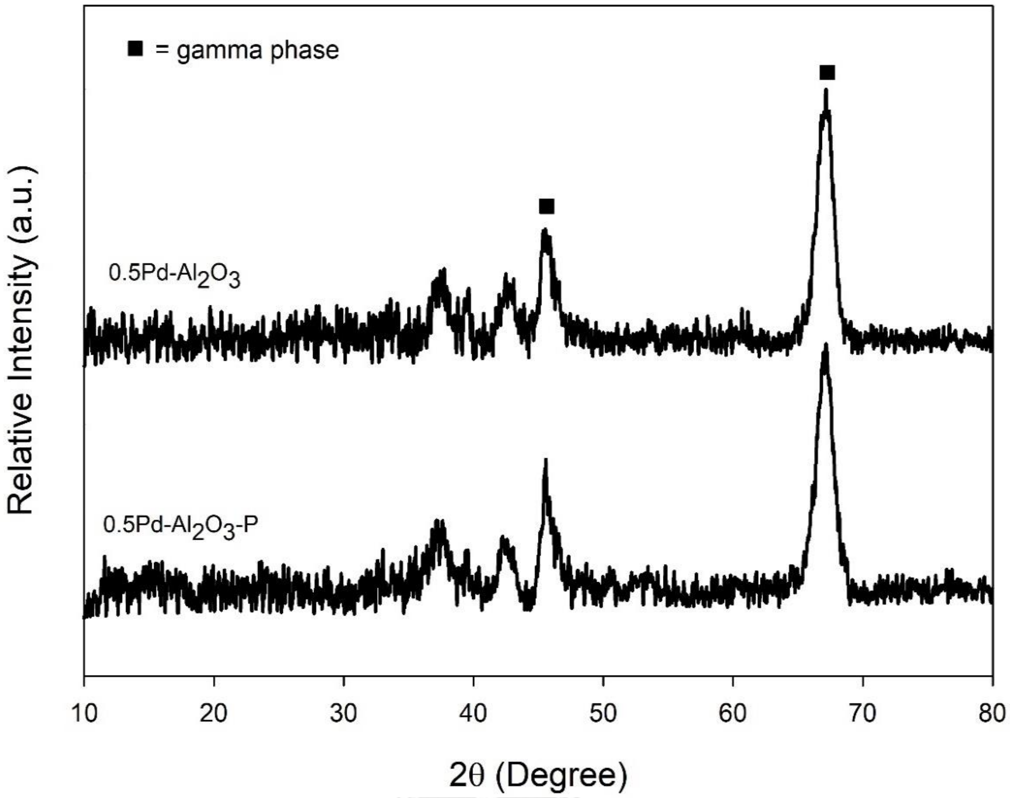


Figure 5.20 XRD patterns of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

5.2.3 Ammonia temperature-programmed desorption (NH_3-TPD)

The surface acidity and strength of acid sites of studied catalysts are the crucial factor for catalytic activity of ethanol dehydration. The NH_3-TPD profiles were calculated and summarized surface acidity for both Pd modified Al_2O_3 and Pd modified Al_2O_3-P catalysts in **Table 5.9**.

Table 5.9 The surface acidity of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

Catalysts	**Number of acid sites (μmol/g cat.)**		
	Weak acid sites	**Moderate to strong acid sites**	**Total acid sites**
0.5Pd-Al_2O_3	140	1107	1247
0.5Pd-Al_2O_3-P	201	986	1187

The NH_3-TPD profiles depicted two different desorption peak of acid sites. The desorption peak at low temperature below 250°C was attributed to weak acid sites and high temperature over 250°C was attributed to strong acid sites. All these profiles were deconvoluted by Gauss curve fitting method for numerical analysis. The NH_3-TPD results of Pd modification on catalysts revealed that Pd addition on Al_2O_3 catalyst increased moderate to strong acid sites. According to the NH_3-TPD results in **Part I**, phosphorous modification improved weak acid sites and reduced moderate to strong acid sites.

5.2.4 Reaction study

In this reaction study, the 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts were investigated the ethanol conversion, product selectivity and product yield. The catalyst performance was tested in reaction temperature of 200, 250, 300, 350, 400°C as shown in **Figure 5.21** to **Figure 5.27**.

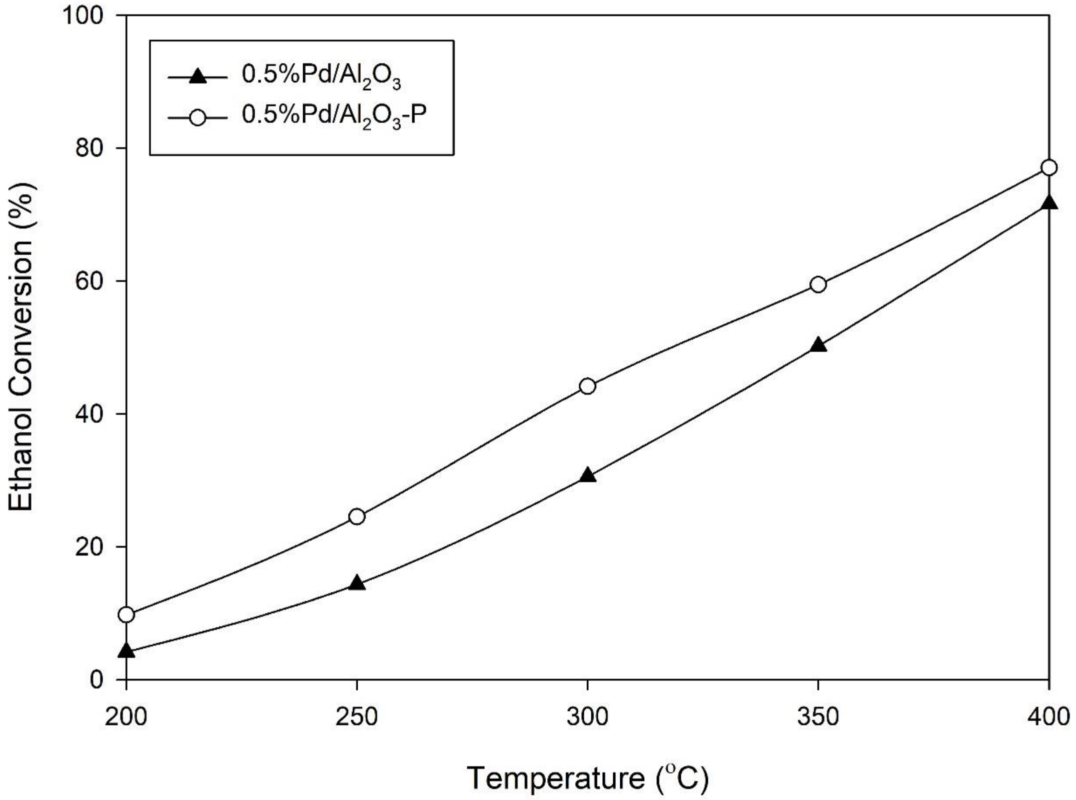


Figure 5.21 Ethanol conversion of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts

From the test performance in **Figure 5.21**, it presented ethanol conversion at reaction temperature from 200 to 400ºC. The ethanol conversion of both 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts obviously increased with increasing the reaction temperature. It was found that 0.5Pd-Al_2O_3-P catalyst exhibited higher ethanol conversion than 0.5Pd-Al_2O_3 catalyst. It ascribed to the large amount of weak acid sites in surface acidity as shown in **Table 5.9**. The 0.5Pd-Al_2O_3-P catalyst exhibited the highest ethanol conversion reaching 77.0% at temperature of 400ºC.

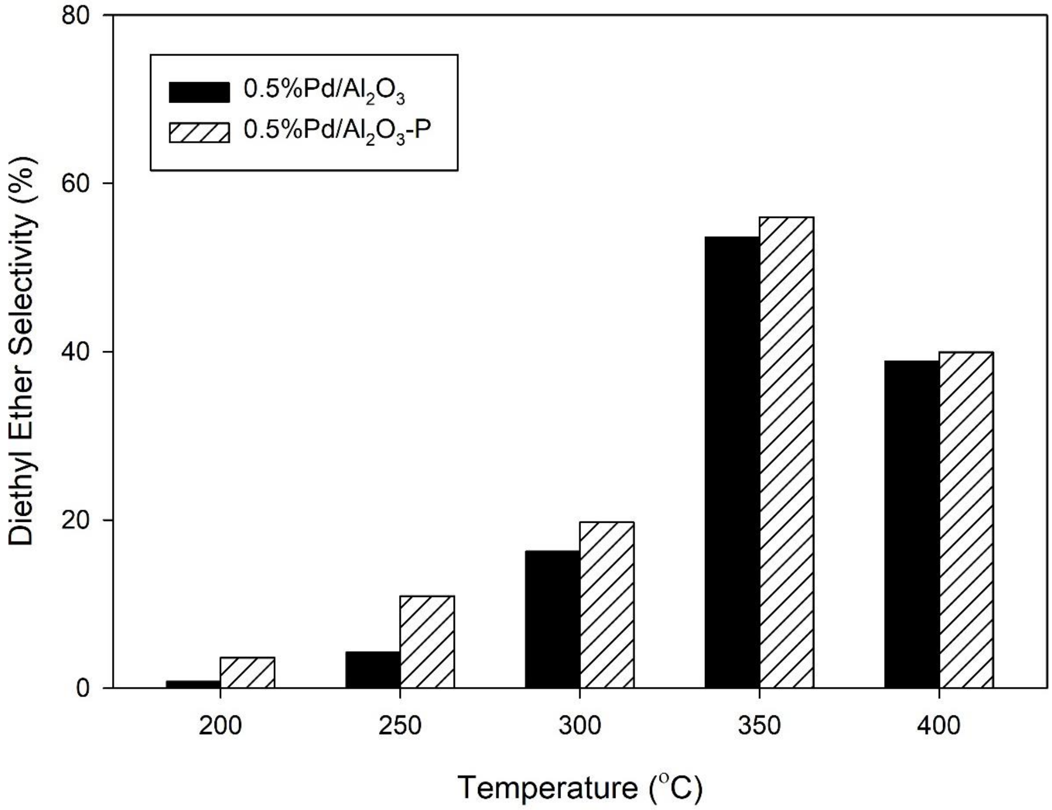


Figure 5.22 Diethyl ether selectivity of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

Figure 5.22 represented diethyl ether selectivity of both studied catalysts. The diethyl ether selectivity of Pd-modified catalysts enhanced with increasing the reaction temperature. At temperature 350°C, both of Pd loading on studied catalysts exhibited the highest diethyl ether selectivity and decreased at high temperature of 400°C caused by its decomposition to ethylene. The 0.5Pd-Al_2O_3-P catalyst exhibited diethyl ether selectivity higher than 0.5Pd-Al_2O_3 catalyst, which the presence of phosphorous enhanced more quantity of weak acid sites [43].

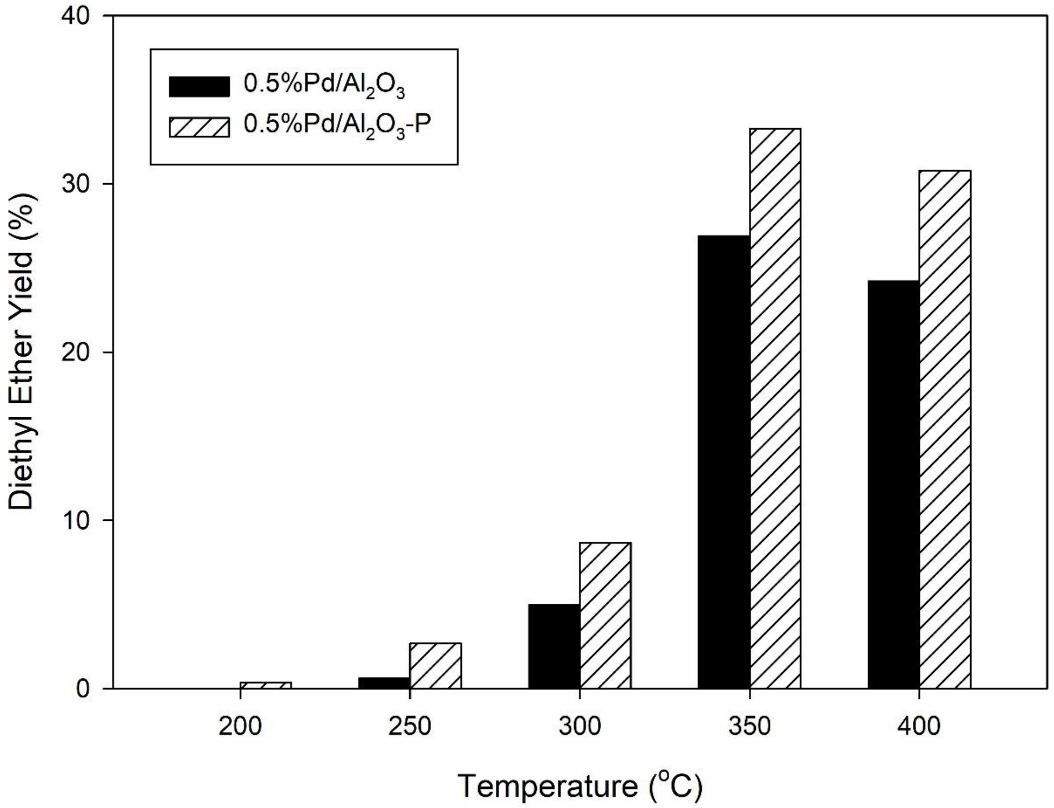


Figure 5.23 Diethyl ether yield of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

Figure 5.23 shows the diethyl ether yield for both 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts. It can be observed that the diethyl ether yield increased with raising the reaction temperature for both catalysts. However, the 0.5Pd-Al_2O_3-P catalyst presented slightly higher diethyl ether yield than the unmodified P catalyst. The highest diethyl ether yield of 33.3% can be obtained from 0.5Pd-Al_2O_3-P catalyst at temperature of 350°C. This can be attributed to higher weak acid sites in the P modification catalysts.

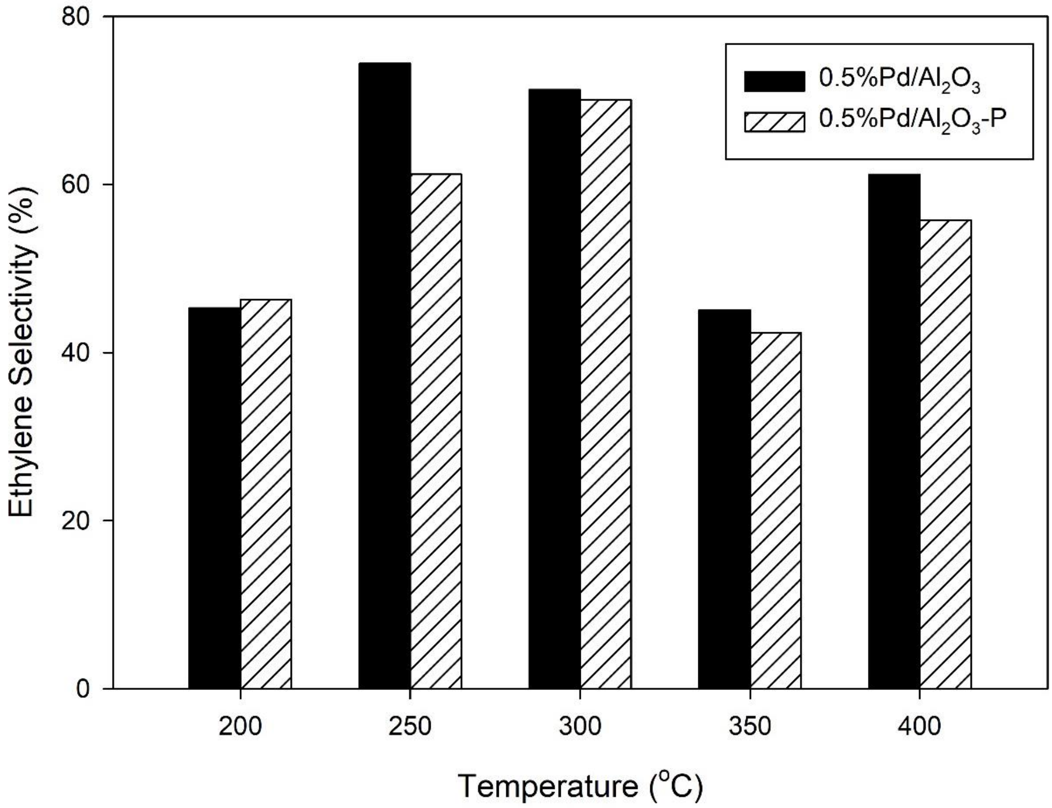


Figure 5.24 Ethylene Selectivity of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

The ethylene selectivity of studied catalysts is illustrated in **Figure 5.24**. At low temperature, both of the Pd-modified catalysts increased with raising the reaction temperature. For 0.5Pd-Al_2O_3 catalyst, it remarkably exhibited the highest ethylene selectivity reaching 74.36% at temperature of 250° corresponding to high amount of moderate to strong acid sites favored to ethylene formation. In addition, phosphorous modification on catalyst played in role of reaction pathway into the diethyl ether caused by weak acid sites related to surface acidity in **Table 5.9** [43].

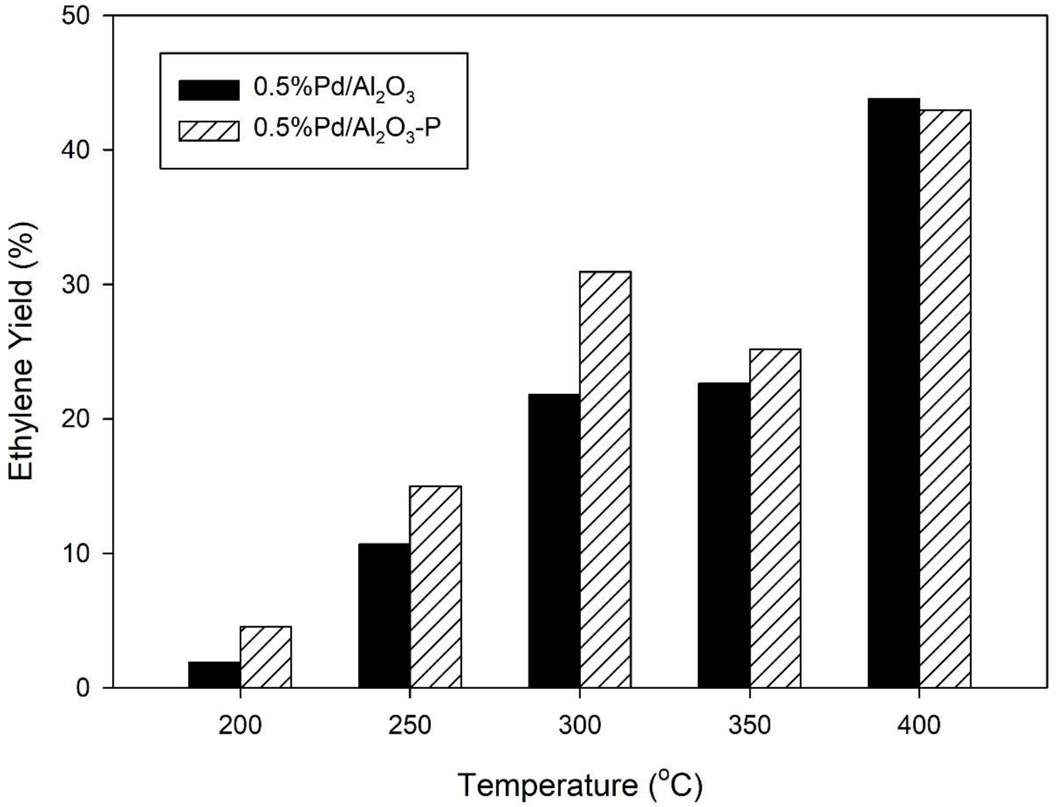


Figure 5.25 Ethylene yield of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

The ethylene yield was calculated by ethanol conversion and ethylene selectivity, which is illustrated in **Figure 5.25**. Both 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts presented similar trend of ethylene yield. The 0.5Pd-Al_2O_3 catalyst exhibited the highest ethylene yield reaching 43.8% at temperature of 400°. Consequently, the Pd addition without phosphorous modification catalyst was suitable to produce ethylene at high temperature.

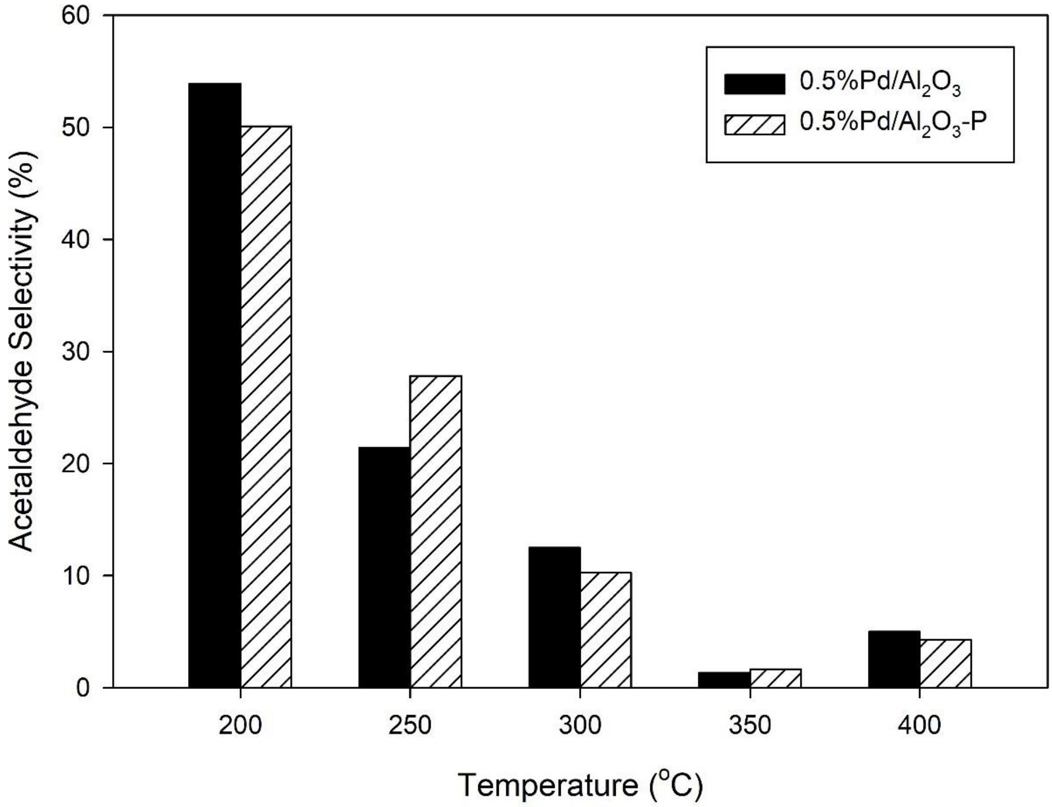


Figure 5.26 Acetaldehyde selectivity of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

For the side reaction of ethanol dehydration, acetaldehyde selectivity of studied catalysts is shown in **Figure 5.26**. Both of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts had similar trend of acetaldehyde selectivity, which decreased with increasing temperature. At low temperature, the acetaldehyde selectivity was observed due to the presence of Pd on catalysts enhanced the dehydrogenation reaction. As the results, acetaldehyde was a major product at low temperature ca. 200°C.

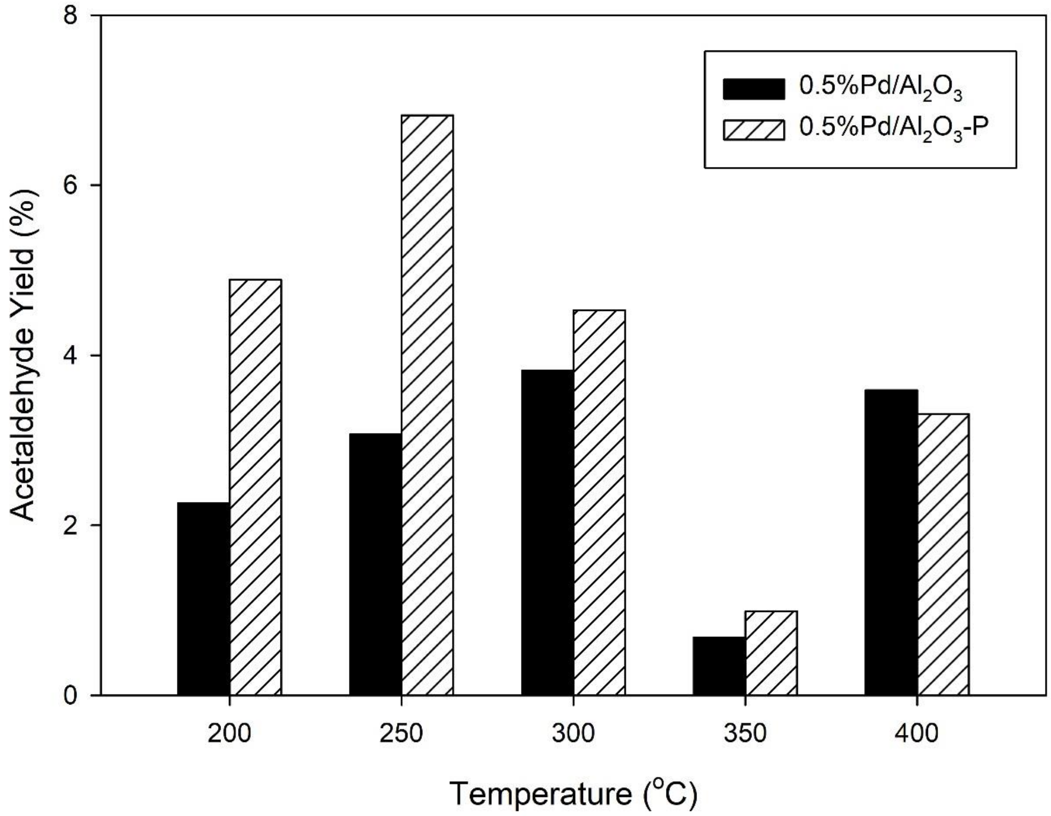


Figure 5.27 Acetaldehyde yield of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts.

The product yields were calculated from the product of ethanol conversion and acetaldehyde selectivity as shown in **Figure 5.27**. The acetaldehyde yield of 0.5Pd-Al_2O_3 catalyst was almost constant at low temperature around 200°C to 300°C and decreased at temperature of 350°C as similar to 0.5Pd-Al_2O_3-P catalyst. The highest acetaldehyde yield was observed by 0.5Pd-Al_2O_3-P catalyst reaching 6.82% at temperature of 250°C, which compared to acetaldehyde yield of 0.5Pd-Al_2O_3 catalyst.

5.2.5 Thermal gravimetric analysis (TGA)

The coke decomposition of 0.5Pd-Al_2O_3 and 0.5Pd-Al_2O_3-P catalysts was investigated by thermal gravimetric analysis. The fresh and spent catalysts were tested for the coke deposition in **Figure 5.28** and **Figure 5.29**.

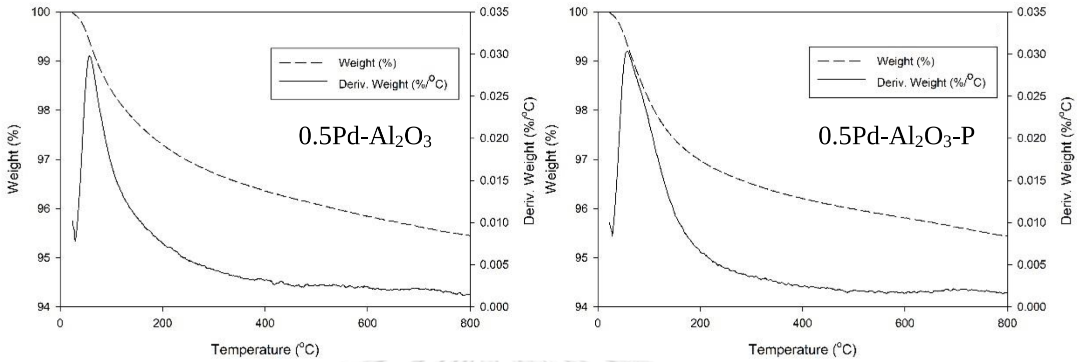


Figure 5.28 TGA/DTA analysis of the fresh catalysts.

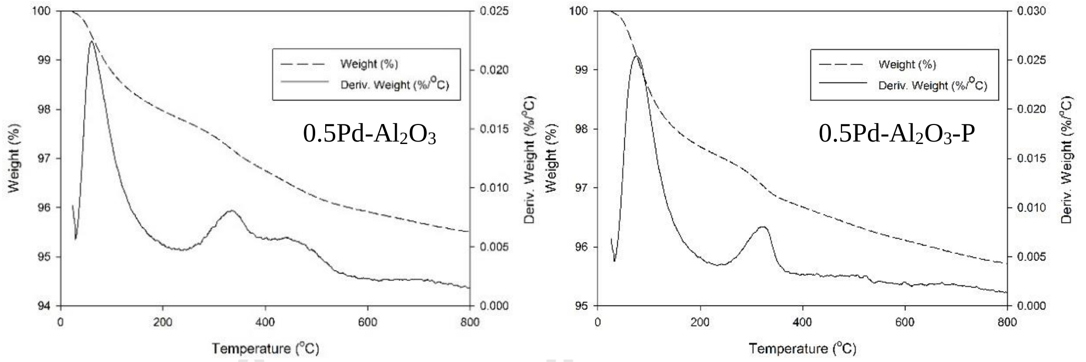


Figure 5.29 TGA/DTA analysis of the spent catalysts.

From the TGA profiles showed similar trend of all catalyst results. The weight loss below 200°C was attributed to the moisture elimination. The weight loss over 200°C was attributed to burning of coke deposition on the catalyst.

Table 5.10 The amount of coke formation in the spent catalysts.

Catalysts	**Temperature (°C)**	**Weight (%)**	**The amount of coke formation (%)**
0.5Pd-Al_2O_3	200	97.97	2.47
	800	95.5	
0.5Pd-Al_2O_3-P	200	97.70	1.98
	900	95.72	

The amount of coke deposition on studied catalysts was evaluated and shown in **Table 5.10**. It noticed that the 0.5Pd-Al_2O_3 catalyst exhibited high amount of coke deposition with 2.47% due to large quantity of strong acid sites corresponding to acidity as determined by NH_3-TPD results as mentioned **Table 5.9**. Significantly, the phosphorous modification reduced the amount of coke deposition on catalyst surface. It was caused by reduction of strong acid sites and increase of weak acid sites on catalyst with phosphorous modification, then improved stability of catalyst as well.

From the results of **Part I** and **Part II**, the catalyst performance can be concluded for better understanding the effect of phosphorous and palladium modification on alumina catalysts.

- Phosphorous modification on catalysts could essentially enhance diethyl ether selectivity because phosphorous improved weak acid sites on surface acidity. [42] [43] The weak acid sites was necessary for diethyl ether product. The P-modified catalyst exhibited the highest diethyl ether yield of 38.41% at temperature of 350°C.

- Pd modification on Al_2O_3-P catalysts affected ethylene selectivity that noticeably escalated with raising the reaction temperature in temperature range 200°C to 300°C. The increase of ethylene selectivity at low temperature 200°C to 300°C was caused by high amount of moderate to strong acid sites that favored to ethylene formation. However, the side reaction as acetaldehyde occurred at low temperature of 200°C to 300°C due to the presence of Pd on catalysts as well.

- Pd modification on Al_2O_3 catalysts were exhibited ethylene selectivity better than Pd modification on Al_2O_3-P corresponding to higher amount of moderate to strong acid sites. The highest ethylene selectivity of Pd modification on Al_2O_3 catalysts reaching 74.36% at temperature of 250°. Nevertheless, the acetaldehyde selectivity was detected at low temperature of 200°C to 300°C as similar to Pd modification on Al_2O_3-P catalysts.

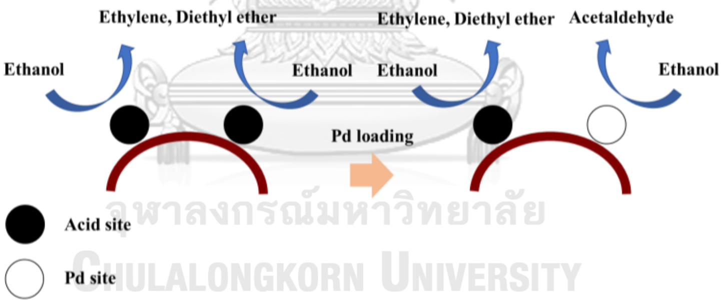
All results obtained can be summarized the characteristics and catalyst performance of Al_2O_3-P, Pd-Al_2O_3-P and Pd-Al_2O_3 catalysts as shown in **Table 5.11**

Table 5.11 The characteristics and catalyst performance of Al_2O_3-P, Pd-Al_2O_3-P and Pd-Al_2O_3 catalysts compared with γ-Al_2O_3 catalyst.

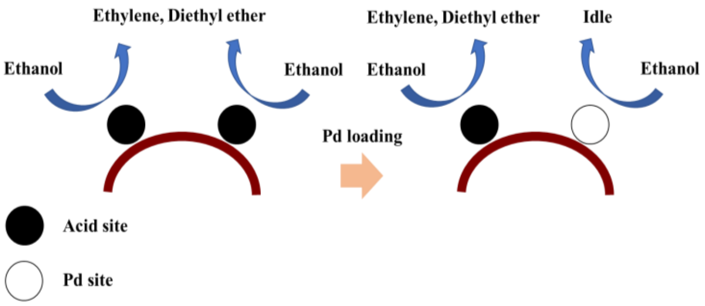
Catalysts	Temperature (°C)	Ethanol conversion (%)	Ethylene selectivity (%)	Ethylene yield (%)	Diethyl selectivity (%)	Diethyl yield (%)	Acetaldehyde selectivity (%)	Acetaldehyde yield (%)	Coke formation (%)
γ-Al_2O_3	200 to 300	o	o	o	o	o	o	o	o
	300 to 400	o	o	o	o	o	o	o	
Al_2O_3-P	200 to 300	+	-	-	+	+	-	+	-
	300 to 400	-	-	-	+	+	-	-	
Pd-Al_2O_3-P	200 to 300	+	+	+	-	-	+	+	-
	300 to 400	-	-	-	+	+	+	+	
Pd-Al_2O_3	200 to 300	+	+	+	-	-	+	+	+
	300 to 400	-	-	-	+	+	+	+	

O described to blank sample for the comparison of phosphorous and palladium addition on catalysts
+ described to increase catalytic performance and characteristic effect from blank sample
- described to decrease catalytic performance and characteristic effect from blank sample

The phenomena of ethanol conversion on catalyst surface is supposed on acid site and Pd site as shown in **Scheme 1** and **Scheme 2**. At temperature 200°C to 300°C, the Pd site dominantly enhanced the dehydrogenation of ethanol to acetaldehyde. In addition, the acid site acted the dehydration of ethanol to diethyl ether and ethylene, while Pd site was idle at temperature 350°C to 400°C.



Scheme 1 The phenomena of ethanol consumption on active site at temperature 200°C to 300°C.



Scheme 2 The phenomena of ethanol consumption on active site at temperature 350°C to 400°C.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The overall results of γ-Al_2O_3 catalyst modified with phosphorous and palladium are investigated to determine the effect of characteristics and catalytic performance on ethanol dehydration reaction. The conclusions and recommendation are described in **Section 6.1** and **Section 6.2**, respectively.

6.1 Conclusions

According to results of **Part I** and **Part II**, the characteristics and catalyst performance are concluded on the effect of phosphorous and palladium modification on alumina catalysts.

1) The characteristics of phosphorous modification on the catalysts are described as follows;

- The amount of phosphorous doping into catalyst does not affect the morphology of catalysts.
- The phosphorous loading is in highly disperses form on catalysts
- The surface area and pore volume decrease with loading of phosphorous, which can attribute to blocking of pores by phosphorous species on catalyst surface and inside channels.
- The phosphorous addition increases weak acid sites, whereas moderate to strong acid sites decrease and total acidity diminishes as well.
- The phosphorous loading on catalyst significantly decreases the amount of coke deposition on catalyst surface.

2) The presence of phosphorous on catalysts enhance the dehydration reaction that produce diethyl ether.

3) The P-modified on Al_2O_3 catalyst exhibits the highest diethyl ether yield of 38.41% at temperature of 350°C.

4) The characteristics of Pd addition on P-modified alumina catalysts are elucidated as follows;

- The addition of Pd on catalysts does not influence on the morphology of catalysts.
- The Pd loading on catalysts is well distributed on catalysts.
- The Pd modification decreases the surface area and pore volume due to Pd contents clog up on surface and diffuse in the support.
- The increasing Pd loading on catalysts gradually decreases weak acid sites as well.
- The modification of Pd promoter is slightly different in the amount of coke formation.

5) The Pd loading on P-modified alumina catalysts escalated ethanol conversion and ethylene selectivity with raising the reaction temperature in temperature range between 200°C to 300°C.

6) The Pd doping on Al_2O_3-P catalysts obviously increases the ethanol conversion and ethylene selectivity at low temperature around 200°C to 300°C. The ethanol conversion and ethylene selectivity can descend order as follows: 0.5Pd-Al_2O_3-P>0.3Pd-Al_2O_3-P>0.1Pd-Al_2O_3-P>0.05Pd-Al_2O_3-P.

7) The gamma alumina catalyst exhibits the highest ethylene yield reaching 74.62% at temperature of 400°C.

8) The characteristics of Pd addition on non-modified phosphorous catalysts are reported as follows;

- The Pd loading on catalysts presents the well disperse form on catalysts.
- The Pd contents display the slightly different amount of coke deposition.
- The modification of Pd species on Al_2O_3 catalyst eliminates weak acid sites.

9) The presence of Pd on catalysts enhances the dehydrogenation reaction at low temperature of 200°C.

10) The 0.5Pd-Al_2O_3 catalyst exhibits the highest ethylene yield reaching 43.79% at temperature of 400° compared to 0.5Pd-Al_2O_3-P catalyst.

6.2 Recommendations

The several techniques should be applied for verifying the characteristics of modified catalysts. However, the catalyst performance should improve in order to increase ethanol conversion and product selectivity. Thus, the recommendations are suggested for further experiments as follows:

1) The type of acid site such as Bronsted acid site and Lewis acid site should be indicated by pyridine adsorbed IR spectra method.

2) The XRF techniques should be used to compare with ICP techniques for error checking.

3) The catalytic stability of $0.5Pd\text{-}Al_2O_3$ and $0.5Pd\text{-}Al_2O_3\text{-}P$ catalysts should be further studied.

4) Other noble metal modified in various loading should be considered for addition on gamma alumina catalysts.

5) The phosphorous loading on other solid catalysts should be examined in order to increase ethanol conversion and diethyl ether selectivity.

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APPENDIX

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

A) Calculation for preparation of phosphorous modified over Al_2O_3 catalyst by acid activation technique

- 5 wt% H_3PO_4 on Al_2O_3 catalyst was prepared as follows:

Chemical

Orthophosphoric acid 85% (H_3PO_4)

Molecular weight = 98 g/mol

Phosphorous atomic weight = 31 g/mole

Based on 1 g of catalyst used,

85 g	of H_3PO_4 in	100 g	of H_3PO_4 solution
5 g	of H_3PO_4 in	5.88 g	of H_3PO_4 solution

Density of H_3PO_4 = 1.685 g/mL

Thus, 5.88 g of H_3PO_4 solution equal to 3.49 mL

Therefore, added 3.49 mL of H_3PO_4 solution into deionized water in amount of 94.12 mL, then stirred the solution with Al_2O_3 catalyst at room temperature for 30 minutes to obtain 5 wt% H_3PO_4 on Al_2O_3 catalyst.

B) Calculation for preparation of palladium modified over Al_2O_3 catalyst by acid activation technique

- 0.5 wt% palladium on Al_2O_3-P catalyst was prepared as follows:

Chemical

Tetraamminepalladium (II) nitrate 10% [$Pd(NH_3)_4(NO_3)_2$]

Molecular weight	= 298.5 g/mol
Palladium atomic weight	= 106.5 g/mole

Based on 1 g of catalyst used, the composition of catalyst would be as follow;

1 g of catalyst	Consisted of palladium to 0.005 g
Palladium	= 0.005 g
Al_2O_3-P catalyst	= 1.000-0.005 g
	= 0.995 g

In 100 g of $Pd(NH_3)_4(NO_3)_2$ solution, there is 3.57 g of Pd contents

Thus, there is 0.005 g of Pd in 0.141 g of $Pd(NH_3)_4(NO_3)_2$ solution

Density of $Pd(NH_3)_4(NO_3)_2$ solution = 1.038 g/mL

Thus, 0.141 g of $Pd(NH_3)_4(NO_3)_2$ solution equal to 0.136 mL or 136 µL

Pore volume of Al_2O_3-P catalyst = 247 µL

Then, add deionized water in the amount of 111 µL into 136 µL of $Pd(NH_3)_4(NO_3)_2$ solution.

APPENDIX B
CALCULATION OF ACIDITY

The acidity of the catalysts is determined from Ammonia temperature-programmed desorption (NH_3-TPD) by calculating area under TCD signal curve as a functional of temperature as follows:

$$\text{Acidity of catalyst} = \frac{\text{Moles of desorp ammonia}}{\text{Amount of dry catalyst}} \text{ x } 100$$

Where moles of ammonia desorbed
= Area underlying the curve of TCD signal x 300 µmole (Ammonia desorbed in mole is calculated from the calibration curve of Micromeritics pulsechemisorp 2750 instrument)

Weight of dry catalyst = 0.1 g
The unit of the catalyst acidity is µmole/g.catalyst

APPENDIX C

CALCULATION CURVE OF REACTANT AND PRODUCTS

The calibration curves of reactant and products were used to calculate the amount of reactant and products obtained from dehydration reaction.

The calibration curves of the reactant and products including ethanol, diethyl ether, ethylene and acetaldehyde are depicted in **Figure C.1** to **Figure C.4** as follows:

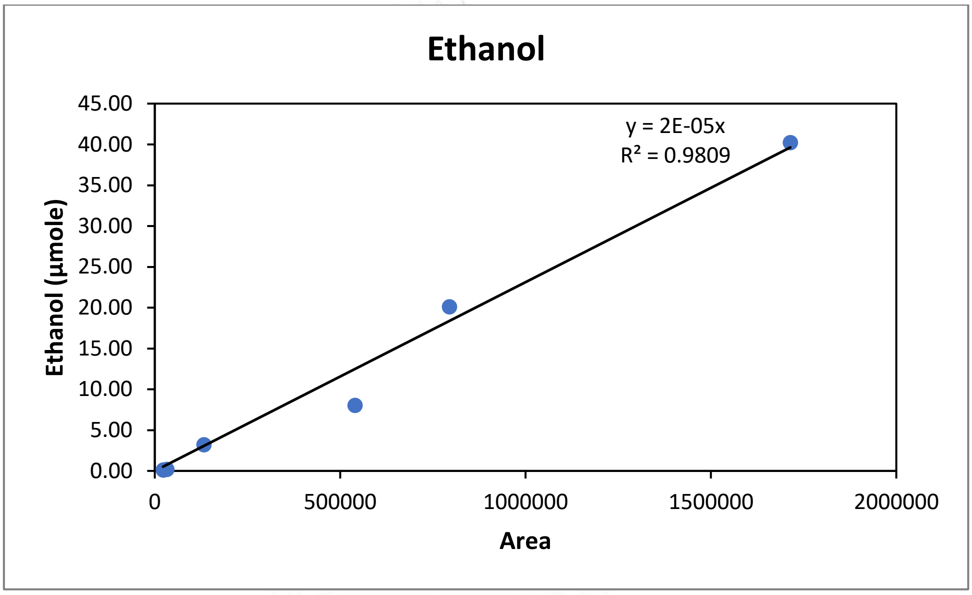


Figure C.1 The calibration curve of ethanol.

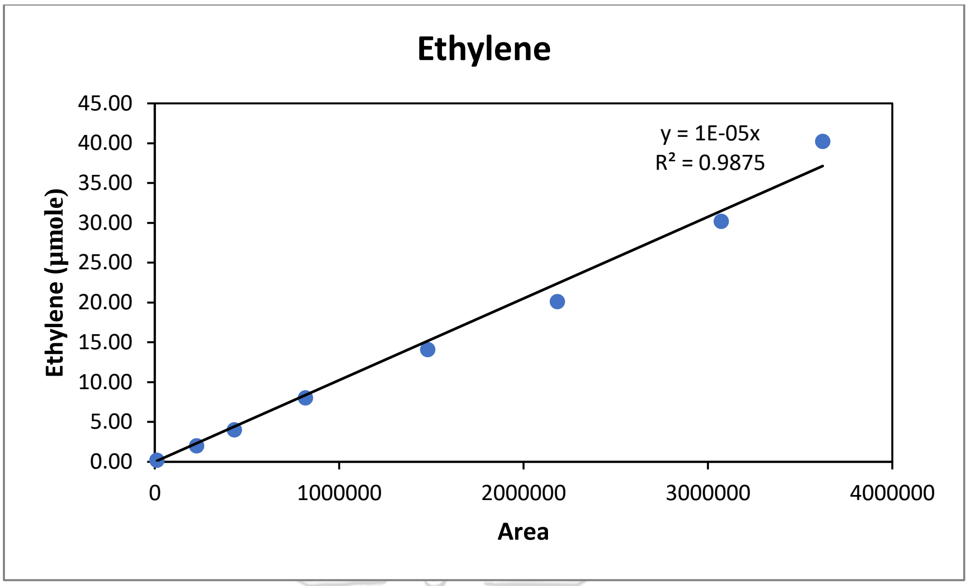


Figure C.2 The calibration curve of ethylene.

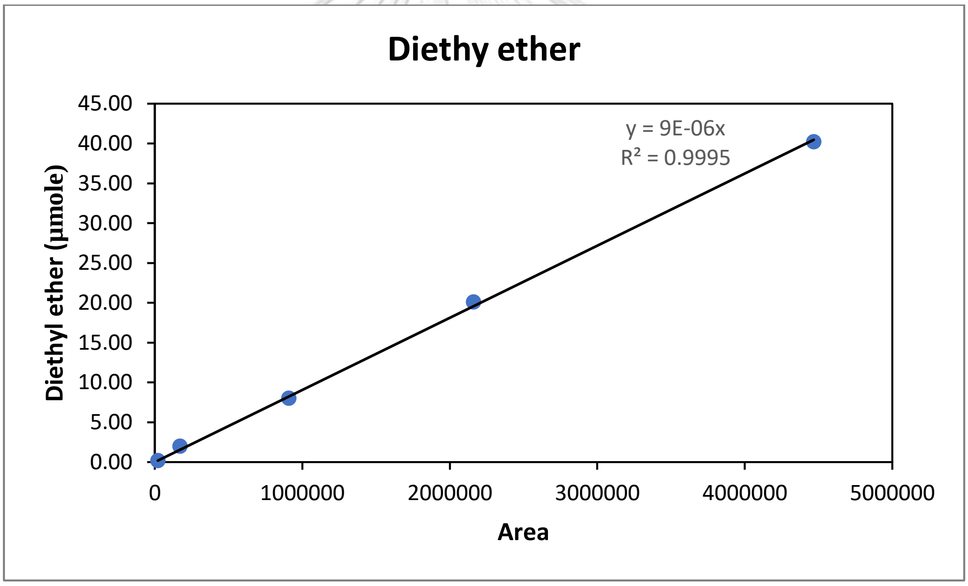


Figure C.3 The calibration curve of diethyl ether.

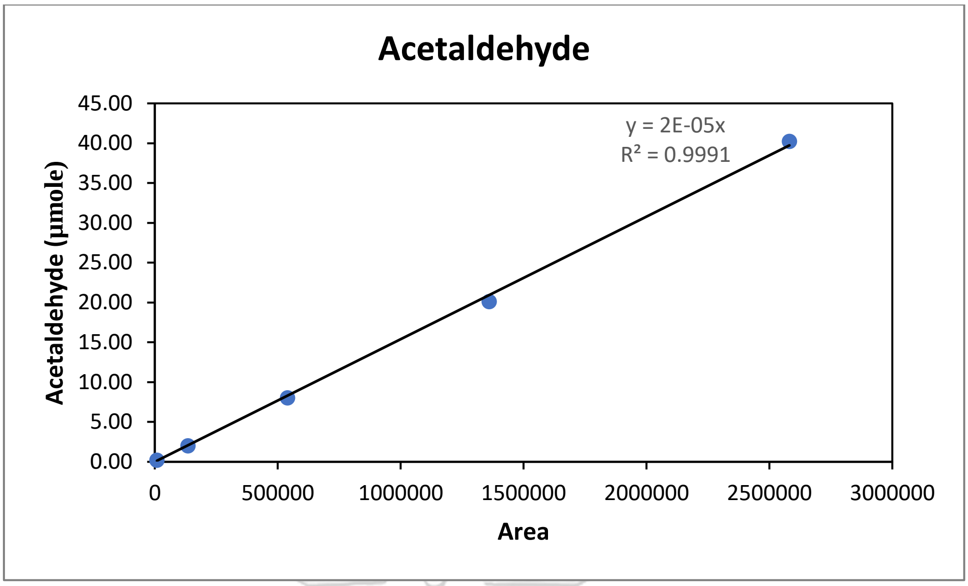
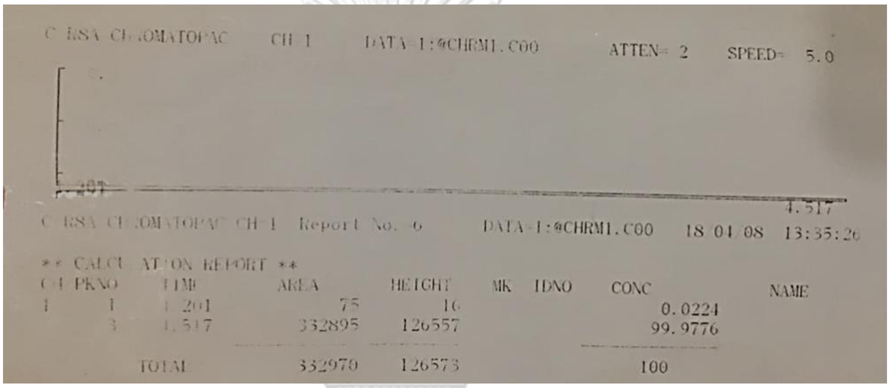


Figure C.4 The calibration curve of acetaldehyde.

APPENDIX D
CHROMATOGRAM

From the chromatograms depicted in **Figure D.1** and **Figure D.2**

Peak position of ethanol	: 4.6 min.
Peak position of ethylene	: 4.1 min.
Peak position of acetaldehyde	: 4.4 min.
Peak position of diethyl ether	: 4.9 min.

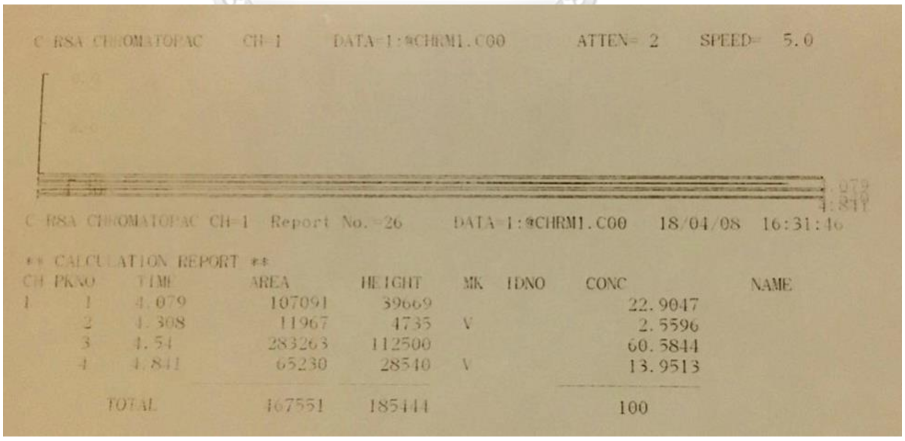


```
C-R8A CHROMATOPAC    CH=1    DATA=1:@CHRM1.C00      ATTEN= 2   SPEED=  5.0

C-R8A CHROMATOPAC CH=1  Report No.=6      DATA=1:@CHRM1.C00   18/04/08  13:35:26

** CALCULATION REPORT **
CH PKNO    TIME         AREA      HEIGHT   MK  IDNO   CONC           NAME
1    1     4.201          75          16              0.0224
     3     4.517      332895      126557             99.9776
                   ----------  ----------        ----------
         TOTAL        332970      126573            100
```

Figure D.1 Chromatogram of the reagent before the reaction.



```
C-R8A CHROMATOPAC    CH=1    DATA=1:@CHRM1.C00      ATTEN= 2   SPEED=  5.0

C-R8A CHROMATOPAC CH=1  Report No.=26     DATA=1:@CHRM1.C00   18/04/08  16:31:46

** CALCULATION REPORT **
CH PKNO    TIME       AREA     HEIGHT   MK  IDNO   CONC           NAME
1    1     4.079     107091     39669              22.9047
     2     4.308      11967      4735   V           2.5596
     3     4.54      283263    112500              60.5844
     4     4.841      65230     28540   V          13.9513
                   --------  --------          ----------
         TOTAL       467551    185444             100
```

Figure D.2 Chromatogram of the reagent after the reaction.

APPENDIX E

CALCULATION OF REACTANT CONVERSION, PRODUCT SELECTIVITY, PRODUCT YIELD

The catalytic performance in ethanol dehydration reaction was evaluated in terms of reactant conversion, product selectivity, product yield.

Reactant conversion

The conversion of reactant is defined as moles of reacted reactant with respect to moles of fed reactant:

$$\text{Reactant conversion (\%)} = \frac{\text{Moles of reacted reactant}}{\text{Moles of fed reactant}} \times 100$$

Product selectivity

The selectivity towards each product is defined as moles of product formed with respect to total moles of product:

$$\text{Product selectivity (\%)} = \frac{\text{Moles of each product}}{\text{Total moles of product}} \times 100$$

Product yield

The product yield of each product is defined in terms of reactant conversion and selectivity of each product.

Product yield (%) = Reactant conversion x Selectivity of each product

APPENDIX F

CATALYTIC TESTING RESULTS

Table F.1 Ethanol conversion, product selectivity from dehydration reaction of ethanol at temperature ranging of 200°C to 400°C.

Catalysts	**Temperature (°C)**	**Ethanol conversion (%)**	**Product selectivity (%)**		
			Diethyl ether	**Ethylene**	**Acetaldehyde**
γ-Al_2O_3	200	0.4	76.6	0.0	23.4
	250	3.1	94.4	2.2	3.4
	300	23.0	89.1	9.7	1.2
	350	61.7	58.9	40.2	0.9
	400	86.6	11.7	86.2	2.2
Al_2O_3-P	200	0.9	86.3	0.0	13.8
	250	3.8	95.2	2.3	2.6
	300	25.4	90.6	8.3	1.1
	350	57.1	67.2	32.0	0.8
	400	76.9	20.0	78.5	1.5
0.05Pd-Al_2O_3-P	200	5.8	2.3	27.6	70.2
	250	18.6	11.1	55.5	33.5
	300	30.8	26.2	62.4	11.4
	350	49.0	56.0	41.3	2.7
	400	68.5	36.0	59.7	4.3
0.1Pd-Al_2O_3-P	200	6.2	3.4	28.8	67.8
	250	20.0	14.0	55.8	30.2
	300	32.3	23.2	66.1	10.7
	350	50.4	51.5	46.3	2.2
	400	70.9	36.4	59.0	4.6
0.3Pd-Al_2O_3-P	200	7.6	3.4	39.7	56.9
	250	21.4	10.4	59.7	29.9
	300	37.0	21.8	67.7	10.5
	350	54.4	53.1	45.2	1.7
	400	72.1	37.5	57.9	4.6
0.5Pd-Al_2O_3-P	200	9.76	3.6	46.3	50.1
	250	24.5	11.0	61.2	27.8
	300	44.1	19.7	70.1	10.3
	350	59.4	56.0	42.4	1.7
	400	77.0	40.0	55.8	4.3

Catalysts	Temperature (°C)	Ethanol conversion (%)	Product selectivity (%)		
			Diethyl ether	Ethylene	Acetaldehyde
0.5Pd-Al_2O_3	200	4.2	0.8	45.3	53.9
	250	14.3	4.3	74.4	21.4
	300	30.6	163	71.3	12.5
	350	50.2	53.6	45.1	1.4
	400	71.6	38.8	61.2	5.0

Table F.2 Product yield from dehydration reaction of ethanol at temperature ranging of 200°C to 400°C.

Catalysts	Temperature (°C)	Product yield (%)		
		Diethyl ether	Ethylene	Acetaldehyde
γ-Al_2O_3	200	0.27	0.0	0.08
	250	2.93	0.07	0.10
	300	20.46	2.22	0.28
	350	36.35	24.79	0.56
	400	10.08	74.62	1.87
Al_2O_3-P	200	0.80	0.0	0.13
	250	3.66	0.09	0.10
	300	23.04	2.11	0.29
	350	38.41	18.28	0.45
	400	15.37	60.34	1.13
0.05Pd-Al_2O_3-P	200	0.13	1.61	4.09
	250	2.06	10.29	6.21
	300	8.05	19.20	3.51
	350	27.45	20.26	1.31
	400	24.66	40.93	2.95
0.1Pd-Al_2O_3-P	200	0.21	1.77	4.17
	250	2.79	11.15	6.04
	300	7.50	21.38	3.45
	350	25.97	23.35	1.12
	400	25.79	41.86	3.24
0.3Pd-Al_2O_3-P	200	0.26	3.03	4.33
	250	2.24	12.78	6.39
	300	8.05	25.08	3.90
	350	28.88	24.54	0.93
	400	27.04	41.72	3.33

Catalysts	Temperature (°C)	Product yield (%)		
		Diethyl ether	Ethylene	Acetaldehyde
0.5Pd-Al_2O_3-P	200	0.35	4.52	4.89
	250	2.68	14.99	6.82
	300	8.68	30.93	4.53
	350	33.29	25.19	0.99
	400	30.77	42.96	3.31
0.5Pd-Al_2O_3	200	0.03	1.9	2.26
	250	0.61	10.66	3.07
	300	4.97	21.79	3.82
	350	26.90	22.62	0.68
	400	24.21	43.79	3.59

APPENDIX G
LIST OF PUBLICATION

Proceeding

Chakkrit Khaochartchai and Bunjerd Jongsomjit, “Catalytic ethanol dehydration to diethyl ether over palladium-modified phosphorous gamma alumina catalysts”. Proceeding of the 27th National Thai Institute of Chemical Engineering and Applied Chemistry Conference (TIChE 2017) "Innovative Chemical Engineering and Technology toward a Sustainable Future", Shangri-La hotel, Bangkok, Thailand, October 18-20, 2017.

VITA

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