Ethanol dehydration with oxygen cofeeding over palladium catalyst supported on
spherical silica particle with ceria modification

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ดีไฮเดรชันของเอทานอลที่มีการป้อนร่วมของออกซิเจนบนตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับซิลิกาอนุภาคทรงกลมที่ปรับปรุงด้วยซีเรีย

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กาญจนี สินไชย : ดีไฮเดรชันของเอทานอลที่มีการป้อนร่วมของออกซิเจนบนตัวเร่ง
ปฏิกิริยาแพลเลเดียมบนตัวรองรับซิลิกาอนุภาคทรงกลมที่ปรับปรุงด้วยซีเรีย. (
Ethanol dehydration with oxygen cofeeding over palladium catalyst
supported on spherical silica particle with ceria modification) อ.ที่ปรึกษา
หลัก : ศ. ดร.บรรเจิด จงสมจิตร

       ปฏิกิริยาเอทานอลดีไฮเดรชันที่มีการป้อนร่วมออกซิเจนบนตัวเร่งปฏิกิริยา
แพลเลเดียมบนตัวรองรับซิลิกาอนุภาคทรงกรมที่ปรับปรุงด้วยซีเรีย ได้ทำการศึกษาในเครื่อง
ปฏิกรณ์ชนิดเบดนิ่งภายใต้ความดันบรรยากาศและมีช่วงอุณหภูมิ 150 - 350 องศาเซลเซียส โดย
ใช้สัดส่วนโมลของออกซิเจนต่อเอทานอล 2.2 ตัวเร่งปฏิกิริยาทั้งหมดถูกเตรียมด้วยวิธีเคลือบฝัง ซึ่ง
มีเตตระแอมมีนแพลเลเดียมคลอไรด์โมโนไฮเดรตเป็นสารตั้งต้นของตัวเร่งปฏิกิริยาแพลเลเดียม
และซีเรียมไนเตรตเฮกซะไฮเดรตเป็นสารตั้งต้นของซีเรีย จากการศึกษาผลของการปรับปรุงซีเรีย
บนตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับซิลิกาพบว่าตัวเร่งปฏิกิริยา Pd/CeO$_2$/SSP มี
ประสิทธิภาพสูงกว่าตัวเร่งปฏิกิริยา Pd/SSP และ CeO$_2$/SSP ที่อุณหภูมิ 200 องศาเซลเซียส
เนื่องจากซีเรียมีตำแหน่งออกซิเจนว่าง ซึ่งสามารถช่วยกักเก็บออกซิเจนให้กับตัวเร่งปฏิกิริยา
แพลเลเดียมนำไปสู่การเกิดเอทิลีนได้ดี อย่างไรก็ตามลำดับการเตรียมตัวเร่งปฏิกิริยาที่ถูกปรับปรุง
ด้วยซีเรียอาจส่งผลต่อพื้นที่ผิว ขนาดของผลึก การรีดิวซ์ และประสิทธิภาพของตัวเร่งปฏิกิริยา โดย
ตัวเร่งปฏิกิริยา Pd/CeO$_2$/SSP ที่ถูกเตรียมด้วยวิธีเคลือบฝังร่วม แสดงค่าการเปลี่ยนแปลงสูงที่สุด
เท่ากับ 66 % ที่อุณหภูมิ 200 องศาเซลเซียส เนื่องจากแพลเลเดียมและซีเรียมีการกระทำระหว่าง
กัน สามารถพิสูจน์จากการรีดิวซ์ที่แตกต่างกัน นอกจากนี้ปริมาณการป้อนร่วมของออกซิเจน ยัง
ส่งผลต่อประสิทธิภาพการเกิดปฏิกิริยา โดยการลดปริมาณสัดส่วนโมลของออกซิเจนต่อเอทานอล
เท่ากับ 1.1 ส่งผลให้ตัวเร่งปฏิกิริยา Pd/SSP มีค่าการเปลี่ยนแปลงลดลงเท่ากับ 29.3 % ที่อุณหภูมิ
175 องศาเซลเซียส และตัวเร่งปฏิกิริยา Pd-CeO$_2$/SP พบค่าการเปลี่ยนแปลงเท่ากับ 31.3 % ที่
อุณหภูมิ 250 องศาเซลเซียส ในทางกลับกันปฏิกิริยาที่ไม่มีการป้อนร่วมของออกซิเจนให้ค่าการ
เปลี่ยนแปลงต่ำกว่าในทุกตัวเร่งปฏิกิริยา นอกจากนี้การเกิดปฏิกิริยาการเผาไหม้ของ
ไฮโดรคาร์บอนโดยใช้ออกซิเจนสามารถเปลี่ยนเอทานอลไปเป็นคาร์บอนไดออกไซด์ได้

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต ....
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Kanjanee Sinchai : Ethanol dehydration with oxygen cofeeding over palladium catalyst supported on spherical silica particle with ceria modification. Advisor: Prof. BUNJERD JONGSOMJIT, Ph.D.

Ethanol dehydration with oxygen cofeeding over palladium catalyst supported on spherical silica particle with ceria modification was carried out in fixed bed reactor under atmospheric pressure and temperature range of 150 °C to 350 °C (O_2/Ethanol molar ratio = 2.2). The results showed that the effect of ceria modification of $Pd/CeO_2/SSP$ catalyst exhibited higher activity than Pd/SSP and CeO_2/SSP at 200 °C. $Pd/CeO_2/SSP$ catalyst yielded very the high ethanol conversion at 200 °C about 57.7 %. However, the preparation method with different sequence of loading has significant effects on crystallite size, surface area, H_2-TPR profile and catalytic activity. $Pd-CeO_2/SSP$ was synthesized by incipient wetness co-impregnation exhibits the highest ethanol conversion at 200 °C about 66.0 % due to its high crystallite size (ca. 5.4 nm) and different interaction between metals and promoter that was proven by H_2-TPR. The results also presented that the various amounts of oxygen cofeed of Pd/SSP catalyst had ethanol conversion at 175 °C about 29.3 % and ethanol conversion of $Pd-CeO_2/SSP$ was observed at 250 °C about 31.3 % for decreased oxygen cofeeding (O_2/Ethanol molar ratio = 1.1), whereas in the absence oxygen cofeeding, it showed less conversion at high temperature for all catalyst. Furthermore, ethanol can be converted to CO_2 from combustion reaction of hydrocarbon with oxygen.

Field of Study:	Chemical Engineering	Student's Signature	....
Academic Year:	2018	Advisor's Signature	....

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, fuel energy has the most important for the world. Bioethanol is the main potential source for substitution of import energy that can become a sustainable fuel instead of fossil fuels. Therefore, the development of new catalysts for ethanol conversion is of importance. Furthermore, ethanol is produced from agricultural raw materials such as sugarcane and cassava, which can stabilize the price of agricultural produce. Ethanol can be used to produce hydrogen and other higher value-added chemicals such as ethylene, diethyl ether, ethyl acetate, 1-3 butadiene, acetaldehyde, etc.[1],[2] that are widely used in many industrial processes. Generally, the production of enriched chemicals from ethanol has many processes, such as dehydration, oxidative dehydrogenation, oxidation, steam reforming, etc. Dissociation of ethanol molecules to ethoxy species, which are additional oxidized to acetaldehyde or dehydrated to ethylene is the key role [3].

Ethylene is the most important intermediate for several products in the chemical industry, such as polyethylene, ethylene oxide, ethylene glycol, and polyvinyl chloride. Normally, ethanol can be directly converted into ethylene with dehydration reaction in atmospheric pressure over several acidic catalysts at high temperature. However, a less studied approach is addition of O_2 or air in the reaction contributing to increase the effectiveness of the reaction. Pestana et al. [4], reported the addition of O_2 to result in coke burning for continuously regenerating the catalysts. The presence of oxygen leads to shift the equilibrium toward the reaction products with high catalytic activity under anaerobic conditions [5]. Thus, oxygen is added to enhance ethylene production efficiently.

Precious metals such as Pd, Pt, or Rh are good catalysts for reaction of ethanol having oxygen added [6],[7]. Palladium particles are one of the most popular transition metals and produced as a result of the very high catalytic activity. It is also widely used in many applications [8]. Several porous materials such as silica,

activated carbons, or alumina are used as supports [7],[8]. However, a mesoporous silica is the option of main research, because of its adequately high surface area, excellent stability, porosity, and the organic groups can be strongly cohesive to its surface [9, 10]. Moreover, previous papers have proposed that the surface of ceria participates within the alcohol oxidation as a cocatalyst [11], [12] and participation of the ceria can activate oxygen in reaction only aerobic conditions in order to refill oxygen [13]. In order to optimize the performance of the catalyst, the preparation method of catalysts should be studied because different preparation methods may affect the interaction between metal, promoter and support. For example, Liu et al.[14] found the sequences of introducing the Ce promoter has an effect on the degree of spatial relations between the Rh and Ce. It is reason for the catalyst prepared by co-impregnation would have better performance in most cases. However, more experiment should perform to confirm this concept and try to explain. At present, the investigation of the palladium and ceria co-catalysts impregnation is rarely reported.

Therefore, this study aims to investigate direct conversion of ethanol to ethylene at temperature ranging from 150-350 °C and atmospheric pressure in catalytic behaviors of Pd/SSP and effect of sequence in method of ceria modification. Then, their catalytic activities were tested with oxygen addition during ethanol reactions. The most efficient catalyst was selected to further study on oxygen cofeed effect.

1.2 Objectives

1. To study Pd catalyst and CeO_2 modification on spherical silica particle (SSP) in ethanol dehydration with oxygen cofeeding.
2. To investigate the effect of different sequence in catalyst preparation with Pd loading and CeO_2 modification in ethanol dehydration with oxygen cofeeding.
3. To compare the effect of amount of ethanol dehydration with oxygen cofeeding.

1.3   Research scope

1. Spherical silica particle (SSP) support was prepared by sol-gel method.

2. Four catalysts of Pd/SSP, Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and coimpregnated Pd-CeO$_2$/SSP were prepared by the incipient wetness impregnation (0.5 wt% of Pd and 5 wt% of CeO$_2$).

3. Characterization of all catalysts with X-ray diffraction (XRD), ammonia temperature programmed desorption (NH$_3$-TPD), temperature-programmed reduction (TPR), scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDX) and N$_2$ physisorption (BET).

4. All catalysts were pre-reduced *in situ* in flowing H$_2$ at 300 °C for 1 h and tested with oxygen cofeed during ethanol reactions at operation temperature between 150 – 350 °C and atmospheric pressure.

5. Comparing the performance of Pd/SSP catalyst and ceria modification with different sequence of loading, which gives the best activity in ethanol reaction.

6. Reaction study of Pd/SSP and the most suitable ceria modification were pre-reduced *in situ* in flowing H$_2$ at 300 °C for 1 h and tested under various amounts of oxygen cofeed (molar ratio of O$_2$/EtOH 2.2, 1.1 and 0) at operation temperature of 150 – 350 °C and atmospheric pressure.

7. Comparing amounts of oxygen cofeed that result in high activity of ethanol reactions.

8. The product gas samples were analyzed by gas chromatography.

1.4   Research methodology

Part I: Comparing the performance of Pd/SSP, CeO$_2$/SSP catalysts and ceria modification under oxygen cofeed during ethanol reactions.

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┌─────────────────────────────────┐
│ Synthesis of spherical silica particle │
│   (SSP) support by sol – gel method   │
└─────────────────────────────────┘
                  │
┌─────────────────────────────────┐
│ Preparation of all catalysts by incipient wetness │
│           impregnation method            │
└─────────────────────────────────┘
```

| Pd/SSP | CeO$_2$/SSP | Pd/CeO$_2$/SSP |

Catalyst testing

Catalyst characterization

Pre-reduced *in situ* in flowing H$_2$ at 300 °C for 1 h and test in ethanol reactions at operating temperature of 150-350 °C and atmospheric pressure

XRD, SEM-EDX, BET

Compare all catalysts that give the best activity in ethanol

Discuss and conclude result of characterization

Investigate between result from experiment and characterization and select the most suitable catalyst to use in part II

Part II: Comparing the performance of ceria modification with different sequence of loading under oxygen cofeed during ethanol reactions.

```
┌─────────────────────────────┐
│  Synthesis of ceria         │
│  modification catalysts     │
│  with different             │
│  sequence of loading        │
└─────────────────────────────┘
            │
            ▼
┌─────────────────────────────┐
│ Preparation of all catalysts│
│ by incipient wetness        │
│ impregnation method         │
└─────────────────────────────┘
```

$Pd/CeO_2/SSP$ $CeO_2/Pd/SSP$ $Pd\text{-}CeO_2/SSP$

Catalyst testing

Catalyst characterization

Pre-reduced *in situ* in flowing H_2 at 300 °C for 1 h and test in ethanol reactions at operating temperature of 150-350 °C and atmospheric pressure

XRD, SEM-EDX, H_2-TPR, BET

Compare all catalysts that give the best activity in ethanol

Discuss and conclude result of characterization

Comparing result from experiment and characterization and select the most suitable catalyst to use in part III

Part III: Comparing the performance of Pd/SSP catalyst and the most suitable ceria modification in oxygen cofeed during ethanol reactions with various amounts of oxygen cofeed.

```
┌─────────────────────────────────┐
│  Use Pd/SSP and select the most │
│ suitable ceria modification from part II │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│ To vary amounts of O₂ cofeed (molar ratio of O₂/EtOH) │
└─────────────────────────────────────────┘
```

$$\text{To vary amounts of } O_2 \text{ cofeed (molar ratio of } O_2/EtOH)$$

| 2.2 | 1.1 | 0 |

Catalyst testing

Pre-reduced in situ in flowing H_2 at 300 °C for 1 h and test in ethanol reactions at operating temperature 150-350 °C and atmospheric pressure

Comparing amount of oxygen that result in effective activity of ethanol reactions.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Properties of mesoporous silica

Mesoporous SiO_2 is the most widely used support because these materials have unique properties, such as high surface area, excellent mechanical, thermal stability, and uniform pore sizes [15]. Silica can be produced from natural sources such as rice husk ash and bagasse ash. Mesoporous silica consists of four main phases, including the hexagonal phase (MCM-41), the cubic phase (MCM-48), lamellar phase and (MCM-50) and spherical particles with hexagonal close packed pores arranged in a radial formation are formed (SSP) [16]. The first three phases were recognized as an unstable phase that will collapse when removing molecules of surfactants. The ability to given structure depends on the special organization of the organic phase [17]. In addition, spherical silica particle (SSP) exhibits a pronounced spherical morphology [16].
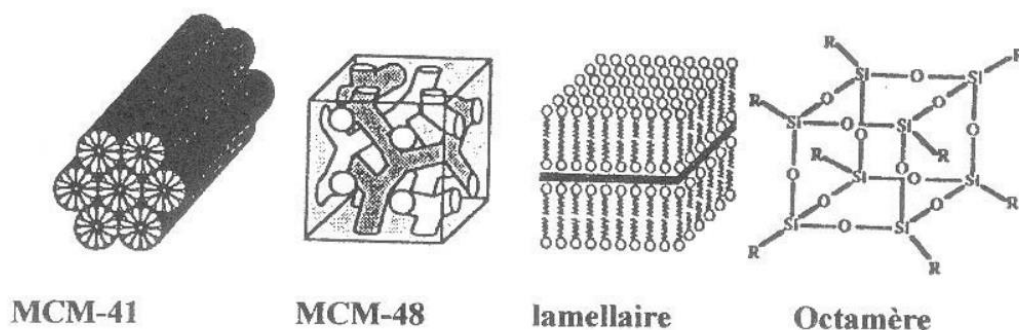
Figure 1 Different structures of Mesoporous SiO_2 family [18].

2.2 Properties of palladium

Palladium (Pd) is a chemical element with an atomic number 46. It is discovered in the 1803 by William Hyde Wollaston. The Physical properties of Palladium is reported in Table 2.1

Palladium platinum, rhodium, ruthenium, iridium, and osmium referred to as the platinum group metals (PGMs). However, these elements have similar chemical properties, but the palladium has lowest density and melting point. Most of the

Palladium and platinum group metals used in catalytic converters that convert up to 90% of harmful gases in cars such as carbon monoxide, nitrogen dioxide and hydrocarbons into less toxic (carbon dioxide, nitrogen and water vapor). Moreover, Palladium is also used in electronics, dentistry, hydrogenation, chemical applications, groundwater treatment and palladium jewelry. Finely divided palladium is a good catalyst and is used for hydrogenation and dehydrogenation reactions.

Table 1 Palladium properties

Properties	Specification
Group, Period, Block	10 , 5 , d
Atomic number, mass	46, 106.42 g/mol
Appearance	A shiny, Silvery white
State at STP	Solid
Density	12.023 g/cm^3
Melting point	1,828.05 K
Boiling point	3,236 K

2.3   Properties of cerium (IV) oxide or ceria (CeO$_2$)

Cerium (IV) oxide or ceria is an important commercial product with the chemical formula CeO_2 and an intermediate in the purification of the element from the ores. Furthermore, the interconvertibility of CeO_x materials is the basis of the use of ceria for an oxidation catalyst. CeO_2 is an active oxide for the oxidation of CO to CO_2 and for ethanol converted to H_2 by partial oxidation or steam reforming. The Physical properties of cerium (IV) oxide is reported in Table 2.2

Table 2 Cerium (IV) oxide or ceria properties

Properties	Specification
Molar mass	172.115 g/mol
Appearance	White or pale yellow solid
Density	7.215 g/cm^3
Melting point	2,670 K
Boiling point	3,770 K

2.4 Ethylene

Ethylene is a hydrocarbon which has the formula C_2H_4. Ethylene is widely used in the chemical industry. Moreover, ethylene is used as intermediate in the petroleum industry. It is produced from crude oil and used as feedstocks to produce ethylene oxide (EO) and polymers such as polyethylene (PE), polyethylene terephthalate (PET), and polyvinylchloride (PVC). Ethylene is also an important natural plant hormone and is used in agriculture to force the ripening of fruits. Normally, ethylene's hydrate is ethanol.

2.5 Ethanol

Ethanol is chemical compound with the chemical formula C_2H_5OH. Ethanol is naturally produced by the fermentation of renewable sources such as corn, sugarcane, or other biomass waste resulting in high ethanol production capacity. Therefore, most ethanol is used as a compound to produce value-added substances such as ethylene, acetaldehyde, diethyl ether and acetic acid. The ethanol properties is shown in Table 2.3.

Table 3 The ethanol properties

Properties	Specification
Molar mass	46.07 g/mol
Appearance	Colorless liquid
Density	0.7893 g/cm^3 (at 20 ℃)
Melting point	159.0 K
Boiling point	351.4 K

2.6   Ethanol reaction

Ethanol is produced directly and indirectly to ethylene with dehydration reaction (reaction 1) using an acid catalyst. In this reaction, ethanol is produced by a reversible high temperature due to exothermic reaction between ethylene and water vapor.

$$C_2H_5OH \leftrightarrow C_2H_4 + H_2O \qquad \Delta H = +44.9\,kj/mol \qquad [1]$$

However, addition of oxygen (cofed oxygen) in ethanol reactions for example, oxidation reaction of ethanol (reaction 2) is practical. The feed composition into the reactor has a significant effect on the product distribution. Particularly, at high temperatures, increase of the O_2/Ethanol ratio in the feed stream results in an increase in the carbon dioxide selectivity.

$$C_2H_5OH + \frac{1}{2}O_2 \leftrightarrow CH_3CHO + H_2O \qquad \Delta H = -242\,kj/mol \qquad [2]$$

In other research, it reported that very small amounts of ethylene was formed in the absence of oxygen gas. This is an indication of the participation of the adsorbed oxygen in the ethylene formation over catalyst. Ethylene is expected to occur on the main catalyst surface due to the oxidative dehydrogenation reaction step. Adsorbed oxygen atoms seem to catalyze dehydration reaction. With an increase in temperature and in oxygen concentration, a bridged structure involving two different sites and an oxygen atom may form on the surface, which may then give ethylene and water. The oxygen atom, which should remain on the surface as a result of this surface reaction step, was probably used in the further oxidation of

surface species in the formation of CO_2 and the other oxygenated reaction products. [19]

2.7 Literature review

In 1971, Samanos et al. [20] studied about ethylene combustion over Pd/SiO_2 and Pd/Al_2O_3 catalysts and reported no differences in the apparent activation energies measured for ethylene combustion over Pd/SiO_2 and Pd/Al_2O_3 catalysts and concluded that CO_2 was formed primarily from ethylene.

In 2004, Han Y.F. et al. [21] investigated kinetics of ethylene combustion in the synthesis of vinyl acetate over a Pd/SiO_2 catalyst. CO_2 formation as a function of the partial pressures of C_2H_4 and O_2 exhibited a positive order with respect to O_2 and a negative reaction order with respect to C_2H_4. However, CO_2 production occurs via combustion of ethylene and/or acetic acid.

In 2006, Gucbilmez Y. and Dogu T. [19] studied ethylene and acetaldehyde production by selective oxidation of ethanol using mesoporous V-MCM-41 catalysts. Ethylene selectivity showed a significant increase with an increase in temperature over 300 °C, while relatively high acetaldehyde selectivities were observed at lower temperatures. Experimental results showing the formation of acetaldehyde and not showing the formation of ethylene in the absence of gas-phase oxygen and the catalyst deactivation observed in such conditions suggested a redox mechanism involving the surface lattice oxygen of the catalyst in acetaldehyde production, while the involvement of adsorbed oxygen was concluded to take place in the formation of ethylene.

In 2007, Kawakami T. et al. [22] investigated vapor-phase oxidation of ethylene to acetic acid over $Pd\text{-}H_4SiW_{12}O_{40}/SiO_2$ and explained that an appropriate ratio of Pd to acidic surface to maximize the interface is important for an efficient catalyst. Excess Pd to the acidic sites causes the formation of CO_2 to a considerable extent.

In 2010, Lippit M.J. and Nieuwenhuys B.E. [23] studied the low temperature (200 °C – 400 °C) activity of Cu/Al_2O_3 and Ag/Al_2O_3 catalysts in the dehydrogenation, dehydration and oxidation reaction of ethanol directly into ethylene oxide. In addition, the promoting effect of adding Li_2O and CeO_2 has been investigated. The presence of O_2 is very important to prevent carbon deposition for catalysts.

From literature review, Pd catalyst was used in promoter to several reactions and not have other report that used Pd in active site in ethanol dehydration to ethylene with oxygen cofeeding. CeO_2 most likely used for promoter in oxidative reaction because CeO_2 perform O_2 storage for active site promoter. Another important point is the preparation method should be investigated since different preparation methods might have an effect on the interaction between metals and promoter or metals and support. Therefore, all factors resulting in this work.

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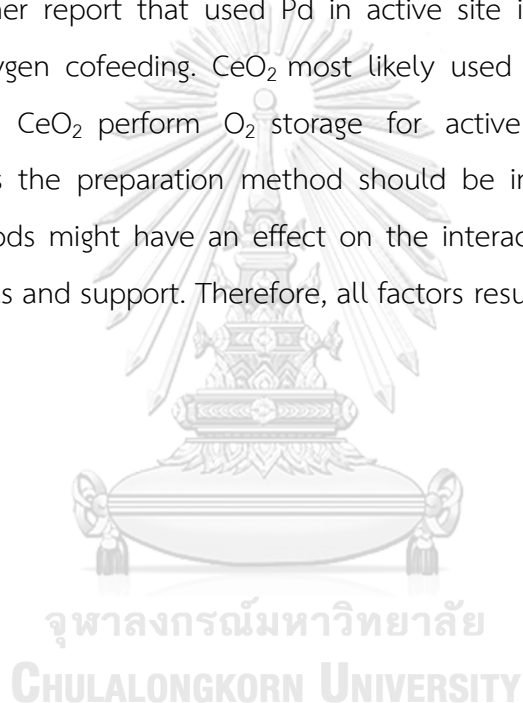
CHAPTER 3

EXPERIMENT

This chapter explains the details of the support synthesis with the sol-gel reaction, the synthesis of all catalysts by incipient wetness impregnation method, the procedure for testing the reaction of ethanol containing oxygen and calculation of oxygen content. Which all catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption (BET), Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX), temperature programmed reduction (TPR), Ammonia temperature programmed desorption (NH_3-TPD).

3.1　Catalysts Preparation

3.1.1　Synthesis of spherical silica particle (SSP) support

Spherical silica particle (SSP) support was synthesized by sol–gel method using tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), ammonia (NH_3), ethanol (C_2H_5OH) and de-ionized water (H_2O) as reported in Table 3.1. The molar ratio of 1 TEOS: 0.3 CTAB: 11NH_3: 58 C_2H_5OH: 144 H_2O [16].

First, cetyltrimethylammonium bromide was dissloved in the mixed solution of ethanol, de-ionized water and ammonia stirring at 600 rpm for 15 min until the solution is clear. Then, tetraethyl orthosilicate was added in solution. The mixed solution was further stirred for 2 h. To notice the white precipitate was subsequently filtrated and washed with de-ionized water. Then, the precipitate was dried at 110 ℃ overnight in oven and calcined in air at 550 ℃ for 6 h. Finally, the spherical silica particle support was obtained in white powder.

Table 4 The chemical used in synthesis spherical silica particle (SSP) support

Chemical	Formula	Supplier
98 wt% Tetraethyl orthosilicate (TEOS)	$SiC_8H_{20}O_4$	Aldrich
Cetyltrimethylammonium bromide (CTAB)	$C_{19}H_{42}BrN$	Aldrich
30 wt% Ammonia	NH_3	Penreac
99.99 wt% Ethanol	C_2H_5OH	J. T. Baker

3.1.2 Preparation of palladium loaded on spherical silica particle

This section describes preparation of 0.5 wt% palladium loaded on spherical silica particle that was synthesized by incipient wetness impregnation method. Precursor of palladium is tetraamminepalladium (II) chloride monohydrate ≥99.99% trace metals basis and formula is $Pd(NH_3)_4Cl_2 \cdot H_2O$ available from Aldrich.

To prepare the catalyst, palladium precursor was first dissolved in de-ionized water. After impregnation, the catalyst was placed at room temperature for 2 h to ensure that completely distributed. Finally, drying at 110 °C overnight in oven and calcine in air at 400 °C for 4 h.
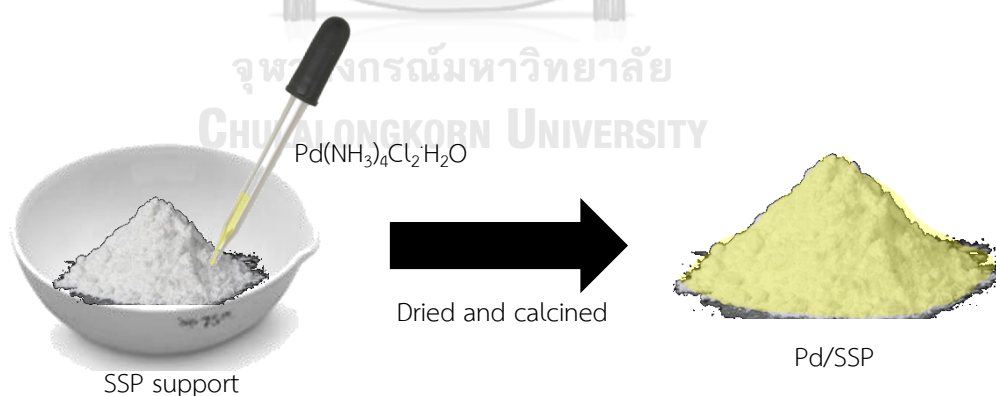
Figure 2 Diagram of Pd/SSP catalyst preparation by incipient wetness impregnation method.

3.1.3   Preparation of of ceria loaded on spherical silica particle

5 wt% ceria loaded on spherical silica particle that was synthesized by incipient wetness impregnation method. Precursor of ceria is cerium (III) nitrate hexahydrate 99.999% trace metals basis [$Ce(NO_3)_3 \cdot 6H_2O$] available from Aldrich.

To prepare the catalyst, ceria precursor was first dissolved in de-ionized water. After impregnation, the catalyst was placed at room temperature for 2 h to ensure that completely distributed. Finally, drying at 110 °C overnight in oven and calcine in air at 500 °C for 2 h.
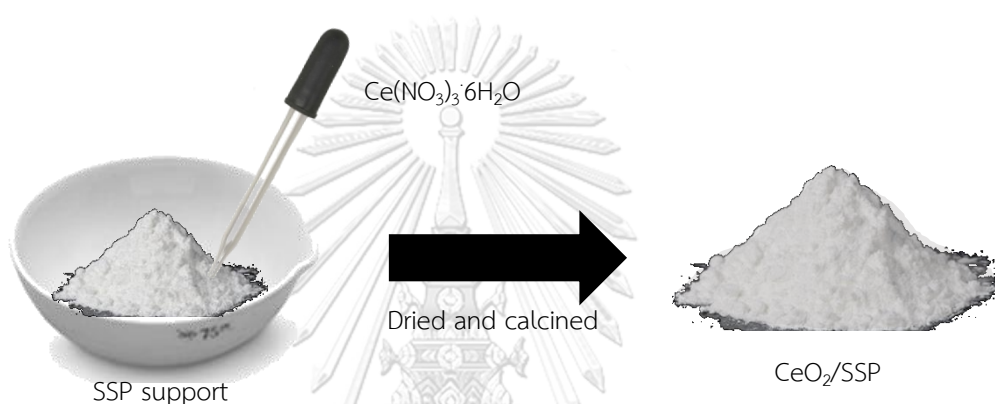
Figure 3 Diagram of CeO_2/SSP catalyst preparation by incipient wetness impregnation method.

3.1.4   Preparation of ceria modified on Pd/SSP and sequence of loading

Ceria modification was prepared by incipient wetness impregnation method. Cerium(III) nitrate hexahydrate 99.999% trace metals basis [$Ce(NO_3)_3 \cdot 6H_2O$] available from Aldrich was dissolved in de-ionized water an optimum composition to obtain 5 wt% of CeO_2. By dividing the sequence of loading as follows.

- **Pd/CeO_2/SSP**

First, ceria precursor was dissolved in de-ionized water and dropping on SSP support. The catalyst was placed at room temperature for 2 h. and dried in oven at 110 °C overnight. Next, palladium precursor solution was dropped on sample. After impregnation, the catalyst was placed for 2 h at room temperature. Then, drying in oven at 110 °C overnight and calcine in air at 400 °C for 4 h.
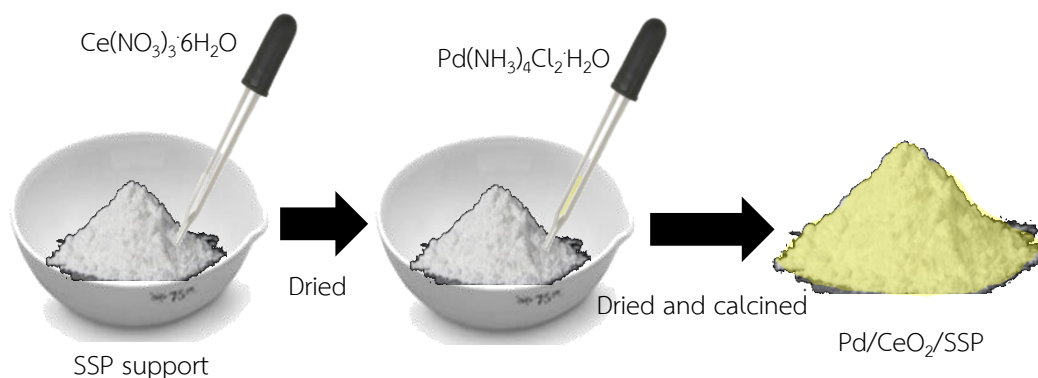
Figure 4 Diagram of Pd/CeO$_2$/SSP catalyst preparation by incipient wetness impregnation method.

- **CeO$_2$/Pd/SSP**

The CeO$_2$/Pd/SSP catalyst was prepared by incipient wetness impregnation technique. Palladium precursor solution was dropped on SSP support and placed at room temperature for 2 h. Then, drying at 110 °C overnight after that ceria precursor was dropped on the sample and kept at room temperature for 2 h. Finally, CeO$_2$/Pd/SSP catalyst was dried at 110 °C overnight and calcined in air at 400 °C for 4 h.
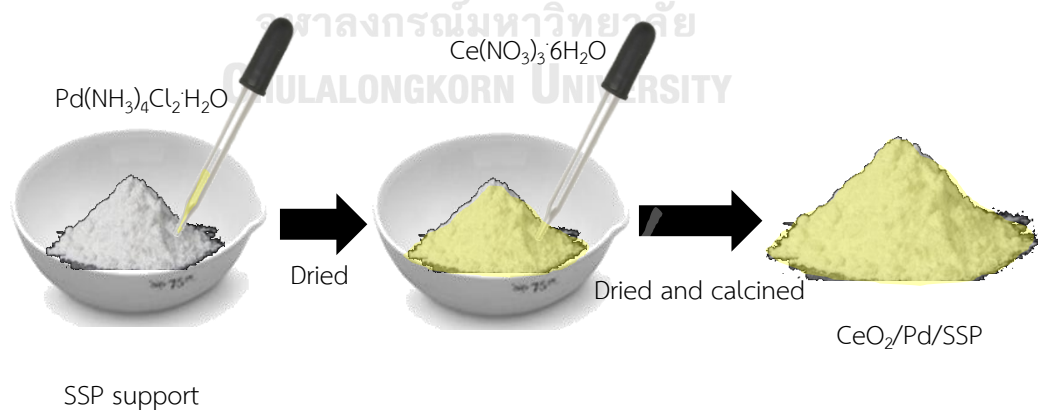
Figure 5 Diagram of CeO$_2$/Pd/SSP catalyst preparation by incipient wetness impregnation method.

- **Pd-CeO$_2$/SSP**

Preparation of this catalyst is done by incipient wetness coimpregnation method. Ceria and palladium precursors were dissolved with distillated water and dropped on SSP support. The catalyst was placed at room temperature for 2 h. After that, drying overnight in oven at 110 ℃ and calcine at 400 ℃, 4 h in air atmosphere.

$Ce(NO_3)_3 \cdot 6H_2O$

$Pd(NH_3)_4Cl_2 \cdot H_2O$

Dried and calcined

SSP support
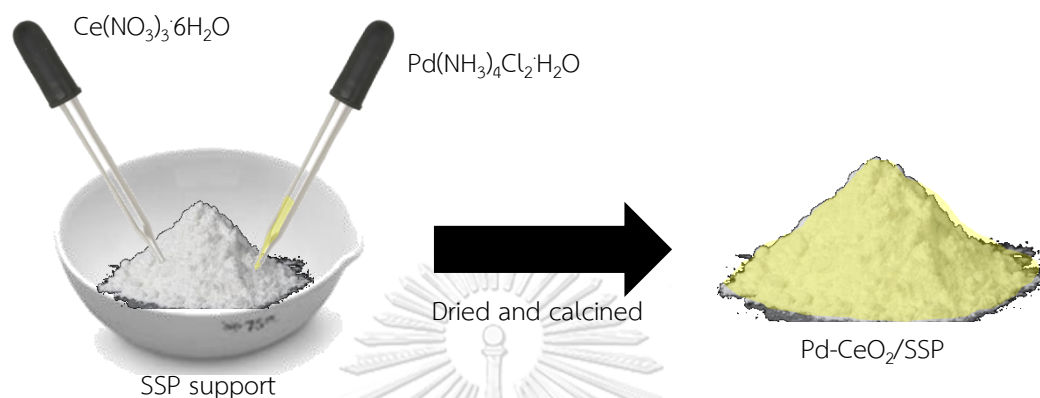
$Pd\text{-}CeO_2/SSP$

Figure 6 Diagram of Pd-CeO$_2$/SSP catalyst preparation by incipient wetness coimpregnation method.

3.2   Catalysts characterization

3.2.1   X-ray diffraction (XRD)

All catalysts were characterized by Bruker D8 Advance X-ray diffractometer with Cu K$_\alpha$ (λ = 1.54439 Å) for analyzing the phase composition of catalysts. The XRD patterns of all catalysts were scanned at a rate of 2.4° min^{-1} in the 2θ range of 20 to 80° with resolution 0.04°.

3.2.2   Nitrogen physisorption (BET)

N$_2$ physisorption (N$_2$ adsorption at −196 ℃ in a Micromeritics ASPS 2000) was performed to determine surface areas, pore size and pore volume of the different catalysts and using BET and BJH method to analyzing.

3.2.3   Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscope (SEM) technique (Hitashi mode S-3400N, Japan) was used to obtain morphology and elemental distribution at the surface of the catalysts. The SEM was operated using the back-scattering electron mode at 15 kV. The EDX was performed using Link Isis series 300 program.

3.2.4   Temperature programmed reduction (TPR)

The reduction behavior of all catalysts were appraised by temperature programmed reduction. 0.1 g of samples were packed in a U-tube glass with 0.01 g of quartz wool and pretreated in nitrogen flow at 250 °C for 1 h. Temperature of reduction profile was ramped from 40 °C to 500 °C with heating rate of 10 °C/min during flowing of 10% H_2 in air.

3.2.5   Ammonia temperature programmed desorption (NH₃-TPD)

Acidity of catalysts was analyzed by Micromeritics chemisorp 2750 pulse chemisorption system. In exploration, 0.1 g of catalysts was packed in a U-tube glass with 0.01 g of quartz wool and pretreated at 500 °C for 1 h under helium flow. After that, the samples were saturated with 15% of NH_3/He and the physisorbed ammonia was desorbed under helium gas flow after saturation. In order to desorb the chemisorbed NH_3, the catalyst was heated from 40 °C to 500 °C at heating rate of 10 °C /min.

3.3   Ethanol reactions study

3.3.1   Chemicals for the reaction study

1. Absolute ethanol purity of 99.99% available from Merck.
2. Nitrogen gas ultra-high purity of 99.99% available from Linde.
3. Hydrogen gas ultra-high purity of 99.99% available from Linde.
4. Air zero balance nitrogen available from Linde.

3.3.2 Reaction study procedure

3.3.2.1 Normal amount of oxygen

Catalytic reactions of ethanol was carried out in a fixed-bed continuous flow micro reactor in gas-phase. The reactor is made of a borosilicate glass with an outside diameter of 0.012 m, interior diameter 0.010 m and a length 0.495 m was used. In a typical experiment, 0.1 g of catalyst was packed between quartz wool bed in a reactor. The catalyst sample was pre-reduced *in situ* in flowing H_2 at 300 °C for 1 h. Then, ethanol was vaporized and fed by a syringe pump at total flow rate of 1.45 ml/h [weight hourly space velocity (WHSV) = 11.4 h^{-1}] with N_2 as a carrier gas having flow rate of 50 mL/min constantly (O_2/EtOH molar ratio of 2.2). Next, O_2 was added (cofeed) into reaction with N_2. The flow rate of N_2 was decreased to 17.8 mL/min and set the flow rate of air to 35.1 mL/min. Catalytic reaction was operated under the temperature range of 150 to 350 °C and the atmospheric pressure. Finally, all products were analyzed by using 2 types of gas chromatography techniques including, flame ionization detector (FID) equipped with a Shimadzu GC14B (DB-5) that can be separated the light hydrocarbon products and thermal conductivity detector (TCD) instrument is Shimadzu GC8A (Porapak-Q and Molecular sieve 5A) was used to separate inorganic compositions.

1. Bubble flow meter   2. Sampling point   3. Glass tube reactor   4. Temperature controller
5. Syringe pump   6. Pressure regulator   7. Vaporizer   8. Catalyst bed
9. Thermocouple   10. Mass flow controller   11. On-off valve   12. 2-way valve
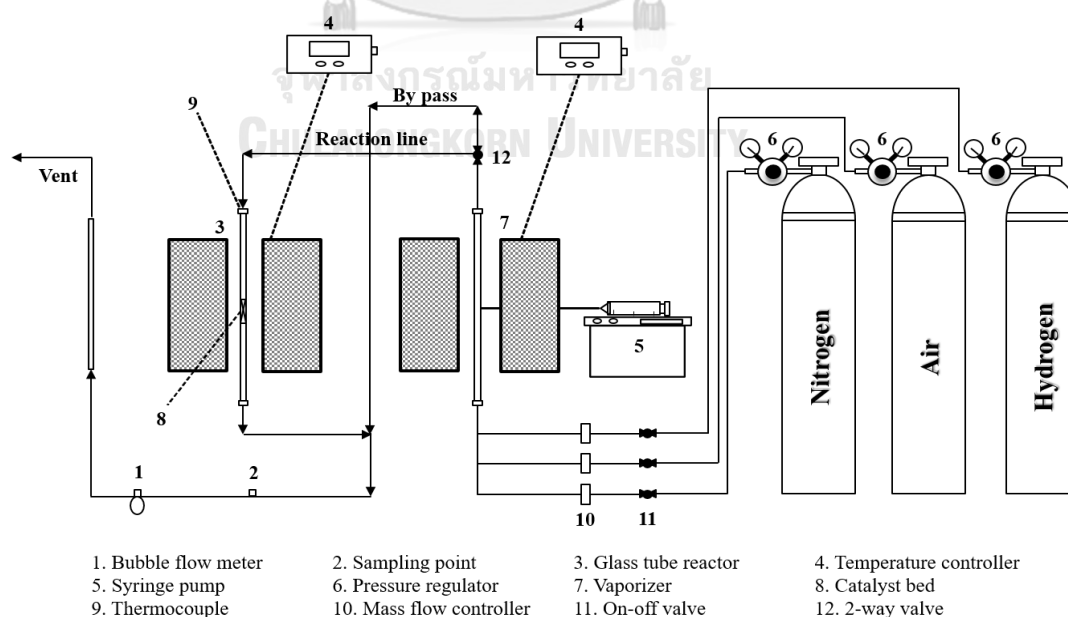
Figure 7 Schematic of Catalytic reaction system in gas phase.

3.3.2.2 Reduced amount of oxygen cofeed

In this catalytic reaction, it has the same method of normal amount of oxygen. However, differently, reducing the amount of oxygen cofeed by half of normal amount of oxygen. Therefore, when O_2 was flew with N_2, the flow rate of N_2 was decreased to 35.4 mL/min and set the flow rate of air to 17.5 mL/min (O_2/EtOH molar ratio of 1.1). Catalytic reaction was tested under the atmospheric pressure and the temperature range of 150 to 350 °C. Then, all products were detected by using flame ionization detector gas chromatography (GC-FID) and thermal conductivity detect or gas chromatography (GC-TCD).

3.4 Research plan

Table 5 Research plan

Plan	Year 2018												Year 2019					
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Study about the theory and literature review																		
Catalysts preparation																		
Catalysts characterization																		
Reaction test																		
Discussion and conclusion																		

3.5 Expected benefits

1. It will obtain the optimum palladium catalyst for ethanol reactions.

2. It will obtain the optimum ceria modification for ethanol reactions.

3. It will obtain the influence of the amount of oxygen in ethanol to ethylene.

CHAPTER 4
RESULTS AND DISCUSSION

Chapter 4 discusses about characterization and catalytic activity of palladium supported on spherical silica particle, ceria modification with different sequence of loading and amount of oxygen in ethanol dehydration with oxygen cofeeding. The results and discussion are divided into three parts. The first part is to study effect of ceria modification, in which catalysts are Pd/SSP, CeO_2/SSP and Pd/CeO_2/SSP. All catalysts were synthesized by incipient wetness impregnation method with palladium of loading 0.5 wt% and ceria loading of 5 wt% and characterized with XRD, SEM-EDX and N_2 physisorption. The second part is investigation effect of ceria modification with different sequence of loading. Catalysts were analyzed with XRD, SEM-EDX, H_2-TPR and N_2-physisorption techniques and comparing catalytic activity with ceria modification in the first part. Finally, the last past is comparing performance of oxygen amount cofeed during ethanol dehydration with different oxygen to ethanol molar ratios (0, 1.1 and 2.2). The catalytic activity of three parts was tested in fixed-bed tubular reactor, which has mixed between oxygen and nitrogen gas as carrier gas and vapor of ethanol pass through. After reaction is complete, the product gas was analyzed with GC- FID and GC- TCD.

PART 1

Comparing the performance of Pd/SSP, CeO$_2$/SSP catalysts and ceria modification under oxygen cofeed during ethanol reactions.

4.1 Characterization of Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP

Three catalysts are synthesized by incipient wetness impregnation. The physical properties of catalysts are analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), and N$_2$ physisorption (BET&BJH).

4.1.1 X-ray diffraction (XRD)
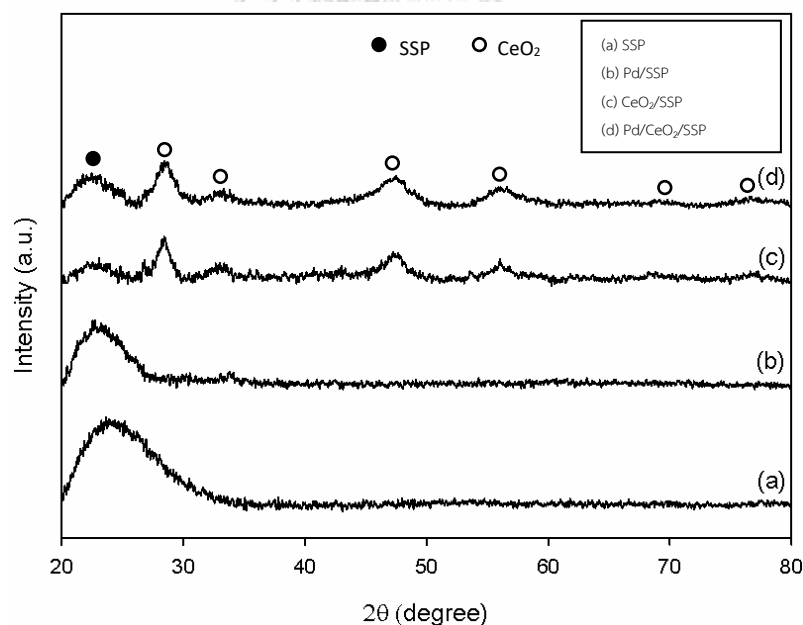
Figure 8 XRD patterns of SSP (a.), Pd/SSP (b.), CeO$_2$/SSP (c.) and Pd/CeO$_2$/SSP (d.)

The crystalline phases of all catalysts were analyzed by XRD method as shown in Figure 8. The XRD patterns of SSP present only amorphous silica in broad peak at 25.3° [15]. In Pd/SSP, it cannot be detected Pd peak because Pd was added only few amounts. A number of reflections at 28.8, 32.8, 47.3, 55.9 and 76.8° show well dispersed CeO$_2$ in the Pd/CeO$_2$/SSP [24].

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

Morphology and element distribution of catalysts can be obtained as proven by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. The morphology of catalysts is shown in Figure 9. Morphologies of spherical silica particles (SSP), CeO_2/SSP, and Pd/CeO_2/SSP are illustrated in Figure 9 (a). (c). and (d). It can be observed that the shape of catalysts seems to be spherical. Morphologies image of Pd/SSP partially change with addition of a low amount of Pd, according to Figure 9 (b). However, the SEM-EDX images of all catalysts confirm that Pd and CeO_2 were sequentially deposited on the surface of SSP.
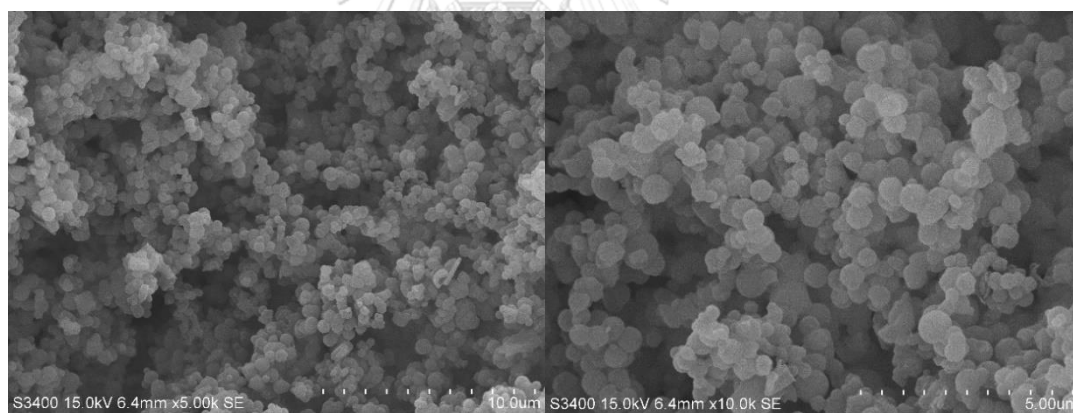
(a).
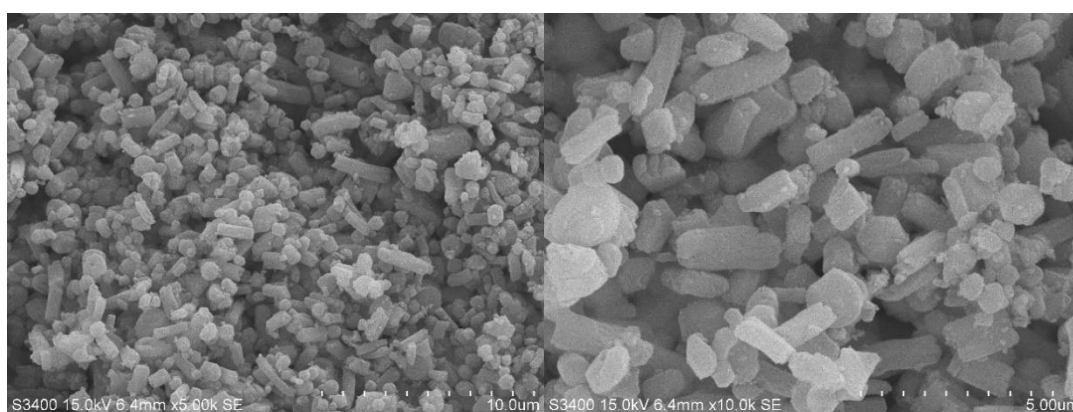
(b).
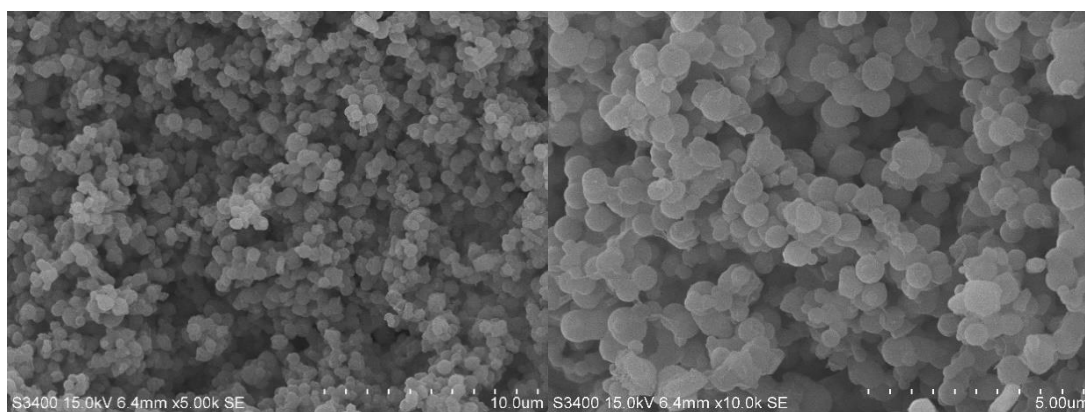
(c).
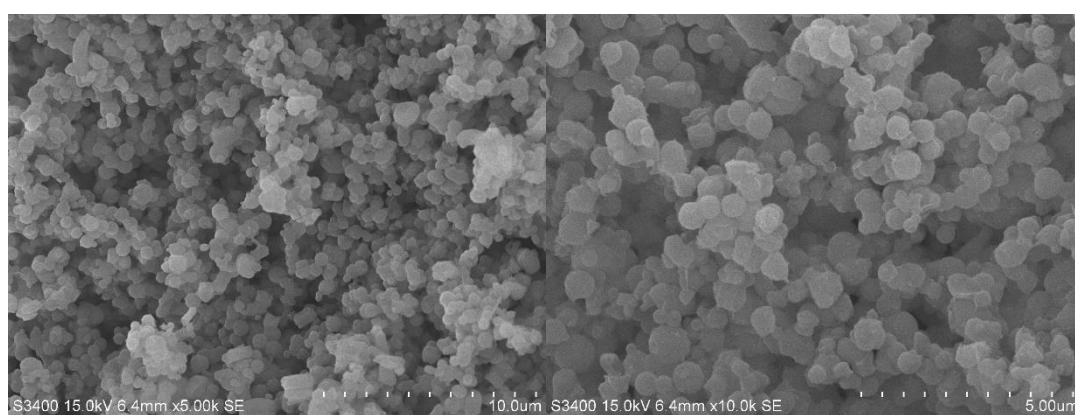
(d).

Figure 9 SEM image of SSP support (a), Pd/SSP (b), CeO_2/SSP (c) and Pd/CeO_2/SSP (d)

respectively.
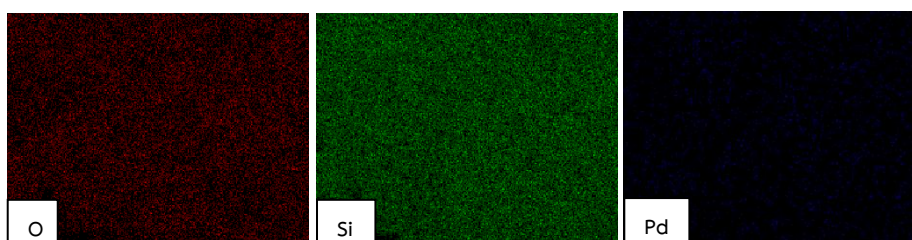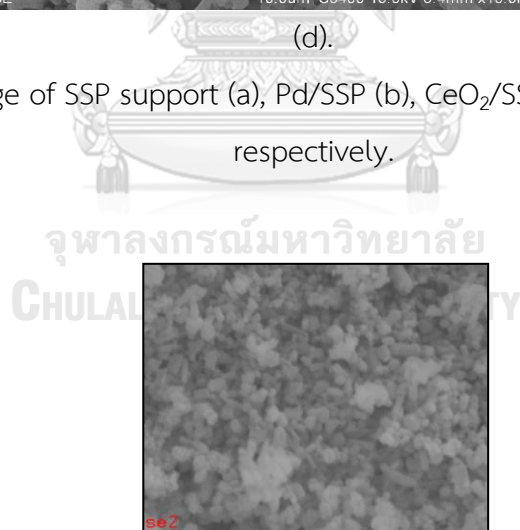
Figure 10 SEM-EDX mapping of Pd/SSP
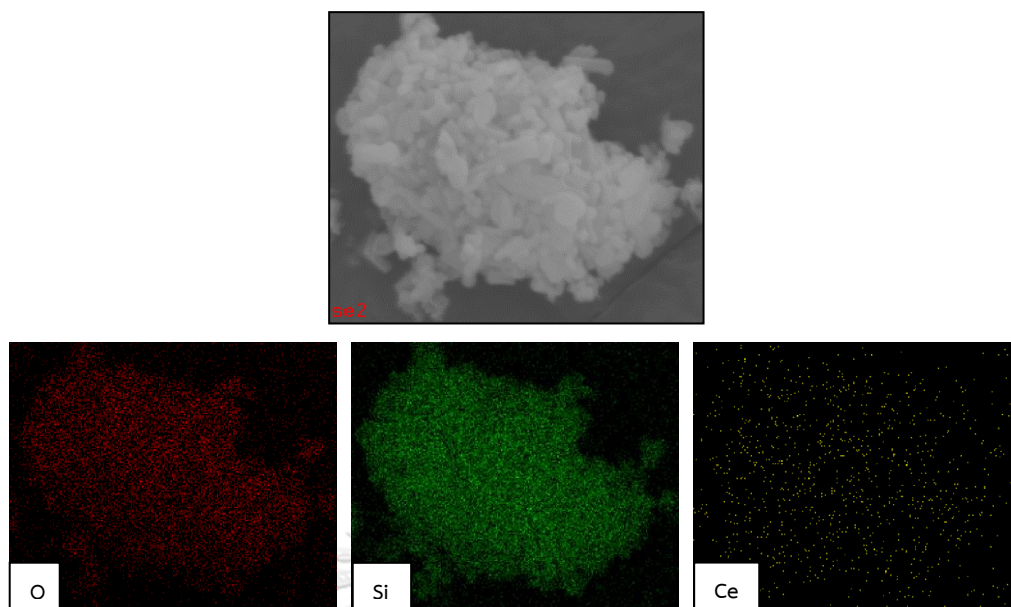
Figure 11 SEM-EDX mapping of CeO$_2$/SSP
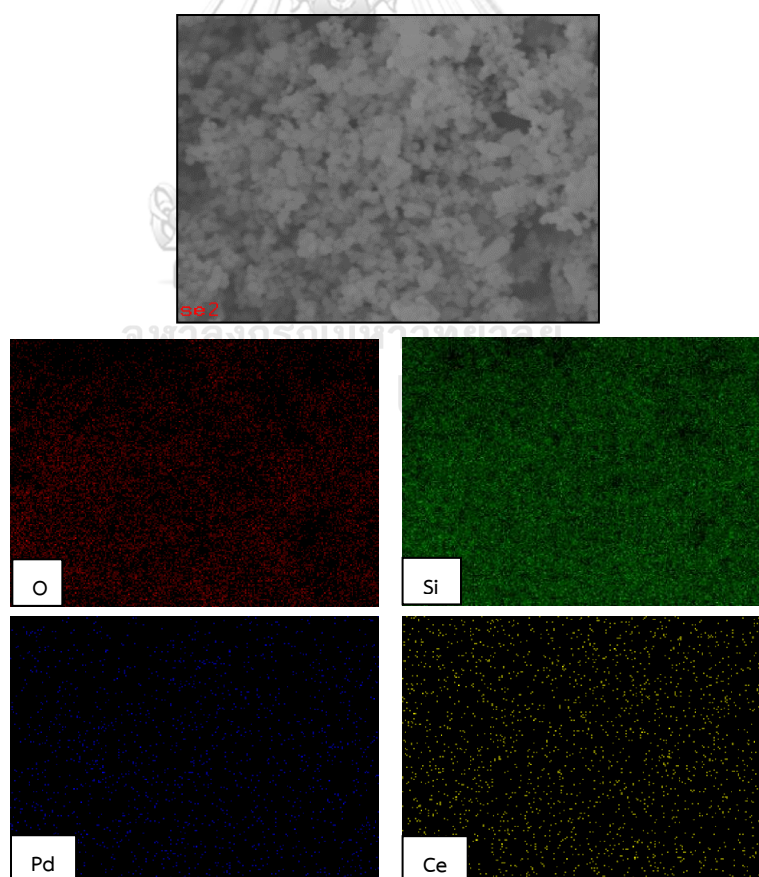
Figure 12 SEM-EDX mapping of Pd/CeO$_2$/SSP

The SEM-EDX mappings of Pd/SSP is illustrated in Figure 10. It reveals element distribution of palladium metal, silicon and oxygen (Pd, Si and O). Element distribution of CeO_2/SSP catalyst had metal cerium, silicon and oxygen (Ce, Si and O) shown in Figure 11 and palladium metal, cerium, silicon and oxygen (Pd, Ce, Si and O) distribution of Pd/CeO_2/SSP as shown in Figure 12. It indicated that all metals have well dispersion on surface catalysts. The amounts of elements distribution in weight percent are shown in Table 6.

Table 6 Element distribution of Pd/SSP, CeO_2/SSP and Pd/CeO_2/SSP (weight percent)

Catalyst	Element distribution (wt %)			
	Pd	Ce	O	Si
Pd/SSP	0.57	-	42.74	56.69
CeO_2/SSP	-	5.42	40.84	53.75
Pd/CeO_2/SSP	0.59	6.19	32.55	60.67

4.1.3 N_2 physisorption (BET&BJH)

Surface area, pore volume, pore size, and isotherm graph of catalysts were investigated by N_2 physisorption technique. The results from N_2 physisorption are reported in Table 7. The high BET surface area of the SSP support is 1064 m²/g, while BET surface area and pore volume decrease after adding of Pd particles. It causes by pore blockage with Pd loading [25]. The pore size can indicate that all catalysts are in mesoporous range (2-50 nm). The isotherms were found to be similar type of isotherm (isotherm type 4) as shown in Figure 13. and appear hysteresis loop in all catalysts. The hysteresis loop is an obvious proof that all catalysts were mesoporous structure.

Table 7 BET surface area, pore size and pore volume of SSP, Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP

Catalyst	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)	Pore size[c] (nm)
SSP support	1064	0.84	2.4
Pd/SSP	675	0.67	3.5
CeO$_2$/SSP	461	0.29	2.9
Pd/CeO$_2$/SSP	809	0.62	2.9

[a] Determined from BET method

[b,c] Determined from BJH desorption method
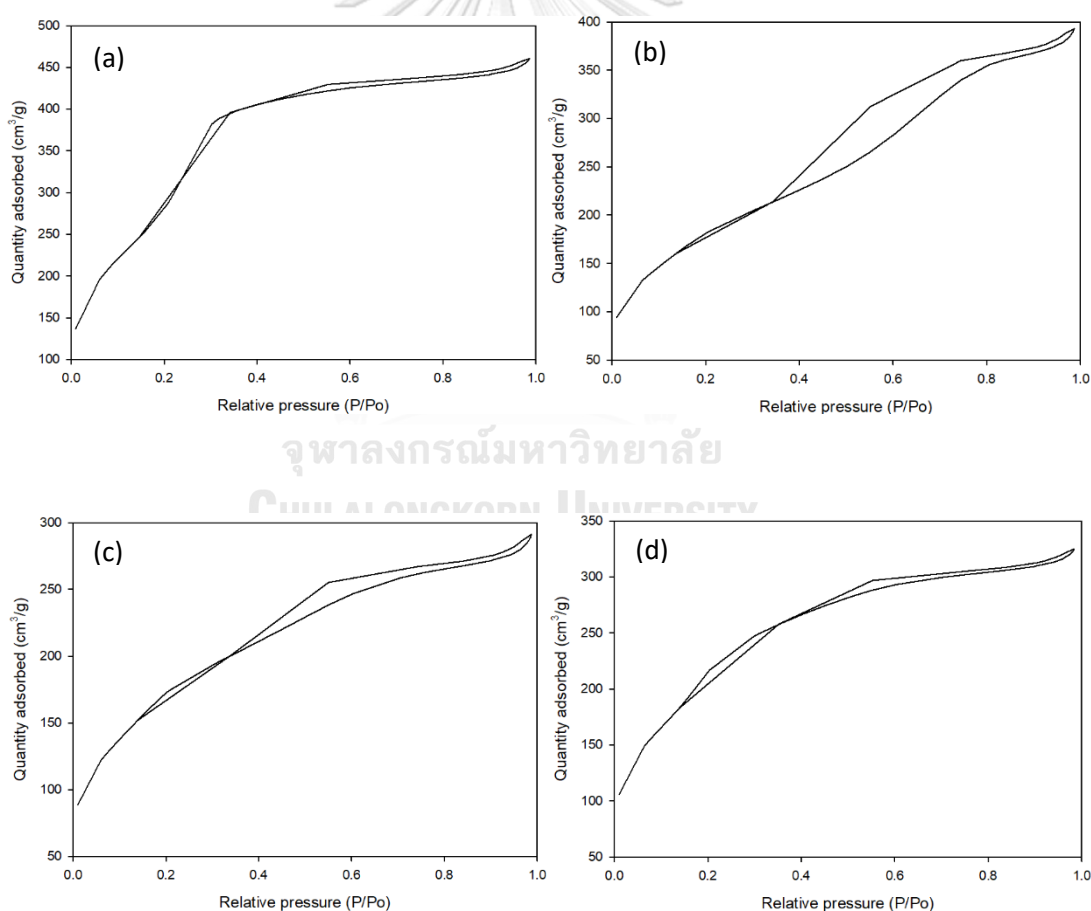
Figure 13 Isotherm graph of catalysts; (a). SSP support (b). Pd/SSP, (c) CeO$_2$/SSP and (d). Pd/CeO$_2$/SSP

4.1.4 Temperature programmed reduction (TPR)

Figure 14 show H_2-TPR results of catalysts. CeO_2/SSP shows TPR peak ranging from 350 to 650 °C was associated with reduction of surface oxygen of CeO_2. H_2-TPR of Pd/SSP shows reduction peaks at 102 °C is ascribed to the reduction of PdO to Pd metal. For Pd-CeO_2/SSP catalyst, one major peak at 204 °C is assigned to the reduction of the species related to the PdO–CeO_2 interaction.
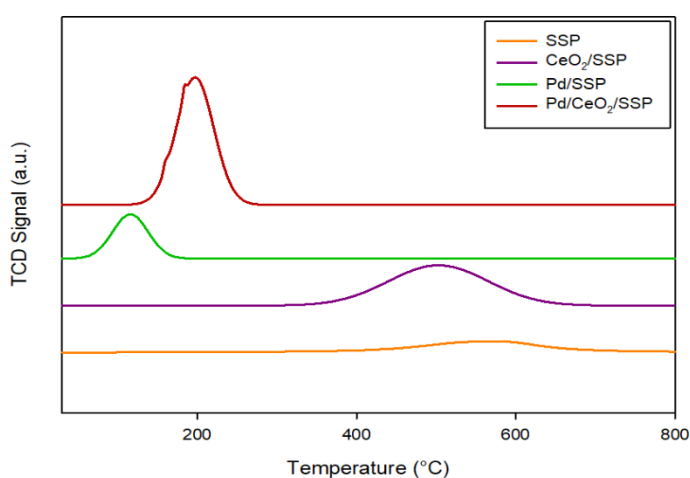
Figure 14 H_2-TPR profile of SSP, CeO_2/SSP, Pd/SSP and Pd/CeO_2/SSP

4.1.5 Ammonia temperature programmed desorption (NH_3-TPD)

NH_3-TPD was used to characterize the acidic properties of catalysts. NH_3-TPD profiles of samples are shown in Figure 15. The NH_3-TPD profile of all catalysts show low temperature (< 200 °C). Table 8 shows acidity of catalysts. For Pd/SSP has highest acidity of 609.19 μmol NH_3/g and CeO_2/SSP is lowest acidity of 194.42 μmol NH_3/g
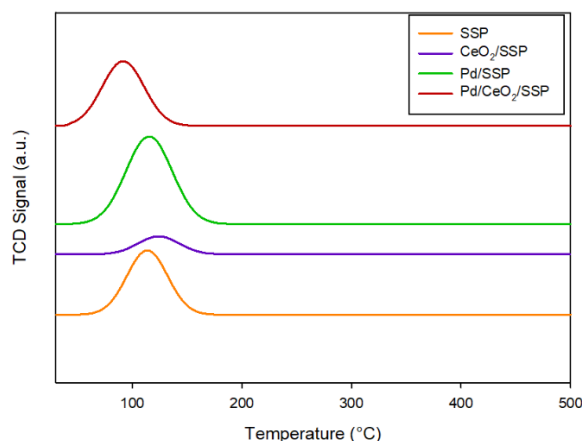
Figure 15 NH$_3$-TPD profile of SSP, CeO$_2$/SSP, Pd/SSP and Pd/CeO$_2$/SSP

Table 8 Acidity of catalysts

Sample	Acidity (μmol NH$_3$/g)
SSP	320.32
CeO$_2$/SSP	194.42
Pd/SSP	609.19
Pd/CeO$_2$/SSP	445.64

4.1.6 Ethanol dehydration reaction with oxygen cofeeding

The catalytic ethanol dehydration with oxygen cofeeding to ethylene over Pd/SSP, CeO$_2$/SSP and ceria modification catalysts was tested in fixed-bed continuous flow microreactor at temperature 150 °C to 350 °C and atmospheric pressure. Table 9 shows conversion and selectivity of all catalysts. The ethanol conversion increases with increased reaction temperature for all catalysts as shown in Figure 17. However, the results obtained from catalytic activity studies indicate ability of Pd/SSP and Pd/CeO$_2$/SSP at low temperature of 175 and 200 °C having the conversion of 51.1% and 57.7%, respectively. On the other hand, CeO$_2$/SSP has low conversion at low temperature.

The ethylene selectivity of Pd/CeO$_2$/SSP was higher than Pd/SSP at 200 °C because of the high ability of CeO$_2$ in oxygen storage for uses in the reaction. For carbon dioxide selectivity, it was found in hydrocarbon combustion that feeding oxygen with hydrocarbon, shows that in Pd/CeO$_2$/SSP has CO$_2$ selectivity lower than Pd/SSP.
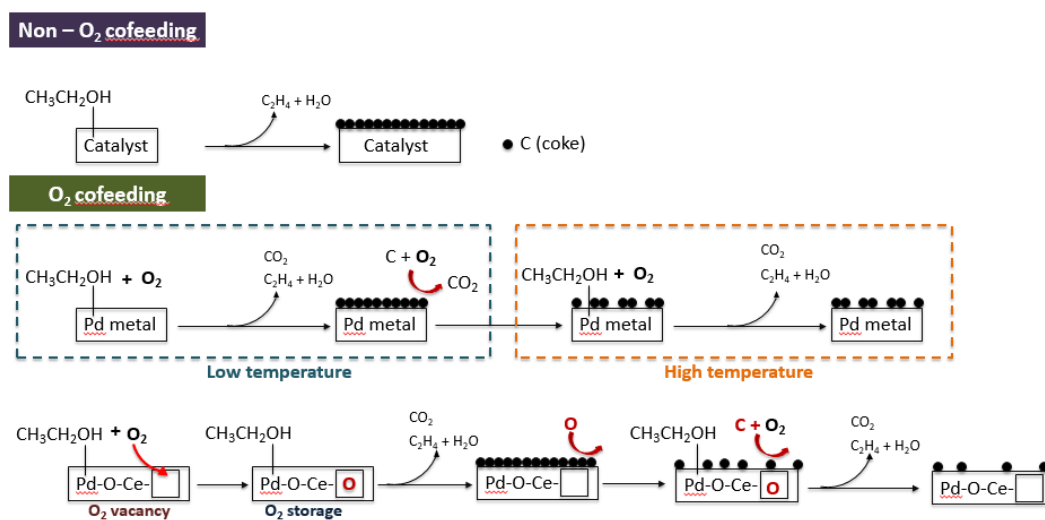
Figure 16 Proposed mechanism of ethanol dehydration reaction with non-oxygen and oxygen cofeeding.

Figure 16 shows mechanism was proposed from experimental. For non-oxygen cofeeding indicated very active catalysts produce coke formation on surface of catalysts. For oxygen cofeeding is divided two types of catalysts; Pd/SSP catalyst was reacted and formed coke after that oxygen in feed contribute to coke burning result in high conversion. For ceria modification catalysts have oxygen vacancy that keep oxygen result in oxygen cannot burn coke. After increasing temperature to 200 °C affect oxygen was release conduce to burned coke together with oxygen in feed that cause coke on surface of catalyst was burned more than Pd/SSP catalyst result in conversion of ceria modification catalysts higher than conversion of Pd/SSP catalysts.

Table 9 Conversion and product selectivity of Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP catalysts

Catalysts	Temperature (°C)	Ethanol conversion (%)	Product selectivity (%)			
			Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
Pd/SSP	150	1.57	6.4	93.6	0.0	0.0
	175	51.1	22.4	9.0	1.1	67.5
	200	50.6	23.3	10.0	1.2	65.5
	250	51.0	21.7	10.0	2.1	66.2
	300	50.8	21.4	12.3	1.5	64.9
	350	54.7	23.7	8.2	2.3	65.7
CeO$_2$/SSP	150	0	0	0	0	0
	175	0	0	0	0	0
	200	0.1	0	100	0	0
	250	0.4	0	100	0	0
	300	3.9	1.4	84.0	4.8	9.8
	350	64.7	7.6	27.9	26.8	37.6
Pd/CeO$_2$/SSP	150	1.5	6.2	93.8	0	0
	175	1.8	5.5	85.7	0	8.8
	200	57.7	26.6	8.9	0	64.6
	250	53.3	27.0	11.8	0	61.2
	300	52.9	25.1	10.1	0.3	64.5
	350	58.9	24.3	9.0	0.5	66.1

Figure 17 Ethanol conversion vs temperature of Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP catalysts.

Figures 17 and 18 show that ethanol conversion and ethylene selectivity, respectively. For Pd/SSP, ethanol can be converted to ethylene at lower temperature (ca. 175 °C). However, when the temperature increases to 200 °C it can be observed that ethanol conversion and ethylene selectivity of Pd/CeO$_2$/SSP were higher than Pd/SSP due to palladium and ceria promoted as seen in Figure 16. It shows that CeO$_2$ is oxygen storage for use in reaction leading to facilitate the formation of ethylene. Figure 19 shows CO$_2$ selectivity of all catalysts at temperature range of 150 °C to 400 °C. CO$_2$ selectivity of Pd/CeO$_2$/SSP is lower than Pd/SSP
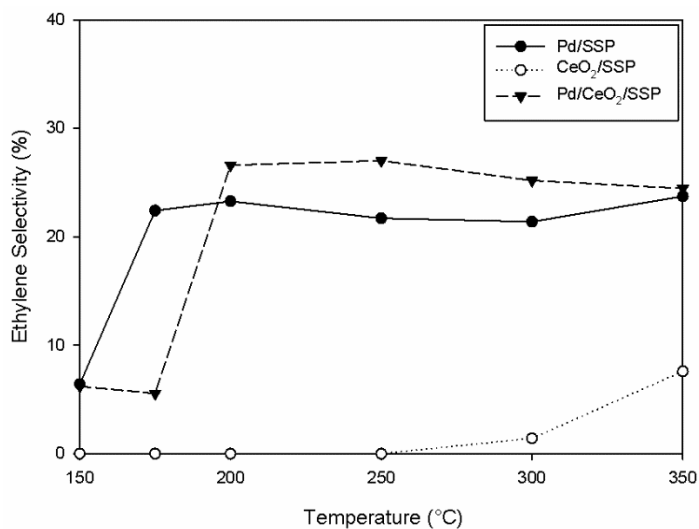
Figure 18 Ethylene selectivity vs temperature of Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP catalysts
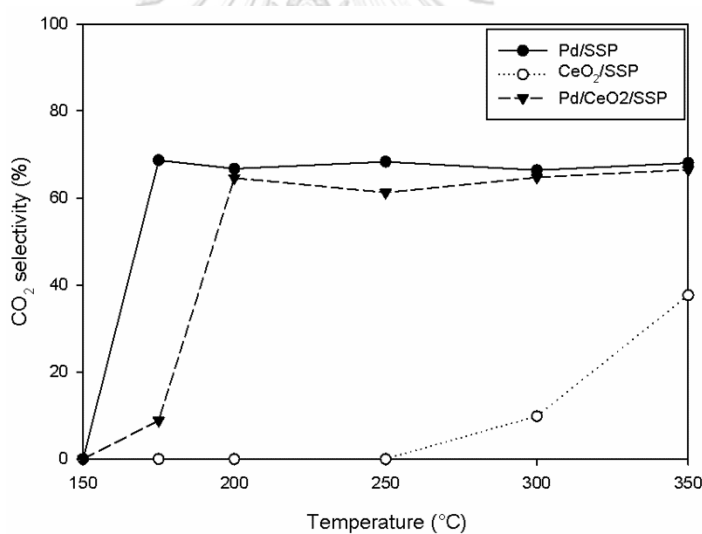
Figure 19 CO$_2$ selectivity vs temperature of Pd/SSP, CeO$_2$/SSP and Pd/CeO$_2$/SSP catalysts

From all results, it can be concluded that the ceria modification on palladium catalysts supported on spherical silica particle importantly affects the catalytic ethanol dehydration with oxygen cofeeding to ethylene.

PART 2

Comparing the performance of ceria modification with different sequence of loading under oxygen cofeed during ethanol reactions.

4.2 Characterization of ceria modification with different sequence of loading catalysts

From part 4.1, ceria modification catalyst gave the highest ethanol conversion and ethylene selectivity. Therefore, in this part ceria modification was investigated with different sequence of loading by incipient wetness impregnation method and calcined at 400 °C for 4 h. The properties of catalysts are investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), H_2-Temperature programmed reduction (H_2-TPR) and N_2 physisorption (BET&BJH).

4.2.1 X-ray diffraction (XRD)

The XRD patterns in Figure 20 show those of $Pd/CeO_2/SSP$, $CeO_2/Pd/SSP$ and $Pd-CeO_2/SSP$, which were measured at diffraction angle (2θ) from 20° to 80°. The diffraction patterns of the ceria modification with different sequence of loading show similar peak of SSP and CeO_2. However, Pd peak did not appear due to Pd was added only few amounts. The XRD patterns of SSP present only reveal the amorphous silica in broad peak at 25.3° and a number of reflections at 28.8, 32.8, 47.3, 55.9, 69.8 and 76.8° show well dispersed CeO_2. Crystallite sizes of $Pd/CeO_2/SSP$, $CeO_2/Pd/SSP$ and $Pd-CeO_2/SSP$ are shown in Table 10. It can be observed that $Pd-CeO_2/SSP$ has the highest crystallite size (ca. 5.4 nm) and lowest crystallite size is obtained from $CeO_2/Pd/SSP$ (ca. 4.6 nm).
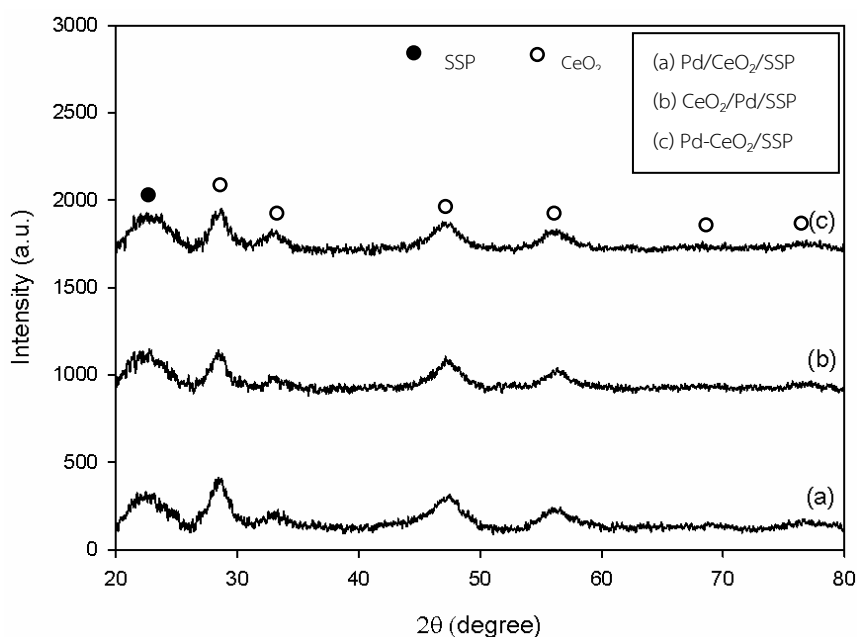
Figure 20 XRD patterns of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP

Table 10 Crystallite size from X-ray diffraction (XRD) technique.

Catalysts	Crystallite Size (nm)
Pd/CeO$_2$/SSP	5.2
CeO$_2$/Pd/SSP	4.6
Pd-CeO$_2$/SSP	5.4

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

Palladium and ceria distribution over spherical silica particles (SSP) support can be obtained as proven by scanning electron microscope (SEM) as shown in Figure 21 and energy dispersive X-ray spectroscopy (EDX) as shown in Figures 22-24. The morphology of Pd/CeO$_2$/SSP catalysts can be observed that the shape of catalysts seems to be spherical. CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP catalysts have similar shape.

This can be concluded that different sequence of loading by incipient wetness impregnation technique may have only little effect on morphology.

(a).

(b).

(c).
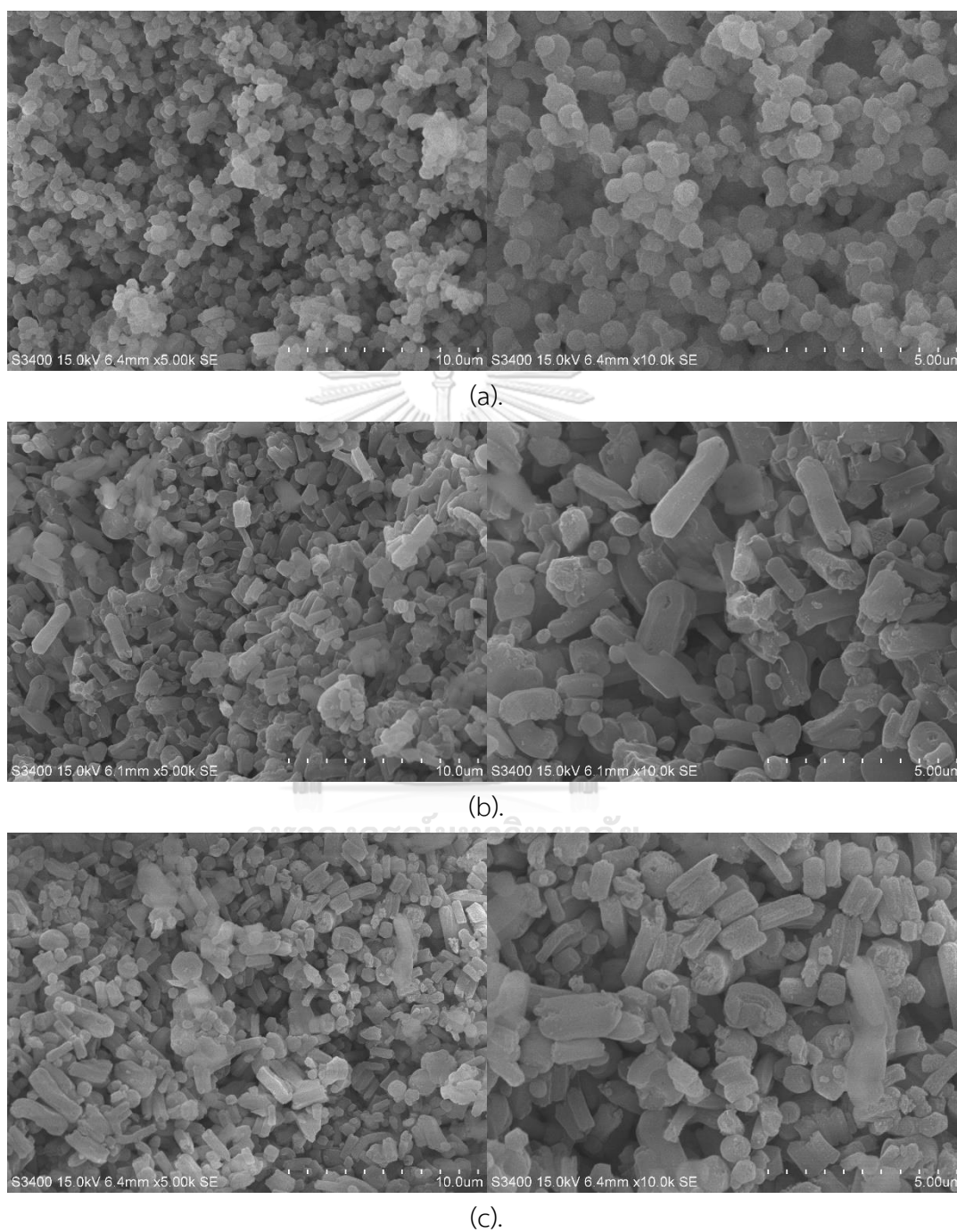
Figure 21 SEM image of (a) Pd/ CeO$_2$/SSP, (b) CeO$_2$/Pd/SSP, (c) Pd-CeO$_2$/SSP
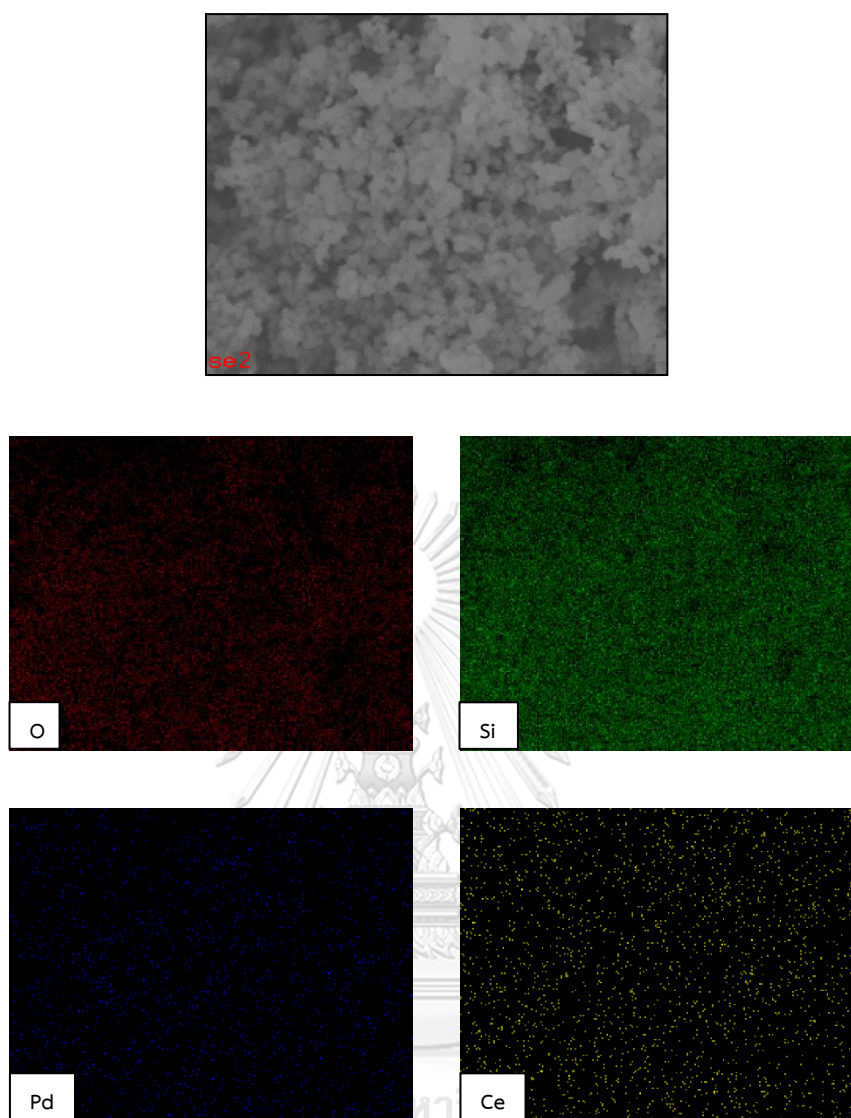
Figure 22 SEM-EDX mapping of Pd/CeO$_2$/SSP
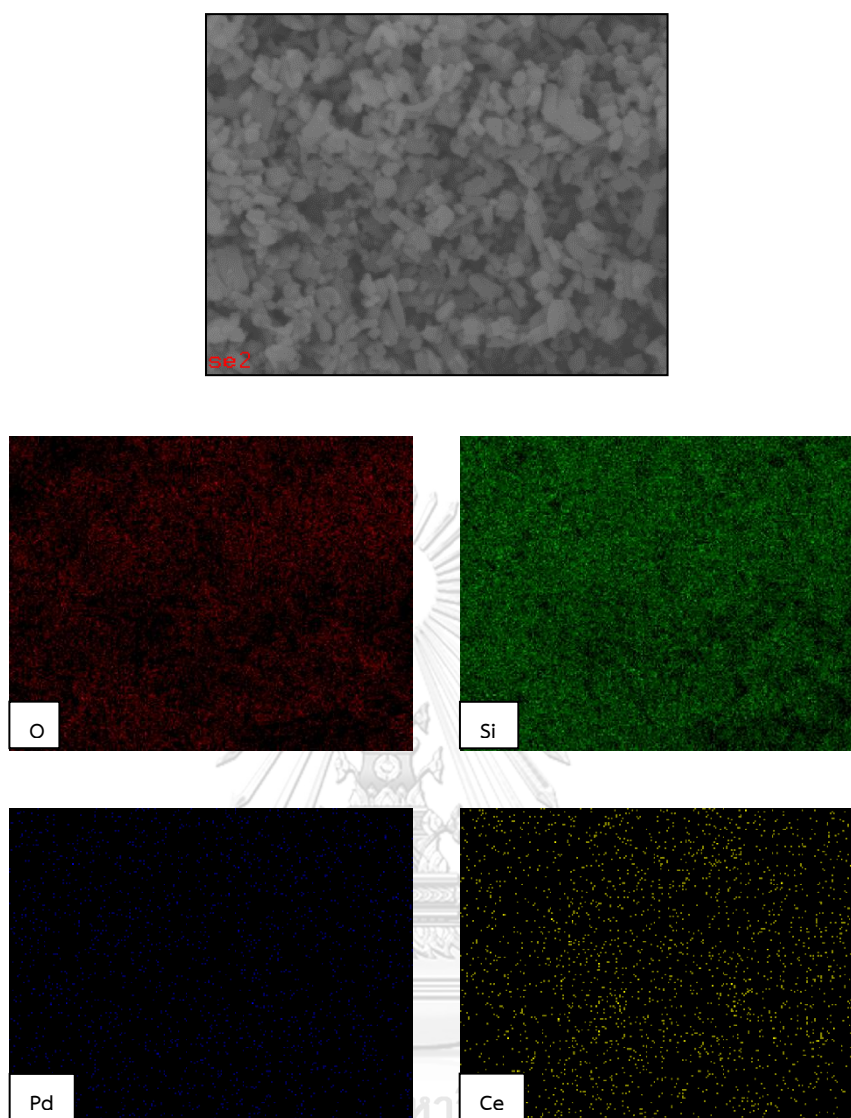
Figure 23 SEM-EDX mapping of CeO$_2$/Pd/SSP
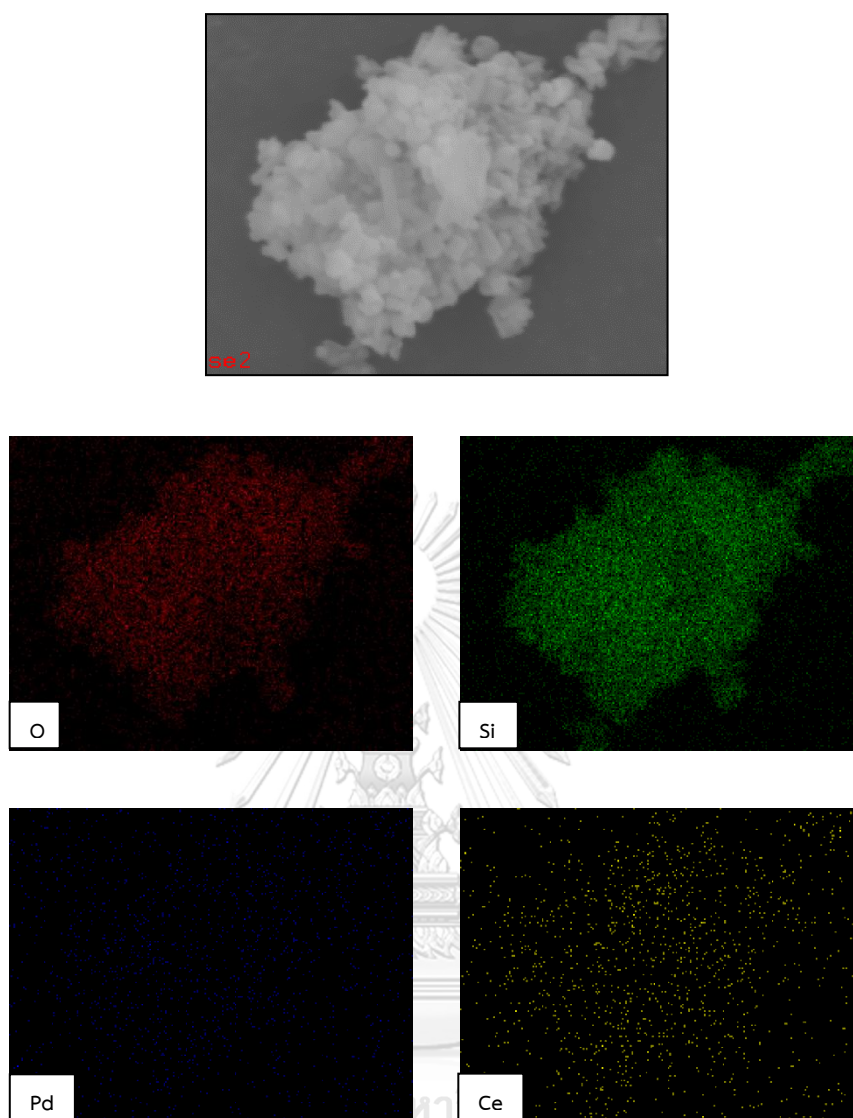
Figure 24 SEM-EDX mapping of Pd-CeO$_2$/SSP

Figures 22 to 24 display element distribution of oxygen (red) , silicon (green), palladium (blue) and cerium (yellow) over $Pd/CeO_2/SSP$, $CeO_2/Pd/SSP$ and Pd-CeO_2/SSP respectively. It can be detected that all metals (Pd, Ce and O) have well dispersion on surface of catalysts from SEM-EDX image. The amounts of elements distribution in weight percent of all catalysts are shown in Table 11.

Table 11 Element distribution of $Pd/CeO_2/SSP$, $CeO_2/Pd/SSP$ and Pd-CeO_2/SSP (weight percent)

Catalyst	Element distribution (wt %)			
	Pd	Ce	O	Si
$Pd/CeO_2/SSP$	0.59	6.19	32.55	60.67
$CeO_2/Pd/SSP$	0.19	6.05	36.01	57.76
Pd-CeO_2/SSP	1.95	7.14	38.39	52.51

4.2.3 H_2-Temperature programmed reduction (H_2-TPR)

Figure 25 show H_2-TPR results of ceria modification with different impregnation sequence of loading. It can be seen from Figure 25 that there were two distinct reduction peaks centered at 140 and 190 °C, respectively. For Pd-CeO_2/SSP catalyst, one major peak at 198 °C and one shoulder peak at 242 °C for $CeO_2/Pd/SSP$, and small shoulder peak at 161 °C and major peak at 204 °C can be observed from TPR profiles indicate a strong interaction between promoters and Pd existed. Therefore, it may be suitable to suppose that the H_2-TPR profiles of the catalysts could be attributed to the reduction of mixed metal oxides.
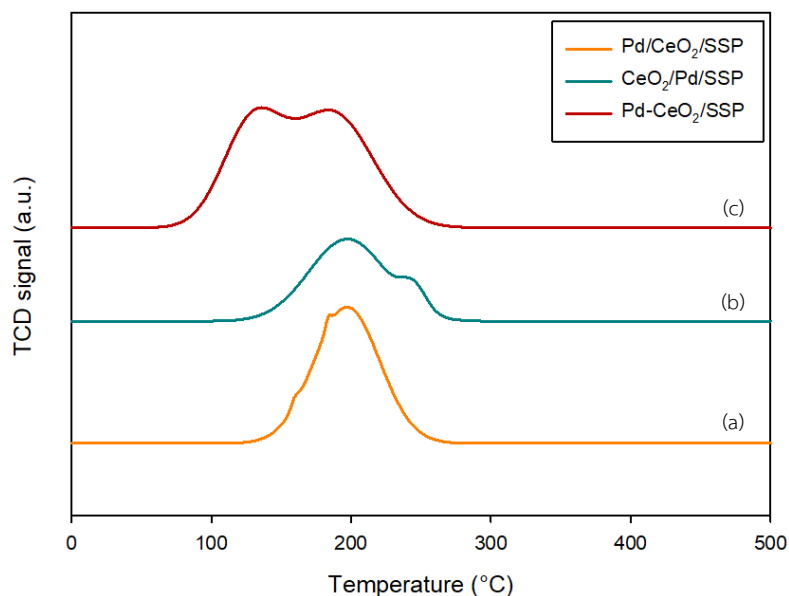
Figure 25 H₂-TPR profile of catalysts with different impregnation sequence. (a) Pd/CeO₂/SSP; (b) CeO₂/Pd/SSP and (c) Pd-CeO₂/SSP

4.2.4 Ammonia temperature programmed desorption (NH₃-TPD)

NH₃-TPD was used to characterize the acidic properties of catalysts. NH₃-TPD profiles of samples are shown in Figure 26. The NH₃-TPD profile of all catalysts show temperature lower than 200 °C. Table 12 shows acidity of catalysts. For Pd-CeO₂/SSP has highest acidity of 521.59 μmol NH₃/g and CeO₂/Pd/SSP is lowest acidity of 339.10 μmol NH₃/g

Table 12 Acidity of catalysts with different impregnation sequence.

Sample	Acidity (μmol NH₃/g)
Pd/CeO₂/SSP	445.64
CeO₂/Pd/SSP	339.10
Pd-CeO₂/SSP	521.59
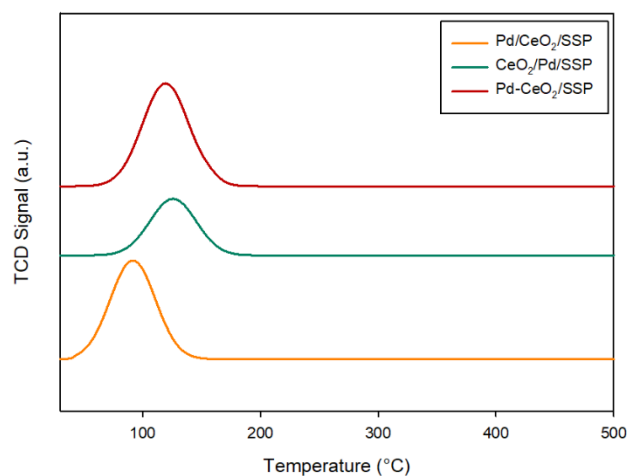
Figure 26 NH$_3$-TPD profile of catalysts with different impregnation sequence. (a) Pd/CeO$_2$/SSP; (b) CeO$_2$/Pd/SSP and (c) Pd-CeO$_2$/SSP

4.2.5 N$_2$ physisorption (BET&BJH).

Table 13 lists the specific surface area, pore volume and pore diameter of catalysts. As can be seen from Table 13, the pore size of the catalysts shows little difference. The highest surface area and pore volume for Pd/CeO$_2$/SSP are 809 m^2/g and 0.62 cm^3/g, respectively. This indicates changes in the specific surface area as the result of impregnation sequence that will fundamentally affect the activity and selectivity of the catalysts.

Table 13 BET surface area, pore size and pore volume of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Pd/CeO$_2$/SSP	809	0.62	2.9
CeO$_2$/Pd/SSP	645	0.45	3.0
Pd-CeO$_2$/SSP	738	0.42	2.7

4.2.6 Ethanol dehydration reaction with oxygen cofeeding

From part 4.1, It indicates that the ceria modification result in the highest conversion and ethylene selectivity in ethanol dehydration with oxygen cofeeding in temperature at 200 °C. In this part, to further optimize the performance of the catalyst, the preparation method should be investigated since different preparation methods might have an effect on the interaction between Pd and promoter using same condition with part 4.1 (temperature programmed 150 °C – 350 °C, atmospheric pressure). The results of all catalyst are shown in Table 14.

Table 14 Conversion and product selectivity of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP catalysts

Catalysts	Temperature (°C)	Ethanol conversion (%)	Product selectivity (%)			
			Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
Pd/CeO$_2$/SSP	150	1.5	6.2	93.8	0	0
	175	1.8	5.5	85.7	0	8.8
	200	57.7	26.6	8.9	0	64.6
	250	53.3	27.0	11.8	0	61.2
	300	52.9	25.1	10.1	0.3	64.5
	350	58.9	24.3	9.0	0.5	66.1
CeO$_2$/Pd/SSP	150	1.0	3.6	96.4	0.0	0.0
	175	2.6	7.4	76.2	0.0	16.4
	200	58.9	20.1	13.2	0.0	66.8
	250	58.1	17.9	13.2	0.1	68.8
	300	59.5	18.8	11.4	0.3	69.5
	350	57.6	18.7	18.2	1.6	61.5
Pd-CeO$_2$/SSP	150	0.4	2.5	97.5	0.0	0.0
	175	1.3	5.7	81.9	0.0	12.4
	200	66.0	29.5	5.3	0.3	64.9
	250	65.3	31.1	5.1	0.3	63.5
	300	65.8	30.4	4.0	0.3	65.4
	350	70.6	34.2	7.0	0.4	58.4

Figure 27 Ethanol conversion vs temperature of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP catalysts.

Ethanol conversion is shown in Figure 27. It can be seen that ethanol conversion of each catalyst increased with increasing temperature. The Pd-CeO$_2$/SSP gave the highest ethanol conversion for 66 % and highest ethylene selectivity of 29.5% as seen from Figure 28 at 200 °C due to synergy effect of Pd-CeO$_2$/SSP catalyst prepared by co-impregnation that may promote the formation of more active site for ethanol formation [14].
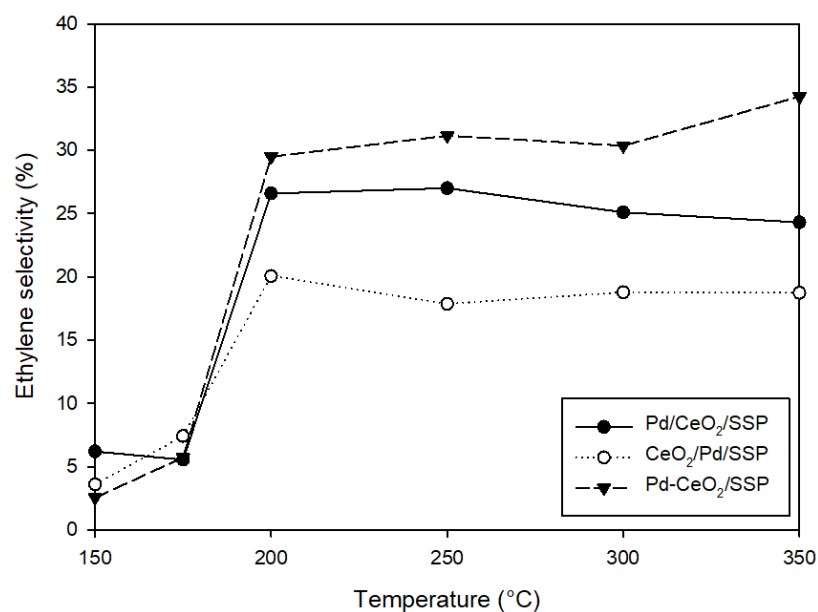
Figure 28 Ethylene selectivity vs temperature of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP catalysts.

Figure 29 shows CO$_2$ selectivity of ceria modification with different sequence of loading. As can be seen from Figure 26, CO$_2$ selectivity of the catalysts shows little different result in impregnation sequence that will not fundamentally affect the activity and selectivity of the catalysts.
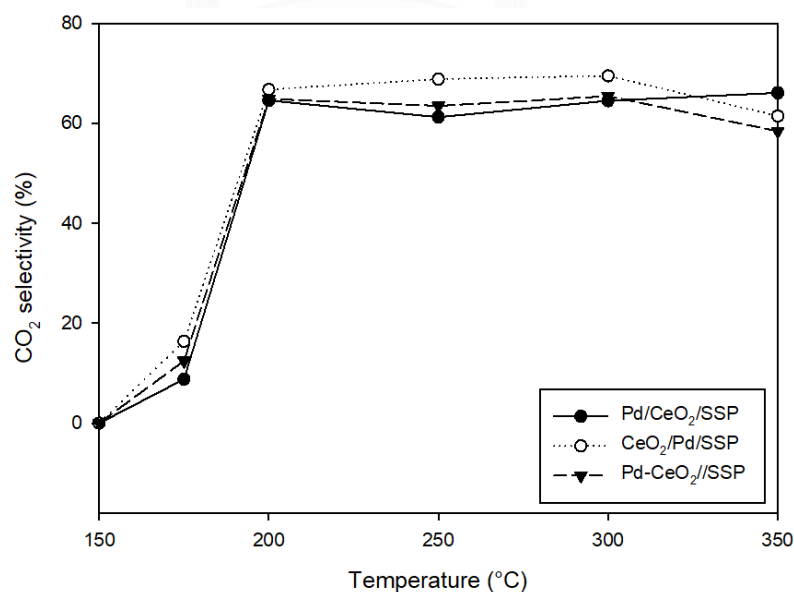
Figure 29 CO$_2$ selectivity vs temperature of Pd/CeO$_2$/SSP, CeO$_2$/Pd/SSP and Pd-CeO$_2$/SSP catalysts.

PART 3

Comparing the performance of Pd/SSP catalyst and the most suitable ceria modification in oxygen cofeed during ethanol reactions with various amounts of oxygen cofeed.

4.3 Ethanol dehydration reaction with oxygen cofeeding with various amounts of oxygen cofeed.

In part 4.3, this work is investigation of various amounts of oxygen cofeed over Pd/SSP and the most suitable ceria modification from part 4.2 in ethanol dehydration in all temperature range (150 °C – 350 °C). The ethanol conversion and products selectivity of Pd/SSP and Pd-CeO$_2$/SSP catalysts with different molar ratio of oxygen to ethanol (0, 1.1 and 2.2) are reported in Table 15. For all catalysts, it shows that the ethanol conversion, ethylene selectivity and CO$_2$ selectivity decreases with decreasing amount of oxygen.

Table 15 Ethanol conversion and products selectivity of Pd/SSP and Pd-CeO2/SSP with various amounts of oxygen cofeed.

Catalyst	O$_2$/EtOH	Temperature (°C)	Conversion (%)	Product selectivity (%)			
				Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
Pd/SSP	0	150	0	0	0	0	0
		175	0	0	0	0	0
		200	0	0	0	0	0
		250	0	0	0	0	0
		300	76.9	76.9	0	23.1	0
		350	62.4	62.4	0	37.6	0
	1.1	150	1.6	5.8	78.9	0.0	15.2
		175	29.3	21.2	18.0	2.8	58.0
		200	35.3	22.0	15.8	2.9	59.4
		250	34.3	21.5	16.3	3.9	58.3

		300	31.1	20.3	19.0	2.5	58.3
		350	30.8	21.4	21.3	1.9	55.4
		150	1.6	6.4	93.6	0	0
		175	51.1	22.4	9.0	1.1	67.5
	2.2	200	50.6	23.3	10.0	1.2	65.5
		250	51.0	21.7	10.0	2.1	66.2
		300	50.8	21.4	12.3	1.5	64.9
		350	54.8	23.7	8.2	2.3	65.7
		150	0	0	0	0	0
		175	0	0	0	0	0
	0	200	0	0	0	0	0
		250	0	0	0	0	0
		300	2.1	82.5	0	17.5	0
		350	3.1	72.6	0	27.4	0
Pd-CeO$_2$/SSP		150	0.5	2.8	97.2	0	0
		175	1.3	6.1	83.8	0	10.1
	1.1	200	2.8	9.2	73.4	0	17.4
		250	31.3	23.4	20.4	0.6	55.6
		300	33.6	24.0	19.3	0.4	56.3
		350	32.5	24.0	23.7	1.0	51.3
		150	0.4	2.5	97.5	0	0
		175	1.3	5.7	81.9	0	12.4
	2.2	200	66.0	29.5	5.3	0.3	64.9
		250	65.3	31.1	5.1	0.3	63.5
		300	65.8	30.4	4.0	0.3	65.4
		350	70.6	34.2	7.0	0.4	58.4

Ethanol conversion of Pd/ SSP and Pd-CeO$_2$/SSP catalysts with different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 is shown in Figures 30 and 31. It can be seen that conversion decreased when O$_2$/Ethanol molar ratio was decreased. This indicated that amount of oxygen cofeeding significantly influenced the activities of catalysts. For Pd/SSP, decreased O$_2$/Ethanol molar ratio resulted in decreased conversion less compared to those of Pd-CeO$_2$/SSP. For Pd-CeO$_2$/SSP. Starting point

of ethanol conversion and ethylene yield (Figures 32 and 33) shift from 200 °C to 250 °C due to amount of O_2 in feed essentially affects CeO_2 in catalyst. Figures 34 and 35 show CO_2 yield indicating that all catalysts has similar trend with ethylene yield when O_2/EtOH molar ratio was decreased.

Figure 30 Ethanol conversion vs temperature of Pd/ SSP and Pd-CeO_2/SSP catalysts with different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (line plot)

Figure 31 Ethanol conversion vs temperature of Pd/ SSP and Pd-CeO_2/SSP catalysts with different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (bar chart)
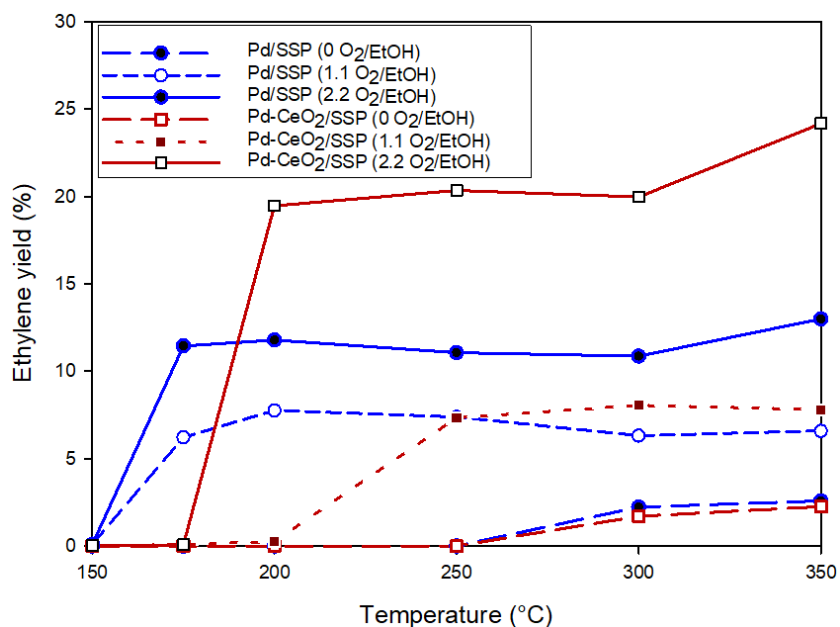
Figure 32 Ethylene yield vs temperature of Pd/ SSP and Pd-CeO$_2$/SSP catalysts with
different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (line plot)
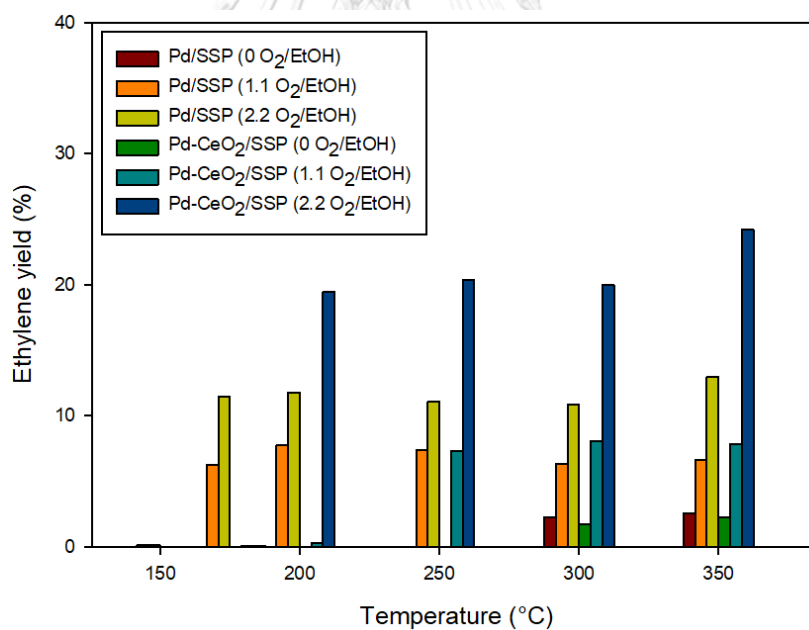
Figure 33 Ethylene yield vs temperature of Pd/ SSP and Pd-CeO$_2$/SSP catalysts with
different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (bar chart)
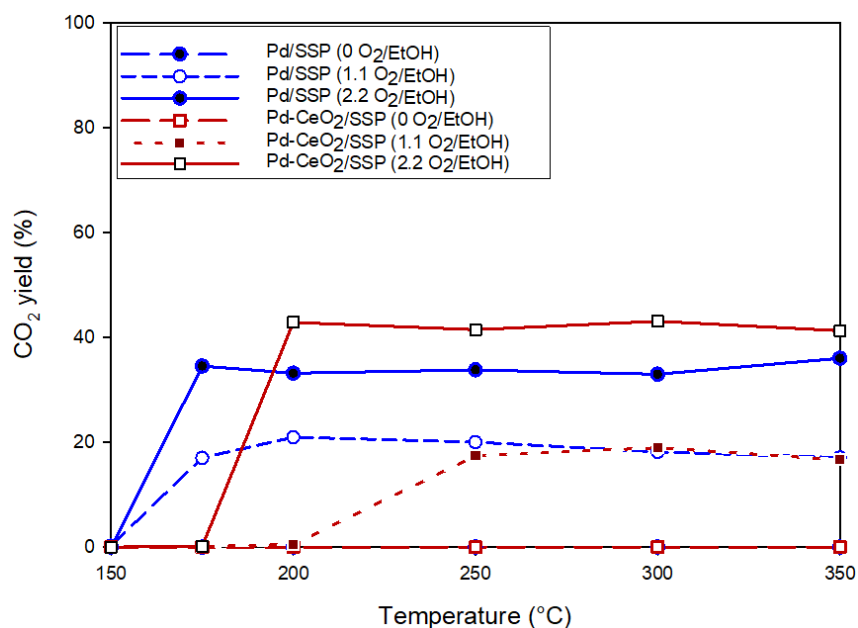
Figure 34 CO_2 yield vs temperature of Pd/ SSP and Pd-CeO_2/SSP catalysts with different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (line plot)

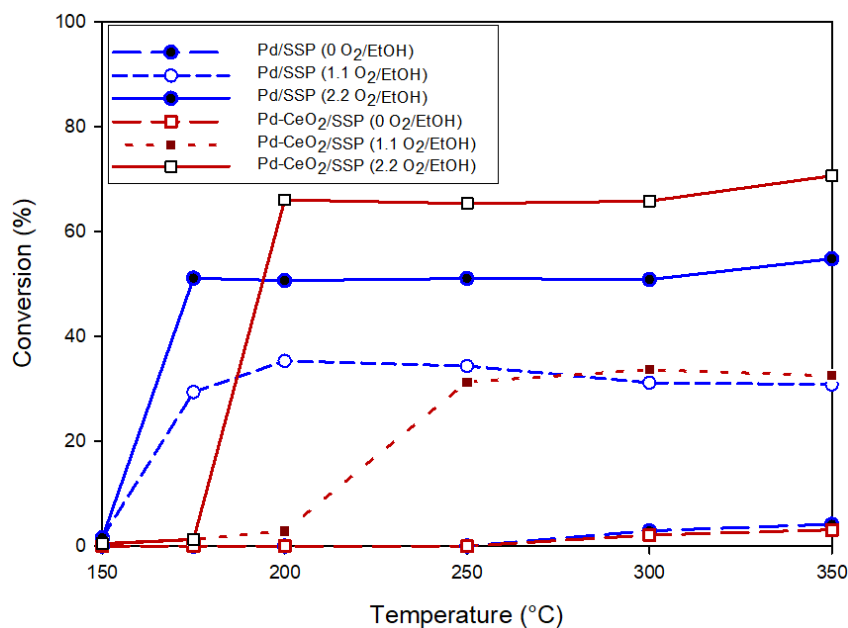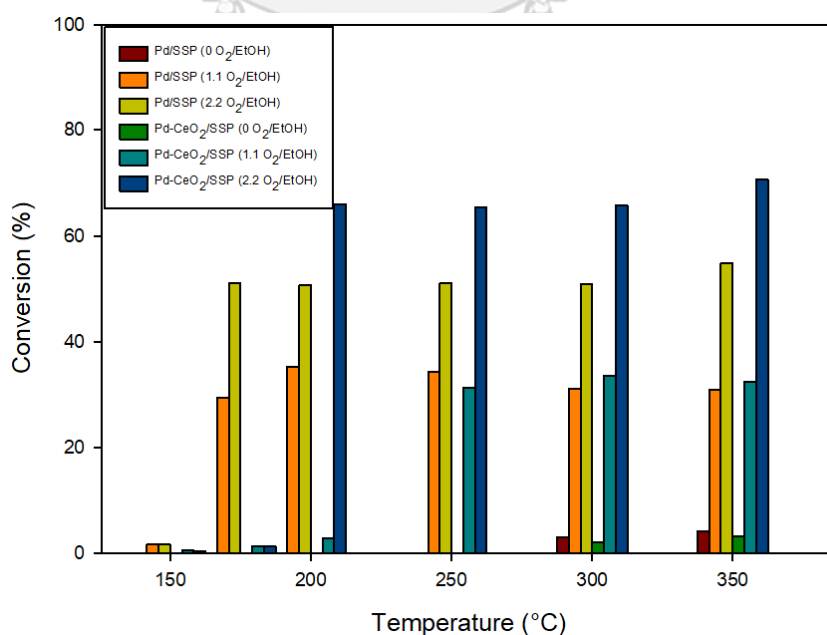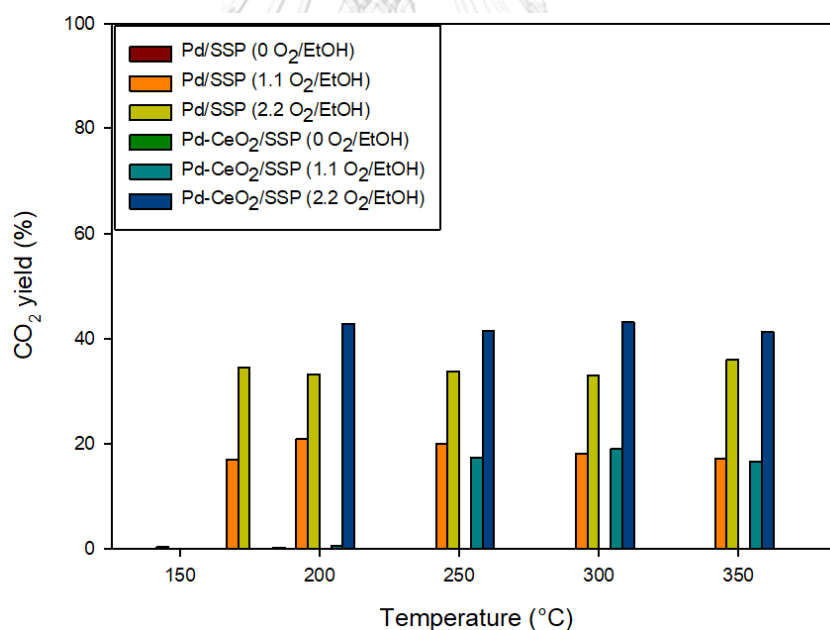**Figure 35** CO_2 yield vs temperature of Pd/ SSP and Pd-CeO_2/SSP catalysts with different molar ration of oxygen to ethanol as 0, 1.1 and 2.2 (chart bar)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In Chapter 5, the results of the experiments are summarized in sections 4.1, 4.2 and 4.3 of Pd/SSP, CeO_2/SSP and ceria modification, which were prepared by incipient wetness impregnation. All catalysts were tested via ethanol dehydration reaction with oxygen cofeeding and characterized with various techniques. Furthermore, the recommendations of this work also include in this chapter. Comparison of results in each part and summarized are as follows.

5.1 Conclusions

In part 1, ethanol conversion and ethylene selectivity of ceria modification of 58% and 27%, respectively were higher than those of palladium or ceria supported on spherical silica particle at 200 °C because CeO_2 can store oxygen in feed for use in reaction with oxygen cofeeding as a result in high catalytic activity. From part 2, the preparation method with different sequence of loading was investigated. This factor affects the reduction behavior, surface area and catalytic activity. For Pd-CeO_2/SSP catalyst, it was prepared via incipient wetness co-impregnation, it exhibits the highest conversion and ethylene selectivity of 67% and 30%, respectively at 200 °C. Finally, part 3 is investigation of oxygen amount in cofeeding by using Pd/SSP catalyst comparing with Pd-CeO_2/SSP from part 2. From the results of the experiment, it was found that the amount of oxygen affecting each catalyst was different. For Pd/SSP, when decreasing the amount of oxygen, the conversion decreased, but the conversion temperature was the same as 175 °C. On the other hand, Pd-CeO_2/SSP exhibits decreased ethanol conversion and starts to have conversion at 250 °C when half of the oxygen was fed. In absence of oxygen cofeeding it shows less conversion at high temperature for all catalyst.

5.2 Recommendations

1. The stability of all catalysts should be investigated in future work.
2. *In situ*-IR technique should be used to study the mechanism of ethanol dehydration to ethylene with oxygen cofeeding.

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APPENDIX

APPENDIX A

Calculation support preparation by Sol-Gel method

For spherical silica particle (SSP) support was prepared by sol–gel method using tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), ammonia (NH_3), ethanol (C_2H_5OH) and de-ionized water (H_2O) as reported. The molar ratio of 1 TEOS: 0.3 CTAB: 11NH_3: 58 C_2H_5OH: 144 H_2O [16].

Precursor

- 98 wt% Tetraethyl orthosilicate (TEOS)
- Cetyltrimethylammonium bromide (CTAB)
- 30 wt% Ammonia
- 99.99 wt% Ethanol

Calculation substances

The molar ratio of 1 TEOS: 0.3 CTAB: 11NH_3: 58 C_2H_5OH: 144 H_2O

- **Tetraethyl orthosilicate (TEOS)**

1 mol of TEOS	208.33	g
Scale down 100 times	2.0833	g
98 g TEOS in solution	100	g
TEOS 2.0833 g in solution	$\frac{2.0833 \times 100}{98}$ = 2.1258	g

- **Cetyltrimethylammonium bromide (CTAB)**

1 mol of CTAB	364.5	g
3 mol of CTAB	364.5x0.3 = 109.3	g
Scale down 100 times	2.0833	g

- **Ammonia**

1 mol of CTAB	17	g
3 mol of CTAB	17 x 11 = 187	g
Scale down 100 times	0.187	g

30 wt% NH_3 in solution	$\dfrac{100 \times 1.87}{30} = 6.23$	g
70 wt% H_2O in solution	$\dfrac{100 \times 1.87}{70} = 4.36$	g
NH_3 from g to ml	$\dfrac{6.23}{0.89} = \underline{7}$	ml

- **99.99 wt% Ethanol**

1 mol of ethanol	46	g
58 mol of ethanol	46 x 58 = 2668	g
Scale down 100 times	<u>26.68</u>	g

- **De-ionized water (H_2O)**

1 mol of water	18	g
144 mol of water	18 x 144 = 2592	g
Scale down 100 times	25.92	g
Water from NH_3 solution	4.36	g
So de-ionized water (H_2O)	25.92 − 4.36 = <u>21.56</u>	g
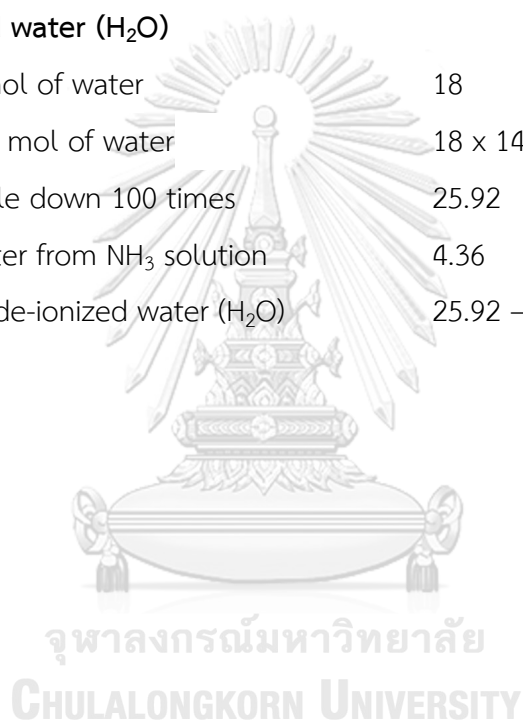
APPENDIX B

Calculation catalyst preparation by incipient wetness impregnation

Metal Loading 0.5 % of Pd on SSP catalyst by incipient wetness impregnation

Precursor

- Tetraamminepalladium(II)chloride in H_2O ≥99.99%   MW = 263.46   g/mol
  ($Pd (NH_3)_4Cl_2 \cdot H_2O$)

- Palladium   MW = 106.42   g/mol

Based on 2 g of 0.5 wt% Pd/SSP

    In catalyst contains   Pd   0.005 x 2 = 0.01   g

                                  SSP   0.995 x 2 = 1.99   g

Based on 1 mole of precursor

    Pd   106.42 g $Pd(NH_3)_4Cl_2 \cdot H_2O$ 263.46 g

    Pd   0.01   g $Pd(NH_3)_4Cl_2 \cdot H_2O$ $\dfrac{0.01 \times 263.46}{106.42}$ = 0.2521 g

Metal Loading 5 % of CeO_2 on SSP catalyst by incipient wetness impregnation

Precursor

- cerium(III)nitrate in H_2O ≥99.99%   MW = 434.23   g/mol
  [$Ce(NO_3)_3 \cdot 6H_2O$]

- CeO_2 MW = 172.23   g/mol

Based on 2 g of 5 wt% CeO_2/SSP

    In catalyst contains CeO_2 0.05 x 2 = 0.1 g

                                    SSP   0.95 x 2 = 1.9 g

Based on 1 mole of precursor

    CeO_2 172.23 g $Ce(NO_3)_3 \cdot 6H_2$ 434.23 g

    CeO_2 0.1   g $Ce(NO_3)_3 \cdot 6H_2$ $\dfrac{0.1 \times 434.23}{172.23}$ = 0.2521 g

In ceria modification catalyst using same calculation method.

APPENDIX C

Calibration curve of Reactant and Product

The calibration curve was calculated by injection substance into GC-FID and detected by chromatogram in area of substance versus amount of injection substance. The calibration curve of reactant and product were shown in Figure AC 1-4
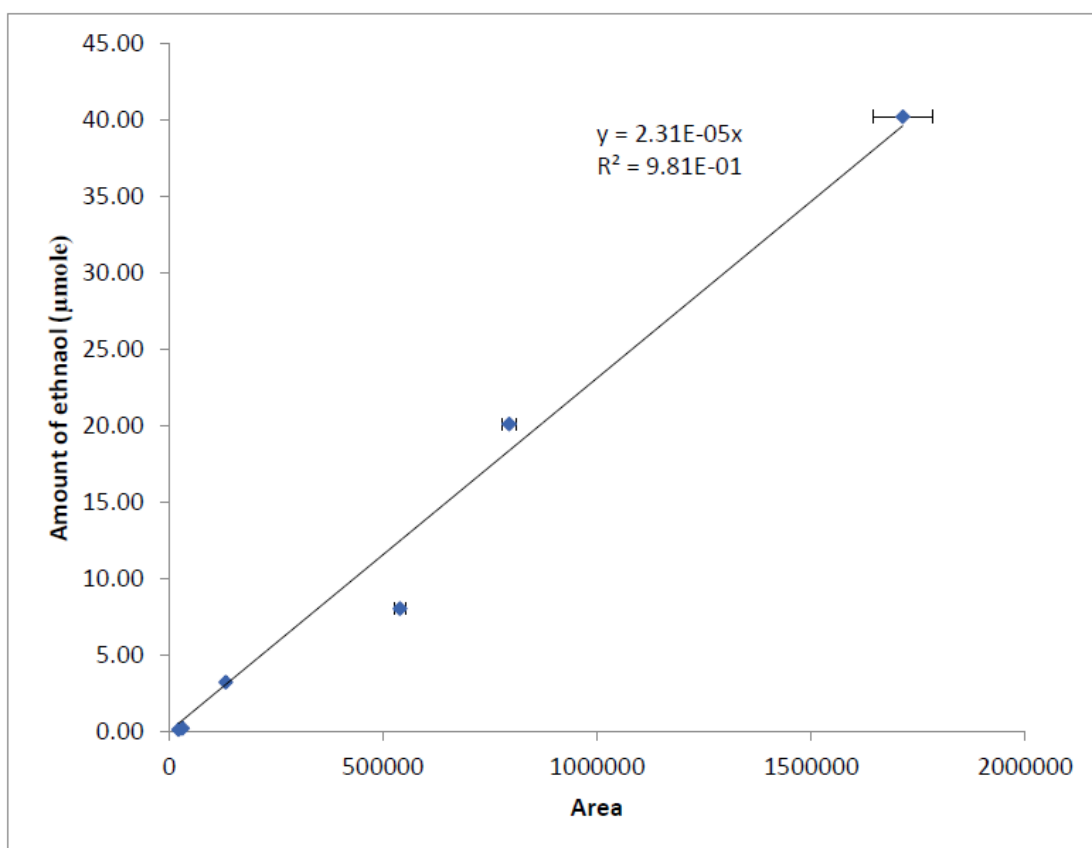
Figure AC 1. The calibration curve of ethanol
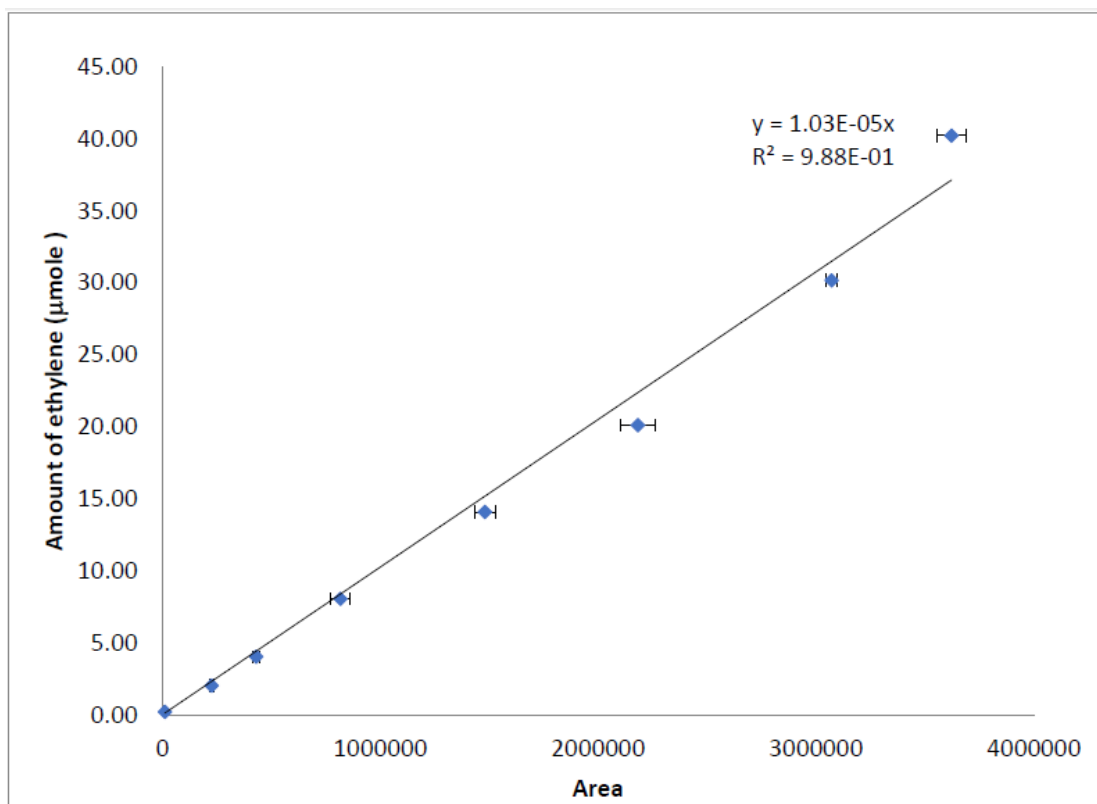
Figure AC 2. The calibration curve of ethylene
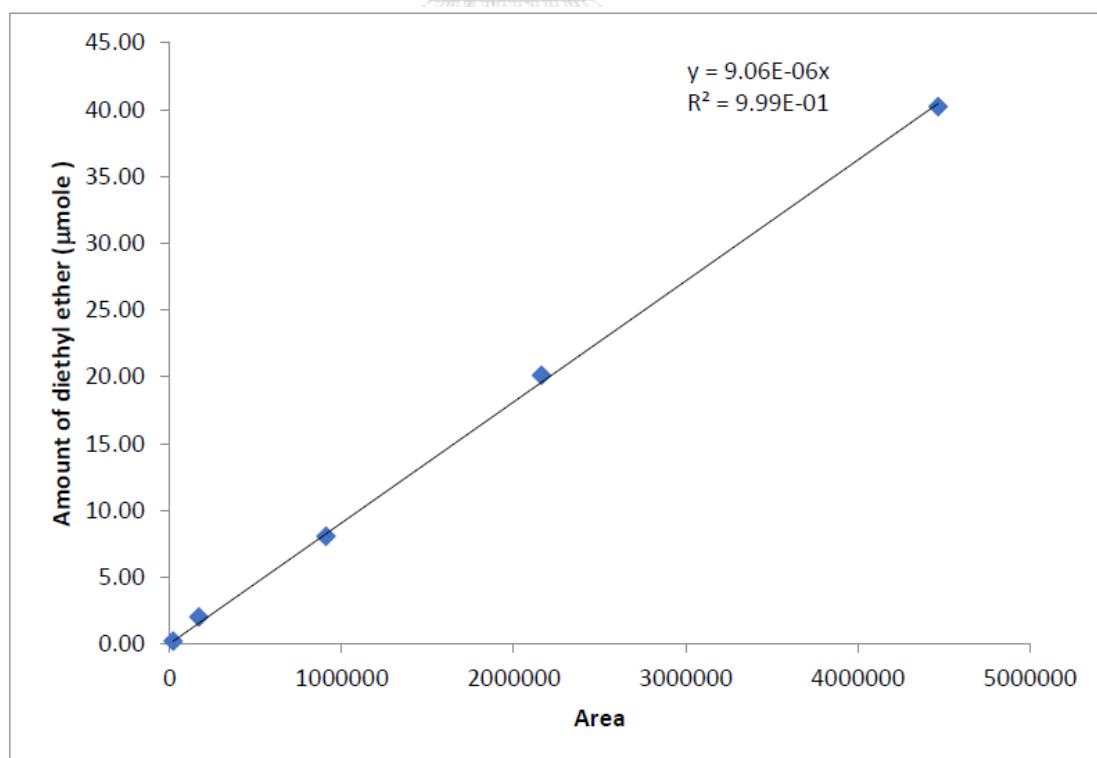
Figure AC 3. The calibration curve of diethyl ether
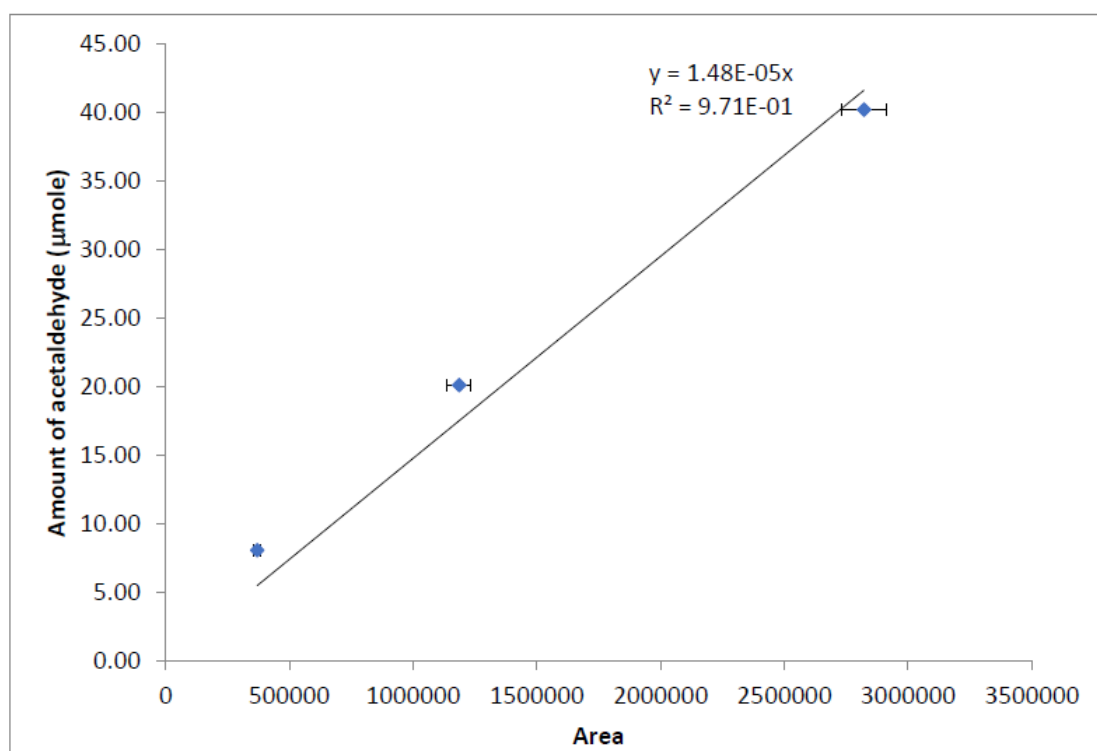
Figure AC 4. The calibration curve of acetaldehyde

APPENDIX D

Calculation of conversion, selectivity, yield rate of reaction and WHSV

Conversion

Reactant conversion (%) $= \dfrac{\text{Mole of reactant after reaction completed}}{\text{Mole of reactant before reaction completed}} \text{X}100 \text{ %}$

Selectivity

Product selectivity (%) $= \dfrac{\text{Mole of desired product}}{\text{Total moles of product}} \text{X}100 \text{ %}$

Yield

Product yield (%) $= \text{Product selectivity} \times \text{Reactant conversion}$

Weight hourly space velocity

WHSV (h^{-1}) $= \dfrac{\text{Mass flowrate of reatant (g/h)}}{\text{weight of catalyst in reactor (g)}}$

APPENDIX E

Catalytic activity, selectivity, yield and rate of reaction of product over all catalysts

Table AF 1. Conversion and selectivity of Pd/SSP, CeO_2/SSP and Pd/CeO_2/SSP

Catalysts	Temperature (°C)	Ethanol conversion (%)	Product selectivity (%)			
			Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
Pd/SSP	150	1.57	6.4	93.6	0.0	0.0
	175	51.1	22.4	9.0	1.1	67.5
	200	50.6	23.3	10.0	1.2	65.5
	250	51.0	21.7	10.0	2.1	66.2
	300	50.8	21.4	12.3	1.5	64.9
	350	54.7	23.7	8.2	2.3	65.7
CeO_2/SSP	150	0	0	0	0	0
	175	0	0	0	0	0
	200	0.1	0	100	0	0
	250	0.4	0	100	0	0
	300	3.9	1.4	84.0	4.8	9.8
	350	64.7	7.6	27.9	26.8	37.6
Pd/CeO_2/SSP	150	1.5	6.2	93.8	0	0
	175	1.8	5.5	85.7	0	8.8
	200	57.7	26.6	8.9	0	64.6
	250	53.3	27.0	11.8	0	61.2
	300	52.9	25.1	10.1	0.3	64.5
	350	58.9	24.3	9.0	0.5	66.1

Table AF 2. Conversion and selectivity of $Pd/CeO_2/SSP$, $CeO_2/Pd/SSP$ and $Pd/CeO_2/SSP$

Catalysts	Temperature (°C)	Ethanol conversion (%)	Product selectivity (%)			
			Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
$Pd/CeO_2/SSP$	150	1.5	6.2	93.8	0	0
	175	1.8	5.5	85.7	0	8.8
	200	57.7	26.6	8.9	0	64.6
	250	53.3	27.0	11.8	0	61.2
	300	52.9	25.1	10.1	0.3	64.5
	350	58.9	24.3	9.0	0.5	66.1
$CeO_2/Pd/SSP$	150	1.0	3.6	96.4	0.0	0.0
	175	2.6	7.4	76.2	0.0	16.4
	200	58.9	20.1	13.2	0.0	66.8
	250	58.1	17.9	13.2	0.1	68.8
	300	59.5	18.8	11.4	0.3	69.5
	350	57.6	18.7	18.2	1.6	61.5
$Pd-CeO_2/SSP$	150	0.4	2.5	97.5	0.0	0.0
	175	1.3	5.7	81.9	0.0	12.4
	200	66.0	29.5	5.3	0.3	64.9
	250	65.3	31.1	5.1	0.3	63.5
	300	65.8	30.4	4.0	0.3	65.4
	350	70.6	34.2	7.0	0.4	58.4

Table AF 3. Conversion and selectivity of Pd/SSP and $Pd-CeO_2/SSP$ with various amounts of oxygen cofeed.

Catalyst	$O_2/EtOH$	Temperature (°C)	Conversion (%)	Product selectivity (%)			
				Ethylene	Acetaldehyde	Diethyl ether	Carbon dioxide
Pd/SSP	0	150	0	0	0	0	0
		175	0	0	0	0	0
		200	0	0	0	0	0
		250	0	0	0	0	0

		300	76.9	76.9	0	23.1	0
		350	62.4	62.4	0	37.6	0
	1.1	150	1.6	5.8	78.9	0.0	15.2
		175	29.3	21.2	18.0	2.8	58.0
		200	35.3	22.0	15.8	2.9	59.4
		250	34.3	21.5	16.3	3.9	58.3
		300	31.1	20.3	19.0	2.5	58.3
		350	30.8	21.4	21.3	1.9	55.4
	2.2	150	1.6	6.4	93.6	0	0
		175	51.1	22.4	9.0	1.1	67.5
		200	50.6	23.3	10.0	1.2	65.5
		250	51.0	21.7	10.0	2.1	66.2
		300	50.8	21.4	12.3	1.5	64.9
		350	54.8	23.7	8.2	2.3	65.7
Pd-CeO$_2$/ SSP	0	150	0	0	0	0	0
		175	0	0	0	0	0
		200	0	0	0	0	0
		250	0	0	0	0	0
		300	2.1	82.5	0	17.5	0
		350	3.1	72.6	0	27.4	0
	1.1	150	0.5	2.8	97.2	0	0
		175	1.3	6.1	83.8	0	10.1
		200	2.8	9.2	73.4	0	17.4
		250	31.3	23.4	20.4	0.6	55.6
		300	33.6	24.0	19.3	0.4	56.3
		350	32.5	24.0	23.7	1.0	51.3
	2.2	150	0.4	2.5	97.5	0	0
		175	1.3	5.7	81.9	0	12.4
		200	66.0	29.5	5.3	0.3	64.9
		250	65.3	31.1	5.1	0.3	63.5
		300	65.8	30.4	4.0	0.3	65.4
		350	70.6	34.2	7.0	0.4	58.4

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