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การกระจายตัวของแพลทินัมและการเคลื่อนที่ของออกซิเจนสำหรับปฏิกิริยาออกซิเดชันของคาร์บอน
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EFFECTS OF MODIFICATION OF γ -Al₂O₃ SUPPORT BY La AND Ce ON Pt DISPERSION
AND OXYGEN MOBILITY FOR CO OXIDATION

Mr. Thanawat Wandondaeng



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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การศึกษาผลของการดัดแปรตัวเร่งปฏิกิริยาแพลทินัมบนแกมมาอะลูมินาด้วยแลนทานัมและซีเรียมที่มีต่อการกระจายตัวของแพลทินัมและการเคลื่อนที่ของออกซิเจนโดยปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์ เติร์มตัวเร่งปฏิกิริยาแพลทินัมบนแกมมาอะลูมินา (0.3wt%Pt) ที่ดัดแปรด้วยแลนทานัมหรือซีเรียมด้วยวิธีเคลือบฝังที่สัดส่วนโดยโมลของแลนทานัมหรือซีเรียมต่ออะลูมิเนียม 0, 0.01, 0.05, 0.10 และ 0.15 ผลของปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์วัดจากค่า light-off temperature (T_{50}) และ turnover frequencies (TOF) สัมพันธ์กับการกระจายตัวของแพลทินัมและการเคลื่อนที่ของออกซิเจนที่ตรวจวัดคุณลักษณะด้วยเทคนิคการเลี้ยวเบนรังสีเอกซ์ (XRD), การดูดซับทางกายภาพของไนโตรเจน, การดูดซับทางเคมีของคาร์บอนมอนอกไซด์ และโปรแกรมอุณหภูมิการคายซับของคาร์บอนไดออกไซด์ (CO_2 -TPD) ผลการทดลองแสดงให้เห็นว่าการเติมแลนทานัมลงบนตัวเร่งปฏิกิริยาแพลทินัมบนแกมมาอะลูมินาจะเพิ่มการกระจายตัวของแพลทินัมและการเคลื่อนที่ของออกซิเจนส่งผลให้ผลของการเกิดปฏิกิริยาออกซิเดชันของคาร์บอนมอนอกไซด์เพิ่มขึ้นอย่างเห็นได้ชัด อย่างไรก็ตามการที่มมีความเป็นต่างของตัวเร่งปฏิกิริยามากเกินไปจะไปลดผลของการเกิดปฏิกิริยาลง ในทางเดียวกันการเติมซีเรียมลงบนตัวเร่งปฏิกิริยาแพลทินัมบนแกมมาอะลูมินาจะเพิ่มการกระจายตัวของแพลทินัมและการเคลื่อนที่ของออกซิเจนเช่นกัน นอกจากนี้การเติมซีเรียมยังไปพัฒนาสมบัติบางชนิดของตัวเร่งปฏิกิริยาส่งผลให้ผลของการเกิดปฏิกิริยาสูงมาก

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Effects of La or Ce modified Pt/ γ -Al₂O₃ catalysts on Pt dispersion and oxygen mobility of catalyst were investigated by CO oxidation reaction. 0, 0.01, 0.05, 0.10 and 0.15 molar ratio of La or Ce to Al was doped on Pt/ γ -Al₂O₃ catalysts (0.3wt%Pt) by impregnation method. The CO oxidation activities in terms of light-off temperature (T_{50}) and turnover frequencies (TOF) corresponded to Pt dispersion, oxygen mobility as characterized by various analytical techniques such as X-ray diffraction (XRD), N₂-physisorption, CO-pulse chemisorption, and temperature programmed desorption of CO₂ (CO₂-TPD). The results indicated that the addition of La on Pt/ γ -Al₂O₃ catalysts increased the dispersion of Pt sites and oxygen mobility of catalyst. As a result, the catalyst activity for CO oxidation was significantly improved. However, too strong basicity of catalysts decreased the CO oxidation activity. In the same way, the addition of Ce on Pt/ γ -Al₂O₃ catalysts can improve the dispersion of Pt sites and oxygen mobility. Furthermore, the addition of Ce can improve some properties of catalysts that result to superior activity.

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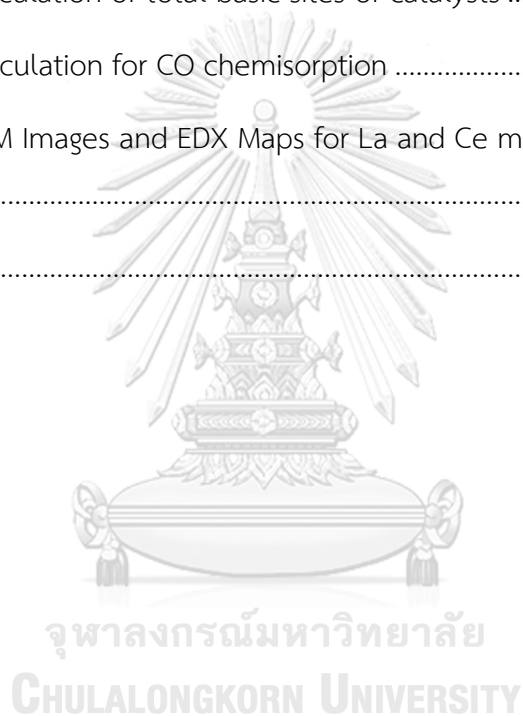
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CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF FIGURES	x
LIST OF TABLES	xii
CHAPTER I INTRODUCTION.....	13
1.1 Introduction.....	13
1.2 Objective.....	3
1.3 The scope of research.....	3
CHAPTER II BACKGROUND AND LITERATURE REVIEWS	2
2.1 Al ₂ O ₃	2
2.1.1 Formation and crystal structure of alumina	2
2.1.2 Application	6
2.2 Modified Al ₂ O ₃ support.....	7
2.3 CO oxidation.....	10
2.3.1 Langmuir-Hinshelwood mechanism.....	10
2.3.2 Mars-van Krevelen mechanism.....	11
2.4 Oxygen mobility.....	12
CHAPTER III EXPERIMENTAL.....	1
3.1 Materials and chemicals	16
3.2 Preparation of catalyst.....	16

	Page
3.2.1 γ - Al_2O_3 support synthesis	16
3.2.2 Preparation of modified γ - Al_2O_3 supports	16
3.2.3 Preparation of modified Pt/ γ - Al_2O_3 catalysts	17
3.3 Catalyst characterization technique	17
3.3.1 N_2 -physisorption	17
3.3.2 Scanning electron microscope (SEM)	17
3.3.3 X-ray diffraction (XRD)	17
3.3.5 CO-Pulse Chemisorption	18
3.3.6 CO_2 temperature programmed desorption	18
3.4 Catalytic activity on CO oxidation reaction	18
CHAPTER IV RESULTS AND DISCUSSION	21
4.1 Effects of La modified Pt/ γ - Al_2O_3 catalysts on Pt dispersion and oxygen mobility for CO oxidation	21
4.1.1 Effect of the modification on the physical and chemical properties of Pt/ γ - Al_2O_3 and La modified Pt/ γ - Al_2O_3 catalysts	21
4.1.2 Catalytic performance and effect of oxygen mobility on CO oxidation over La modified Pt/ γ - Al_2O_3 catalysts	26
4.2 Effects of Ce modified Pt/ γ - Al_2O_3 catalysts on Pt dispersion and oxygen mobility for CO oxidation	29
4.2.1 Effect of the modification on the physical and chemical properties of Pt/ γ - Al_2O_3 and Ce modified Pt/ γ - Al_2O_3 catalysts	29
4.2.2 Catalytic performance and effect of oxygen mobility on CO oxidation over Ce modified Pt/ γ - Al_2O_3 catalysts	33
CHAPTER V CONCLUSIONS AND RECOMMENDATIONS	37

	Page
5.1 Conclusions	37
5.2 Recommendations	37
REFERENCES	38
APPENDIX.....	46
Appendix A Calculation for catalyst preparation	47
Appendix B Calculation of total basic sites of catalysts	49
Appendix C Calculation for CO chemisorption	50
Appendix D SEM Images and EDX Maps for La and Ce modified Pt/ γ -Al ₂ O ₃ catalysts	51
VITA.....	56



LIST OF FIGURES

Figure 2.1 Transformation sequences of aluminum hydroxides.....	6
Figure 2.2 Mars-van-Krevelen mechanism on Au/TiO ₂	12
Figure 2.3 Correlation between the oxygen surface mobility and the strength of metal-oxygen bonds.....	13
Figure 2.4 Correlation between oxygen surface mobility and oxide surface basicity..	13
Figure 2.5 Optical basicity (left) and single bond strength (right) of simple oxides as a function of element electronegativity.....	14
Figure 3.1 Research methodology.....	15
Figure 3.2 Schematic diagram of the reaction line for CO oxidation analyzed by gas chromatographs equipped with molecular sieve 5A columns.....	20
Figure 4.1 XRD patterns of the γ -Al ₂ O ₃ support and La modified Pt/ γ -Al ₂ O ₃ catalysts.....	22
Figure 4.2 Nitrogen adsorption–desorption isotherms of La modified Pt/ γ -Al ₂ O ₃ catalysts.....	23
Figure 4.3 Pore size distribution of La modified Pt/ γ -Al ₂ O ₃ catalysts.....	23
Figure 4.4 CO ₂ -TPD profiles of La modified Pt/ γ -Al ₂ O ₃ catalysts.....	25
Figure 4.5 The CO oxidation results of La modified Pt/ γ -Al ₂ O ₃ catalysts: (A) conversion profiles, and (B) temperature at 50 % conversion versus Pt active sites.....	27
Figure 4.6 Relationship between TOF and Desorbed CO ₂ of La modified Pt/ γ -Al ₂ O ₃ catalysts.....	28
Figure 4.7 XRD patterns of the γ -Al ₂ O ₃ support and Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	29
Figure 4.8 Nitrogen adsorption–desorption isotherms of Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	31
Figure 4.9 Pore size distribution of Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	31
Figure 4.10 CO ₂ -TPD profiles of Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	33

Figure 4.11 The CO oxidation results of Ce modified Pt/ γ -Al ₂ O ₃ catalysts: (A) conversion profiles, and (B) temperature at 50 % conversion versus Pt active sites.....	34
Figure 4.12 Light-off temperature (T_{50}) conversion versus Pt active sites of La and Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	35
Figure 4.13 Relationship between TOF and Desorbed CO ₂ of Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	36
Figure 4.14 Relationship between TOF and Desorbed CO ₂ of La and Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	36
Figure B.1 The calibration curve of carbon dioxide obtained from CO ₂ -TPD profiles.....	49
Figure D.1 SEM images of the La modified Pt/ γ -Al ₂ O ₃ catalyst at 1,000 magnification with molar ratio La/Al: (a) 0, (b) 0.01, (c) 0.05, (d) 0.10, and (e) 0.15.....	51
Figure D.2 SEM images of the Ce modified Pt/ γ -Al ₂ O ₃ catalyst at 1,000 magnification with molar ratio Ce/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15.....	52
Figure D.3 EDX maps for Pt of the La modified Pt/ γ -Al ₂ O ₃ catalyst at molar ratio La/Al: (a) 0, (b) 0.01, (c) 0.05, (d) 0.10, and (e) 0.15.....	53
Figure D.4 EDX maps for Pt of the Ce modified Pt/ γ -Al ₂ O ₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15.....	54
Figure D.5 EDX maps for La of the La modified Pt/ γ -Al ₂ O ₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15.....	55
Figure D.6 EDX maps for Ce of the Ce modified Pt/ γ -Al ₂ O ₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15.....	55

LIST OF TABLES

Table 3.1 Chemical used in catalyst preparation.....	16
Table 4.1 Physical properties of La modified Pt/ γ -Al ₂ O ₃ catalysts.....	24
Table 4.2 Physical properties of Ce modified Pt/ γ -Al ₂ O ₃ catalysts.....	30



CHAPTER I

INTRODUCTION

1.1 Introduction

CO oxidation is known to be structure insensitive which the activity of the reaction depends on the number of active sites of the active metal. Thus, CO oxidation is a suitable model reaction to provide more understanding about the catalyst [1]. Noble metals such as Pt, Pd or Au are widely used for CO oxidation catalyst because they have high catalytic activity at low temperature [2-4]. Among noble metals, Pt is widely used because it has a highly selective desired product [5, 6]. However, a major disadvantage of using noble metals is the price. So, the improvement of catalyst performance has been studied in terms of metal dispersion, preparation methods, an addition of a second metal, and strong metal-supported interaction for low cost catalyst but high performance. Alumina is mostly used as support in Pt catalyst for enhancing properties of Pt catalyst due to its high thermal stability and high surface area especially the γ -Al₂O₃ phase [7, 8].

Due to the price of noble metals, several studies have aimed for the enhancement of Al₂O₃ support properties in order to improve metal dispersion instead of loading high noble metal [9]. There are many researches studied about dopants added to the catalyst for improving catalyst properties can effect to whether dispersion of the metal, interaction and amount of active site can be adsorbed on the γ -Al₂O₃ surface after dopants loading or activity and selectivity are better after achieved reaction. According to Chotikrai et al. [10], the Si modified catalyst not only improved the dispersion of Pt sites but also enhanced the thermal stability of the catalyst. There is a research studied the bimetallic Pt-Sn/ γ -Al₂O₃ have more investigated for improvement selectivity, activity and conversion, for instance, the research of S.H. Vaidya, C.V. Rode, and R.V. Chaudhari studied highly selective liquid phase hydrogenation of diethyl succinate to γ -butyloactone revealed selectivity of γ -butyloactone due to Lewis acidity of Sn^{2+/4+} but this research mentioned to a few

dispersion abilities of Pt by XRD characterization that Pt component was well dispersed over the alumina support [11], but they didn't mention the interaction effect to the Pt dispersion. As a following the research of Mi-Hyun lee result showed the percent dispersion between Pt and Pt/Sn in other weight different, percent dispersion of Pt/Sn is more than Pt about 2-3 times [12]. By the way, Ce often studied and researched of selectivity, activity, conversion, dispersion ability and little interaction between Pt with Ce [13]. The sampling of the dopant such as Ce is a one that has been studied, for Ce support, the size of Pt increased as Ce contents decrease due to less Pt-O-Ce bonds. Not only oxygen active but also Ce elements are necessary for high Pt dispersion. The Pt-loaded on Ce based materials presents high activity than fresh support such as ZrO_2 and Al_2O_3 [14]. According to R.M. Navarro et al. [15], the specific areas for lanthanum, containing to support are higher than corresponding to bare alumina due to higher of BET result, as the reason La can improve excellent dispersion when impregnated on Pt/ γ - Al_2O_3 . According to T. Ekou et al. [16], the high dispersion of Pt particles on Ti/ γ - Al_2O_3 can be attributed to the high reactivity of alumina surface toward metallic precursor species, i.e. to a good interaction between alumina and metal. Doped Ga was studied by E.L. Jablonski et al. [17], the effect of Ga adding to Pt/ γ - Al_2O_3 was studied on the activity, selectivity and deactivation in the propane dehydrogenation revealed that Ga, intimate contact with Pt can occur dilution and blocking effect, leading to a low hydrogen activity, and low H_2 and CO chemisorption capacities but its predominance is improvements in the selectivity to propylene in the propane hydrogenation and decrease of the carbon formation on the catalyst surface. According to Lizseth Rodriguez [18], the addition of Ga to the fresh catalyst, uncalcined, increased the dispersion of Pd except for higher Ga content (0.72%, Ga/Pd = 1.68).

Among of second metals, La and Ce are the interesting dopant that can improve the dispersion of active metal and the thermal stability of catalyst that provides a highly activity of reaction [19, 20]. In addition, La and Ce may improve the oxygen mobility because of its high basicity properties and may solve the problem of decreasing of oxygen mobility by Si loading [10, 21]. In this work, the effects of La or

Ce modified γ - Al_2O_3 supported Pt catalysts on Pt dispersion and oxygen mobility of catalyst were investigated by CO oxidation.

1.2 Objective

To investigate effects of La or Ce modified Pt/ γ - Al_2O_3 catalysts on Pt dispersion and oxygen mobility of catalyst by CO oxidation activity.

1.3 The scope of research

Effects of La or Ce loading on Pt dispersion and oxygen mobility of La or Ce modified γ - Al_2O_3 supported Pt catalysts in CO oxidation.

1.3.1 Synthesis of (La, Ce) modified γ - Al_2O_3 by varying Loading of La or Ce with dopant/Al molar ratios 0.01, 0.05, 0.10 and 0.15 via incipient wetness impregnation method.

1.3.2 Preparation of La modified Pt/ γ - Al_2O_3 catalysts and Ce modified Pt/ γ - Al_2O_3 catalysts via 0.3wt%Pt.

1.3.3 Characterization of the catalysts by N_2 -physisorption, SEM-EDX, XRD, CO_2 -TPD, CO pulse chemisorption.

1.3.4 Catalytic reaction test in CO oxidation.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

The purpose of this chapter provides the fundamental concept and literature review for this thesis. The first section of the chapter describes the fundamental information about properties of Al_2O_3 and applications. Next section describes the metal modified Al_2O_3 supports. After that, the fundamental of CO oxidation was mentioned. Finally, the fundamental of oxygen mobility was described.

2.1 Al_2O_3

Aluminum oxide is an oxide of aluminum, occurring in nature as various minerals such as bauxite, corundum, etc. It is commonly called alumina. There are many applications in industry as adsorbents, catalysts or catalyst carriers, coatings, and soft. Because of their excellence thermal stability and a wide range of chemical, physical and catalytic properties [22-24].

2.1.1 Formation and crystal structure of alumina [25]

Alumina can exist in many metastable phases before transforming to the most stable α -alumina (corundum form). Chi (χ), kappa (κ), eta (η), theta (θ), delta (δ), and gamma (γ) are six primary metastable phases of alumina that were presented by the Greek letters. The temperature range and sequence of each phase transformation depends on various factors such as a degree of crystallinity and impurities of the starting alumina precursor [24]. Alumina precursor and calcination condition significantly influence the resulting powder properties. The sequences of phase transformation from alumina precursor to the thermodynamically stable α -alumina phase are irreversible, as depicted in the literature are also approximates (Fig. 2.1).

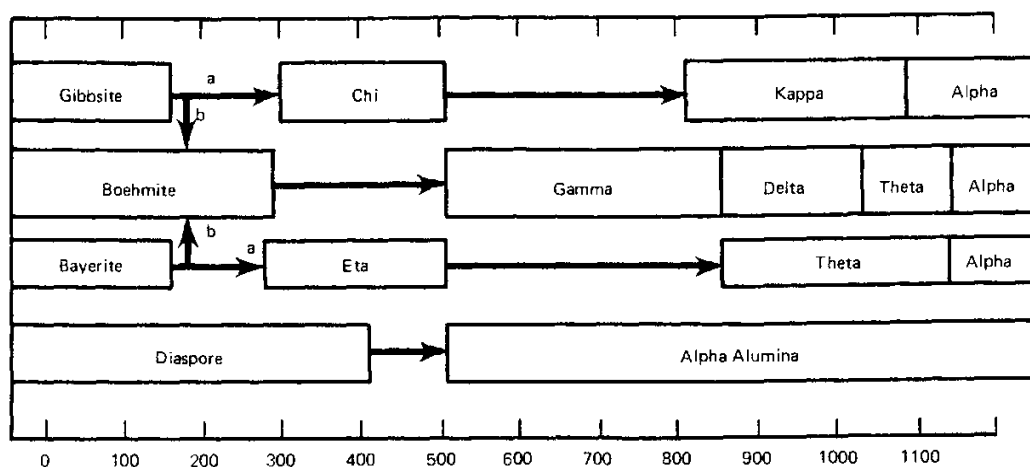


Figure 2.1 Transformation sequences of aluminum hydroxides [25].

Aluminum trihydroxide ($\text{Al}(\text{OH})_3$) and aluminum oxide hydroxide (AlOOH) exhibit polymorphism and exist in many forms of structure. The framework of all aluminum hydroxides consists of double oxygen layers stacking with the aluminum ions located in octahedrally coordinated interstices. The symmetry of the overall structure for each hydroxide is determined by the distribution of hydrogen, whereas the packing of oxygen ions inside the layer can be either hexagonal or cubic. It has been suggested that the mechanism of dehydration for the particular hydroxide is controlled by the relative distance between hydroxyl groups, both within and between the layers.

The phase transformation sequence commonly begins with aluminum hydroxides ($\text{Al}(\text{OH})_3$ and AlOOH) transforming to the low-temperature phase of alumina (η and χ) at the temperature around 150-500 °C, and afterward to high-temperature phase (δ , θ , κ) at the temperature around 650-1000 °C. Finally, α -alumina, the thermodynamically stable phase, is formed at the temperature around 1100-1200 °C. Furthermore, γ -alumina is widely used in the industry that transforms by boehmite at the temperature around 500-800 °C.

2.1.2 Applications

Aluminium oxide catalyzes a variety of reactions that are useful industrially. In its largest scale application, aluminium oxide is the catalyst in the Claus process for converting hydrogen sulfide waste gases into elemental sulfur in refineries. It is also useful for dehydration of alcohols to alkenes. Aluminium oxide serves as a catalyst support for many industrial catalysts, such as those used in hydrodesulfurization and some Ziegler-Natta polymerizations [23].

In the present, aluminium oxide is widely used as a support of the catalyst because of their high surface area, thermal stability, and porous materials. There are many researches about aluminium oxide that used as a support of the catalyst. According to A. Manasilp, et al. [26], the effect of water vapor, carbon dioxide, CO and oxygen concentrations, temperature, and Pt loading on the activity and selectivity of selective CO oxidation over Pt/Alumina catalyst for fuel cell applications was studied. The results show that the single-step sol-gel made Pt/alumina catalysts have the high levels of activity and selectivity necessary for catalyzing the preferential oxidation of 1% or less CO in the hydrogen-rich fuel processor gas all the way down to a few ppm of CO. The sol-gel technique provides a high surface area stable catalyst and despite the fact that some of the Pt are not accessible to gas phase species, results in high activity catalysts. Water vapor in the feed increases the activity of the catalysts dramatically and in the absence of water vapor, CO₂ in the feed stream decreases the activity of the catalysts significantly. In addition, C. K. Costello, et al. investigated the deactivation and regeneration phenomenon during room temperature CO oxidation over the Au/ γ -Al₂O₃ catalyst. They reported that metallic Au is important in activating the oxygen molecule, and the Au cation with a hydroxyl ligand provides the pathway for the conversion of CO to CO₂. It is the requirement of such an ensemble that makes the activity of a catalyst very sensitive to the preparation details and pretreatment conditions. The model also provides a mechanistic explanation of chloride poisoning [27]. Furthermore, B. Li, et al. studied the effect of Ni loading on catalyst bed temperature in the oxidative steam reforming of methane over α -Al₂O₃ supported Ni catalysts with various Ni loadings (0.2-10 wt.%). The results suggested that methane

conversion increased monotonically with Ni loading amount. However, the bed temperature profile was much dependent on W/F (catalyst weight to a total flow rate of the introduced gases) conditions. At low W/F, the highest bed temperature increased substantially with Ni loading. On the other hand, at medium W/F, the highest bed temperature decreased with Ni loading in the range of 0.2-0.9 wt.%, while beyond this loading, the highest bed temperature increased moderately [28]. According to L. Zhang, et al. [29], the role of silver species on Ag/Al₂O₃ catalysts for the selective catalytic oxidation of ammonia to nitrogen was studied. They reported that the Ag species state and Ag particle size have a significant influence on the Ag/Al₂O₃ activity and N₂ selectivity of the selective catalytic oxidation of NH₃ at low temperature. Ag⁰ is proposed to be an active species on the H₂ pretreated catalyst at low temperature (<140 °C). It is evident that well-dispersed and small particle Ag⁰ enhances catalytic activity at low temperature, whereas large particle Ag⁰ is related to a high N₂ selectivity. On the other hand, Ag⁺ could also be the active species at temperatures above 140 °C.

2.2 Modified Al₂O₃ support

Although the high activity and selectivity of alumina supported noble metal catalyst, the major disadvantage of noble metal is the price. There are many researches about the improvement of alumina support for reducing the noble metal loading. The addition of second metal in the catalyst is the simple way to improve Al₂O₃ supported noble metal catalyst. This improvement not only improve the dispersion of noble metal, but also enhance the other properties of the catalyst. According to S. Damyanova, et al. [30], the effect of CeO₂ loading on the surface and catalytic behaviors of CeO₂-Al₂O₃-supported Pt catalysts for the reaction of CO₂ reforming of CH₄ were studied. Pt catalysts supported on mixed CeO₂-Al₂O₃ carriers with different CeO₂ loading (0.5–10.3 wt.%) were prepared by wetness impregnation method. The results show that the addition of cerium oxide led to improving the catalytic performance of the reforming of methane with CO₂. Pt catalyst with 1 wt.% of CeO₂ exhibited the highest specific activity and stability, due to the increase in the metal–

support interface area, caused by the higher Pt dispersion. In addition to W. Lin, et al. [31], the effects of the support and residual chlorine ions for total oxidation of methane at low temperature over Pd/TiO₂/Al₂O₃ were investigated. The results show the addition of titania to alumina enhanced the reduction as well as the oxygen mobility of palladium oxide and thus generated catalyst with much higher activity for the reaction. Furthermore, the existence of residual chlorine ions on the catalyst surface would lower the oxygen mobility and reducibility of the supported palladium oxide and consequently inhibit the activity of the catalyst for methane total oxidation.

Y. Zhang, et al. studied the effect of zirconia modified γ -Al₂O₃ supported Cu on methanol synthesis from CO₂ hydrogenation. The results show that the addition of zirconia can improve the catalytic performance of Cu/ γ -Al₂O₃ catalyst used for methanol synthesis from CO₂ and H₂. Furthermore, zirconia modified Cu/ γ -Al₂O₃ catalyst is beneficial in enhancing the dispersion of the supported CuO species, indicating there is strong interaction between the CuO and ZrO₂ species, which is responsible for the enhanced catalytic performance of Cu based catalyst supported on zirconia modified γ -Al₂O₃ catalyst [32].

G. Avgouropoulos, et al. investigated the catalytic performance of alkali (K⁺ and Na⁺)-promoted Pt/Al₂O₃ catalysts for the complete oxidation of ethanol present in trace amounts (500 ppm) in the air. The results suggest that the alkali-promoted catalysts do not produce acetic acid and are significantly more active than un-promoted Pt/Al₂O₃, especially when they have been pre-reduced. The most effective catalyst was Pt/Al₂O₃ (K/Al = 0.10), in which complete oxidation of ethanol to CO₂ was achieved at ~220 °C, while complete oxidation of ethanol over the un-promoted catalyst was obtained at 280 °C [33].

E. N. Ndifor, et al. studied the synthesis of alumina-supported platinum catalysts modified by vanadium for the complete oxidation of naphthalene. The results show that the activity of an alumina-supported platinum catalyst for naphthalene total oxidation is promoted by a small amount of vanadium added during the impregnation step of catalyst preparation. Only 0.5%V was found to promote the activity of the 0.5%Pt/ α -Al₂O₃ catalyst. The activity enhancement has been related to the presence of a more easily reducible vanadium species coupled with the enhanced number of surface Pt sites.

On the other hand, the higher vanadium loadings had a negative effect, as they suppressed activity because of the presence of crystalline V_2O_5 has been suggested to account for the lower activity observed for catalysts with higher vanadium content [34]. W. Yao, et al. studied the promotional effect of Y_2O_3 on the performance of $Ag/\alpha-Al_2O_3$ catalyst for epoxidation of propylene with molecular oxygen. They reported that the presence of a small quantity of Y_2O_3 in the Ag catalyst can adjust its surface basic sites and evidently improve the activity of the epoxidation of propylene to propylene oxide [35]. J.C.S. Araujo, et al. investigated the effects of La_2O_3 on the structural properties of $La_2O_3-Al_2O_3$ prepared by the sol-gel method and on the catalytic performance of $Pt/La_2O_3-Al_2O_3$ towards steam reforming and partial oxidation of methane. The results show that the $Pt/12La_2O_3-Al_2O_3$ catalyst shows the highest catalytic activity and stability in the partial oxidation of methane. The higher stability of La_2O_3 -containing catalysts during partial oxidation of methane cannot be easily connected to the anchoring of Pt particles due to the similarity of the bonding energies of both $Al-O-Pt$ and $La-O-Pt$. In addition, the metal-support interface and the nature of the support have important roles in the accessibility and stability of Pt sites [36]. I. Witonska, et al. researched the addition of Bi into SiO_2 or Al_2O_3 supported Pd catalysts for hydrodechlorination of 2,4-dichlorophenol. They reported that the presence of Bi show the high activity, selectivity, and stability of $Pd-Bi/support$ (SiO_2 , Al_2O_3) systems containing up to 5 wt.% of bismuth constitute a premiss to their possible application in the chemical industry [37]. L. Sun, et al. investigated the effects of Y_2O_3 -modification to $Ni/Y-Al_2O_3$ catalysts on autothermal reforming of methane with CO_2 to syngas. The results show that the addition of Y_2O_3 into $Y-Al_2O_3$ supported Ni catalysts presented better activity and stability than $Ni/Y-Al_2O_3$ catalyst in autothermal reforming of methane. Furthermore, Y_2O_3 has important effects on preventing Ni sintering and carbon deposition, which result in good activity and stability of the Y_2O_3 modified $Ni/Y-Al_2O_3$ catalysts [38]. N. Chotigkrai, et al. researched the effect of Si addition to $Pt/Y-Al_2O_3$ on Pt dispersion and oxygen mobility for CO oxidation $Pt/xSiO_2/Al_2O_3$ catalysts. The results suggest that the catalytic activity of CO oxidation over $Pt/xSiO_2/Al_2O_3$ catalysts apparently depended not only on Pt dispersion but also

oxygen mobility of the supports. The significant relationship between TOF and desorbed CO₂ also strengthened the effect of oxygen mobility relating to support basicity. The desorbed CO₂ as representative of oxygen mobility was substantially decreased with increasing amount of Si addition on the γ -Al₂O₃. However, Pt dispersion was greatly improved by 82 and 45 % on 0.6 and 1.2 wt% SiO₂-doped Al₂O₃ supported Pt catalysts and declined afterward. Among the various Pt/xSiO₂/Al₂O₃ catalysts prepared in this study, the one containing 0.6 wt% SiO₂ showed the highest catalytic activity because it maximized Pt dispersion while minimizing diminution of the oxygen mobility [10]. Furthermore, J. Ohyama, et al. [39] studied the effect of FeOx modification of Al₂O₃ on its supported Au catalyst for hydrogenation of 5-hydroxymethylfurfural. The results show that the apparent catalytic activity of the FeOx modified Al₂O₃ supported Au (Au/FeOx/Al₂O₃) catalysts increased as an increase of Fe loading up to 10 wt.% (3–4 times higher than Au/Al₂O₃). Therefore, the dispersed Fe₂O₃ on Al₂O₃ is effective to enhance the activity of Au catalysts for the hydrogenation because of the formation of exposed small Au clusters.

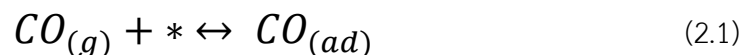
Among of second metals, La and Ce are the interesting dopant that can improve the dispersion of active metal and the thermal stability of catalyst that provides a highly activity of reaction [19, 20]. Furthermore, La and Ce may improve the oxygen mobility because of its high basicity properties and may solve the problem of decreasing of oxygen mobility by Si loading [10, 21].

2.3 CO oxidation

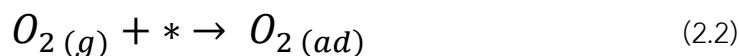
2.3.1 Langmuir-Hinshelwood mechanism

It is generally admitted that CO oxidation on transition metal followed a Langmuir-Hinshelwood mechanism. The carbon monoxide and oxygen molecules can adsorb on transition metal and take place at metal dispersed catalysts. The mechanism has been proposed during the CO oxidation [40]:

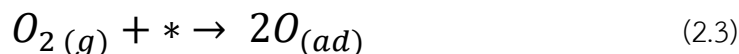
1) CO is adsorbed on surface of metal catalysts;



2) Oxygen is adsorbed on surface of metal catalysts;



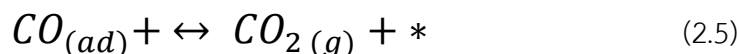
3) Oxygen on surface is dissociated to form oxygen adatoms;



4) Adsorbed CO molecule reacted with adsorbed oxygen to form CO₂



5) Adsorbed CO₂ is desorbed from active site



Where * is a vacant active site

2.3.2 Mars-van Krevelen mechanism

Mars-van Krevelen mechanism is participation of lattice O atom in CO oxidation reaction which has been proposed to explain the CO₂ and CO₃²⁻ formation upon metal oxide exposure to CO. In this case, the oxygen atoms on the surface must be reactive enough to allow the adsorption of CO at these sites. Such sites do not exist on perfect stoichiometric surfaces and require some corrugation. Once CO has adsorbed on metal site and approached the activated O atom, an electron transfer takes place from the molecule to the surface and the cationic sites are reduced. As a result, CO binds to one surface O forming CO₂, or to two surface O forming carbonates CO₃²⁻, at the same time that titanium cations are reduced [41].

The Mars-van Krevelen mechanism on Au/TiO₂ is shown in Fig. 2.2. The CO adsorbed on Au nanoparticle then reacted with activated surface lattice oxygen species at the perimeter of the Au-TiO₂ interface and CO₂ product desorbed to gas phase. Oxygen lattice site was replenished by dissociative adsorption of O₂ at them. At higher temperatures (>80°C), migration of surface lattice oxygen and surface oxygen vacancies also gives access to neighboring oxygen surface lattice sites [42].

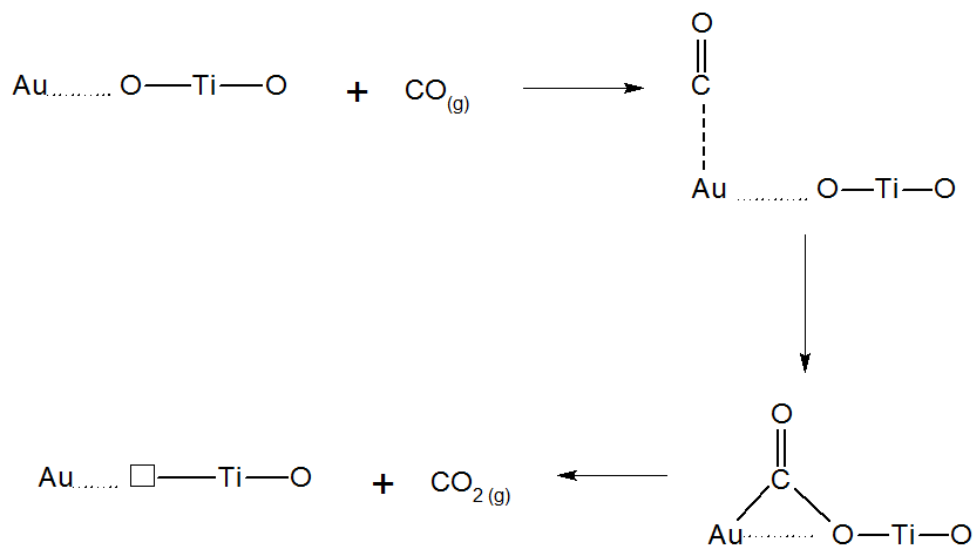


Figure 2.2 Mars-van-Krevelen mechanism on Au/TiO₂

2.4 Oxygen mobility

According to the surface mobility of reactant species plays a crucial role in catalysis, which has been considered as an elementary step of reaction mechanisms [43-47]. This led many researchers tends to establish the surface mobility phenomena. For example, H₂ mobility as called “H₂ spillover” has been vastly studied due to H₂ is essential in several reactions including hydrogenation, isomerization, and etc, as discussed in many reviews [44, 45], while O₂ spillover seemed to be the less popular topic. However, O₂ mobility has also been extensively studied by D. Martin and D. Duprez using the temperature-programmed isotopic exchange of ¹⁸O₂ with ¹⁶O [46]. They reported the rate of oxygen diffusion over several oxides and pointed out the correlation between oxygen surface mobility and metal-oxygen bonds strength as shown in Figure 2.2. Weak bonding strength results in high rate of oxygen diffusion on the surface.

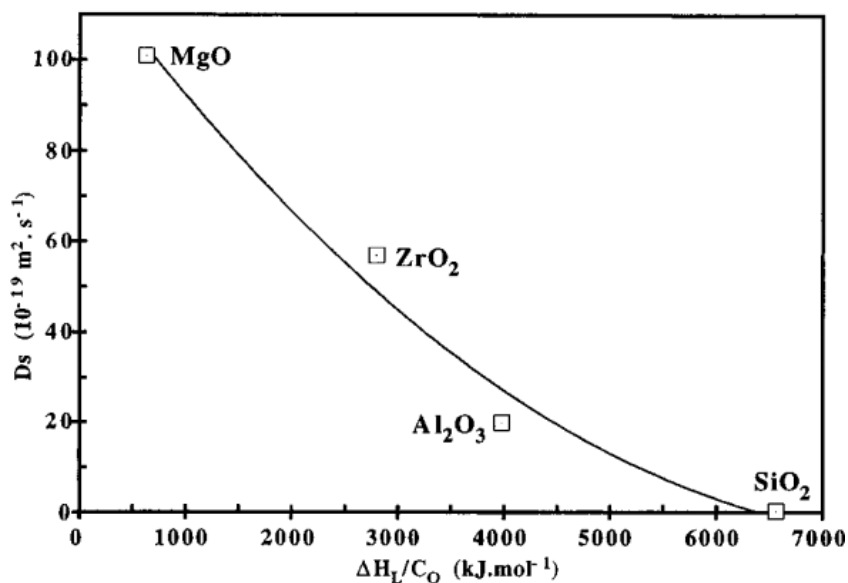


Figure 2.3 Correlation between the oxygen surface mobility and the strength of metal-oxygen bonds [46].

Furthermore, they also revealed that oxygen mobility can be practically linked to the surface basicity of oxides, as the rate of oxygen diffusion increased with the amount of surface basicity (Fig. 2.3). This study was consistent with recent work of V. Dimitrov and T. Komatsu [48]; they established the relation of optical basicity and single bond strength of simple oxides as a function of electronegativity as depicted in Figure 2.4. It was found that simple oxide which has low electronegativity causes the weak strength of metal-oxygen bonds and high optical basicity.

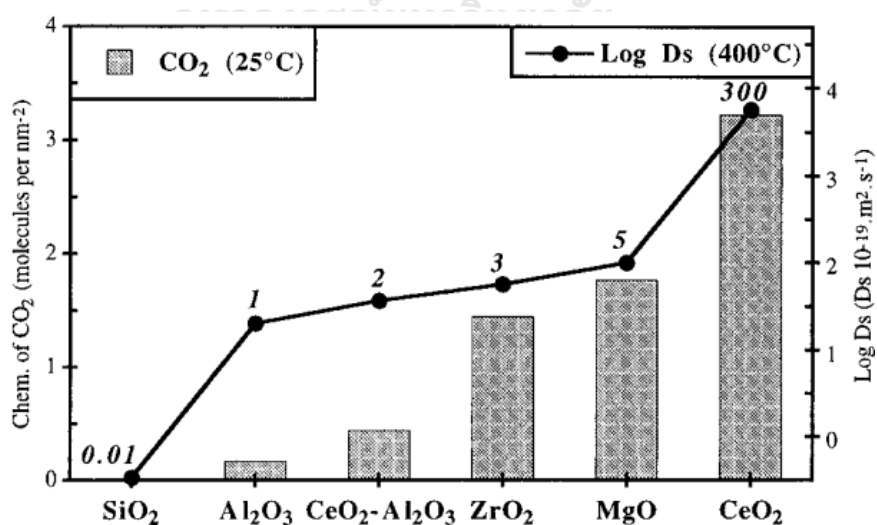


Figure 2.4 Correlation between oxygen surface mobility and oxide surface basicity [46]

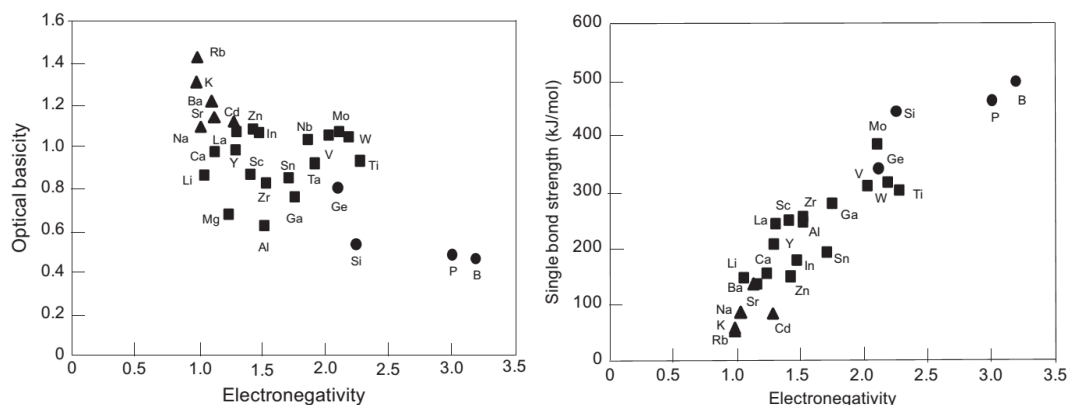


Figure 2.5 Optical basicity (left) and single bond strength (right) of simple oxides as a function of element electronegativity [48].

Oxygen mobility has been reported to influencing combustion temperature of coke generated in propane dehydrogenation on various oxides supported Pt catalysts [43]. It was found that the coke combustion temperatures increased following the reverse order of oxygen mobility of the supports, suggesting that the oxygen transfer over supports was a rate-determining step in the coke combustion process.

CHAPTER III EXPERIMENTAL

This chapter provides the detail of chemicals, catalyst preparation, characterization and catalytic reaction test. The research methodology is showed in Fig. 3.1

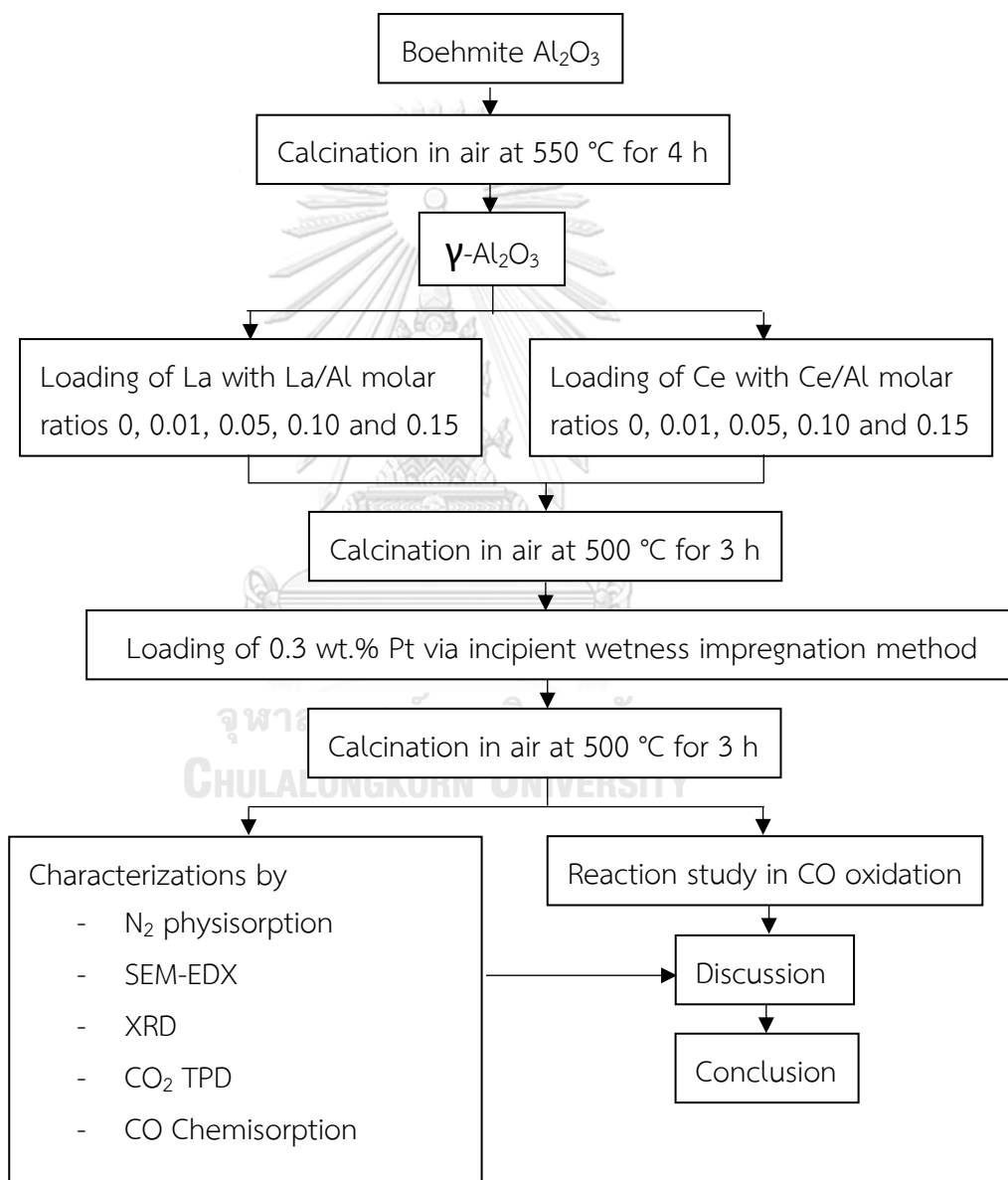


Figure 3.1 Research methodology

3.1 Materials and chemicals

The chemicals used in catalyst preparation are listed in Table 3.1.

Table 3.1 Chemical used in catalyst preparation

Chemicals	Chemicals name	Purity (%)	Suppliers
Boehmite Al ₂ O ₃	Boehmite Al ₂ O ₃	100	Plural
H ₂ PtCl ₆	Chloroplatanic acid	38	Aldrich
La(NO ₃) ₃ ·6H ₂ O	Lanthanum nitrate hexahydrate	99	Himedia
Ce(NO ₃) ₃ ·6H ₂ O	Cerium (III) nitrate hexahydrate	99.5	Acros

3.2 Preparation of catalyst

The details of the preparation method for modified γ -Al₂O₃ supported Pt catalysts are present as follows:

3.2.1 γ -Al₂O₃ support synthesis

The γ -Al₂O₃ support was synthesized by calcination of boehmite Al₂O₃ in tube furnace at 550 °C, heating rate is 10 °C/min for 4 h with air flow.

3.2.2 Preparation of modified γ -Al₂O₃ supports

The modified γ -Al₂O₃ supports were prepared by incipient wetness impregnation methods. 2 g of γ -Al₂O₃ was doped with an aqueous solution of lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) or cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) via different the molar ratios of dopant/Al at 0, 0.01, 0.05, 0.10 and 0.15, respectively. The solution of the metal precursor was slowly dropped onto the γ -Al₂O₃ support to obtain the desired ratio and dried in oven 110 °C overnight before calcined in a tube furnace at 500 °C, heating rate 10 °C/min for 3 h with air flow. The La-modified γ -Al₂O₃ support and the Ce-modified γ -Al₂O₃ support was obtained

3.2.3 Preparation of modified Pt/ γ -Al₂O₃ catalysts

Modified γ -Al₂O₃ supported Pt catalysts were prepared by incipient wetness impregnation using aqueous solution of chloroplatinic acid (H₂PtCl₆·6H₂O) to yield in 0.3 wt% Pt. The aqueous solution of Pt precursor was slowly dropped on transition modified γ -Al₂O₃ support to obtain the desired mole ratio of the catalyst. After impregnation, the catalyst was dried in an oven at 110 °C overnight and then calcined in air 500 °C for 3 h. The obtained catalyst was noted as Pt/ γ -Al₂O₃, Pt-0.01La, Pt-0.05La, Pt-0.10La and Pt-0.15La for La-modified Pt/ γ -Al₂O₃ catalysts and Pt-0Ce, Pt-0.01Ce, Pt-0.05Ce, Pt-0.10Ce and Pt-0.15Ce for Ce-modified Pt/ γ -Al₂O₃ catalysts.

3.3 Catalyst characterization technique

The characterization technique was used to gain more understanding of catalyst structure and texture properties.

3.3.1 N₂-physisorption

The surface area, pore volume, and pore diameter were measured by the Brunauer–Emmet–Teller (BET) method on a Micromeritics ASAP 2020 instrument. The measurements were performed with nitrogen as adsorbate at liquid nitrogen temperature following the samples pretreatment at 200 °C under vacuum 12 h.

3.3.2 Scanning electron microscope (SEM)

The elemental distribution on a surface of the catalysts was investigated with SEM-EDX using Link Isis series 300 program SEM (JEOL model JSM-5800LV).

3.3.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were analyzed by X-ray diffractometer (Bruker D8 Advance) using Cu K α irradiation at a range between 20 ° and 80 ° with a step of 0.05 ° s⁻¹. The lattice parameter and d-spacing were calculated based on Bragg's law. Crystallite size was calculated by Scherrer equation

3.3.5 CO-Pulse Chemisorption

The active sites of platinum metal were determined by CO pulse chemisorption technique using Micromeritics ChemiSorb 2750 and ASAP 2101C V.3.00 software. 50mg of catalysts was reduced in H₂ at 500°C for 1h. After reduction, H₂ was driven with He at 510 °C for 10 min and cooled down with He. After cooling down, the 20 µl of CO gas was fed to the catalyst by syringe injection at a flow rate of He is 25 ml/min at 30 °C. CO was pulsed until catalysts were saturated. The active sites of the Pt catalysts were calculated by assuming that ratio of CO_{adsorbed}/Pt atom is unity.

3.3.6 CO₂ temperature programmed desorption

The basicity of the catalyst was determined by CO₂-TPD. 50 mg of catalysts were treated in He at 510 °C for 1 h before cooling down to 30 °C. After that, 20 ml/min of CO₂ was applied through the sample for 20 min. Then, CO₂-saturated sample was purged with He until baseline stable. The TPD profile was recorded with TCD (Micromeritics 2750) with a heating rate 10 °C/min.

3.4 Catalytic activity on CO oxidation reaction

The catalytic reaction test was performed in CO oxidation, which the apparatus for this reaction test was assembled as a Figure 3.2. The 50 mg of catalyst sample was packed into the quartz reactor 5 mm inside diameter that was placed in the furnace that it was heated by variable voltage. After that, He was used for displacement the air in the reactor before reduction. The sample was reduced with H₂ at 500 °C, heating rate 10 °C/min for 1 h. The H₂ remained in the quartz reactor would be purged by He at 510 °C for 30 min before cooling down at ambient temperature. The reactant gas mixture (1% CO, 2% O₂ and balanced He) was flown through the catalyst bed at a total flow rate of 100 ml/min (GHSV ≈ 30600 h⁻¹) and maintained at the desired temperature for 20 min. The concentration of CO was monitored by an on-line GC-8ATP (Shimadzu) gas chromatograph equipped with a TCD detector and a Molecular Sieve 5A column.

Catalytic activity was evaluated in term of the light-off temperature, defined as the temperature at 50% conversion was obtained. The calculation of CO conversion was based on CO consumption, determined by using the following equation (3.1). The turnover frequency (TOF) of the catalysts at 150 °C was calculated based on Pt active sites measured by CO chemisorption and at CO conversion < 20% following equation (3.2).

$$\%CO \text{ conversion} = \frac{mol_{CO,in} - mol_{CO,out}}{mol_{CO,in}} \times 100 \quad (3.1)$$

$$TOF = \frac{\text{rate of reaction}}{\text{metal active sites}} \quad (3.2)$$



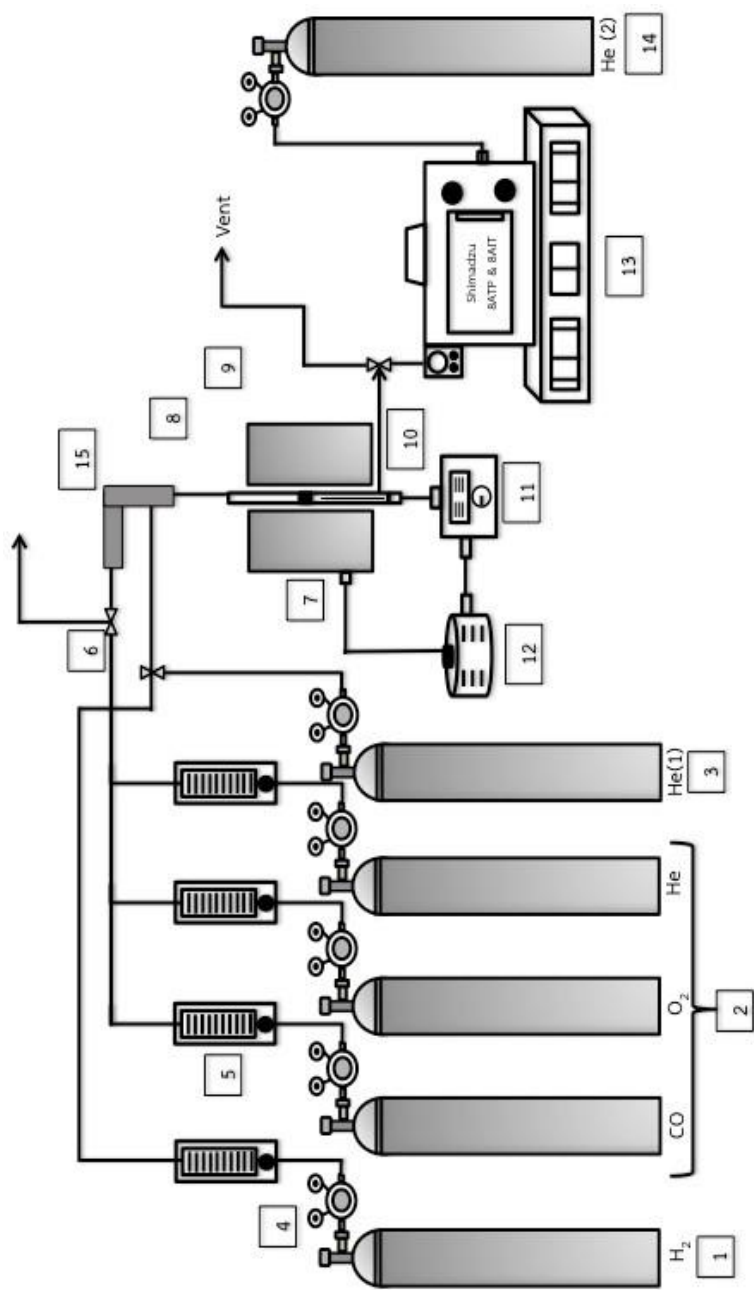


Figure 3.2 Schematic diagram of the reaction line for CO oxidation analyzed by gas chromatographs equipped with molecular sieve 5A columns. 1. H₂ gas 2. Reactant gas mixture 3. He Carrier gas (1) 4. Regulator 5. Mass flow controller 6. Three ways valve 7. Furnace 8. Quartz reactor 9. Packed bed 10. Thermocouple 11. Temperature controller 12. Variable Voltage 13. Gas Chromatograph 14. He Carrier gas (2) 15. Heating tape

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion in this chapter consist of two parts, including the effect of La (La/Al molar ratio 0.01, 0.05, 0.10, 0.15) modified Pt/ γ -Al₂O₃ on Pt dispersion, oxygen mobility and catalytic activity of CO oxidation of La modified Pt/ γ -Al₂O₃ catalysts and the second part, the effect of Ce (Ce/Al molar ratio 0.01, 0.05, 0.10, 0.15) modified Pt/ γ -Al₂O₃ on Pt dispersion, oxygen mobility and catalytic activity of CO oxidation of Ce modified Pt/ γ -Al₂O₃ catalysts. The catalyst characteristics were investigated by N₂-physisorption, SEM-EDX, XRD, CO₂-TPD, and CO pulse chemisorption technique.

4.1 Effects of La modified Pt/ γ -Al₂O₃ catalysts on Pt dispersion and oxygen mobility for CO oxidation

4.1.1 Effect of the modification on the physical and chemical properties of Pt/ γ -Al₂O₃ and La modified Pt/ γ -Al₂O₃ catalysts

The XRD patterns of the γ -Al₂O₃ supports and La modified γ -Al₂O₃ on Pt at $2\theta = 20^\circ$ to 80° are shown in Fig. 4.1. The XRD of the unmodified γ -Al₂O₃ showed the expected main peaks at $2\theta = 38^\circ$, 46° and 67° , corresponding to the (311), (400) and (440) planes, respectively [49]. After Pt metal was loaded to γ -Al₂O₃, the characteristic peaks of Pt were not observed. This may be due to well dispersion of Pt on support or very low amount of Pt loading [50]. In the same way, the characteristic peaks of La were not seen in the XRD patterns of Pt-0.01La, Pt-0.05La, Pt-0.10La and Pt-0.15La probably due to the low amount of La loading. However, the addition of La led to the decrease in peak intensities of γ -Al₂O₃. This suggests that the crystallinity of γ -Al₂O₃ was decreased.

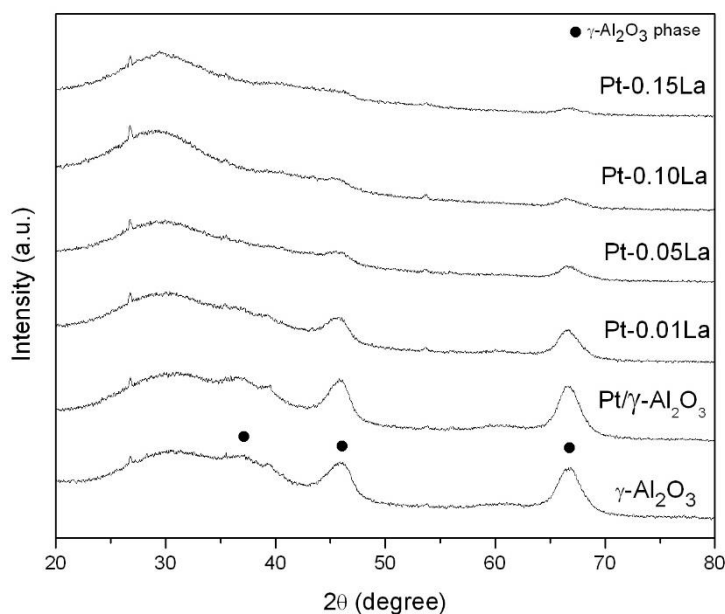


Figure 4.1 XRD patterns of the γ - Al_2O_3 support and La modified Pt/ γ - Al_2O_3 catalysts

The textural properties of the synthesized catalysts were determined by N_2 physisorption methods and the results are shown in Table 1 and Figs. 4.2-4.3. Fig. 4.2 shows that all samples exhibited type IV isotherms, a characteristic of mesoporous materials [51]. The BET surface area of the unmodified catalyst was $210 \text{ m}^2/\text{g}$. It was decreased to 203, 162, 107 and $75 \text{ m}^2/\text{g}$ with the increase of La loading to 0.01, 0.05, 0.10 and 0.15 molar ratio, respectively. This may be owing to the covering surface on Al_2O_3 surface by La content [52, 53]. Similarly, the pore volume of the samples was decreased by increasing the La loading. After La addition, the pore size of Pt/ γ - Al_2O_3 catalyst was decreased from 6.2 nm to 5.8 and 5.9 nm with increasing La content to 0.01 and 0.05 molar ratio, respectively. The decreasing of pore size diameter probably due to the accumulation of La_2O_3 and pore blockages [10]. However, the molar ratio of La/Al higher than 0.10 led to the increasing of pore size diameter and a shift of pore size distribution of La modified catalysts, as shown in Fig. 4.3, to the larger pore may occur by an amorphous structure when high loading La content was used. These results correspond to the XRD results as previously explained [54, 55].

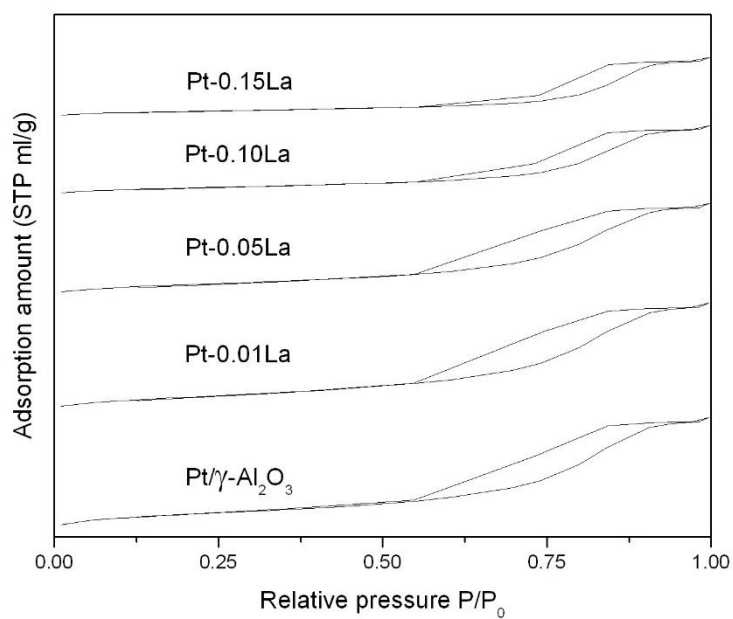


Figure 4.2 Nitrogen adsorption-desorption isotherms of La modified Pt/ γ -Al₂O₃ catalysts

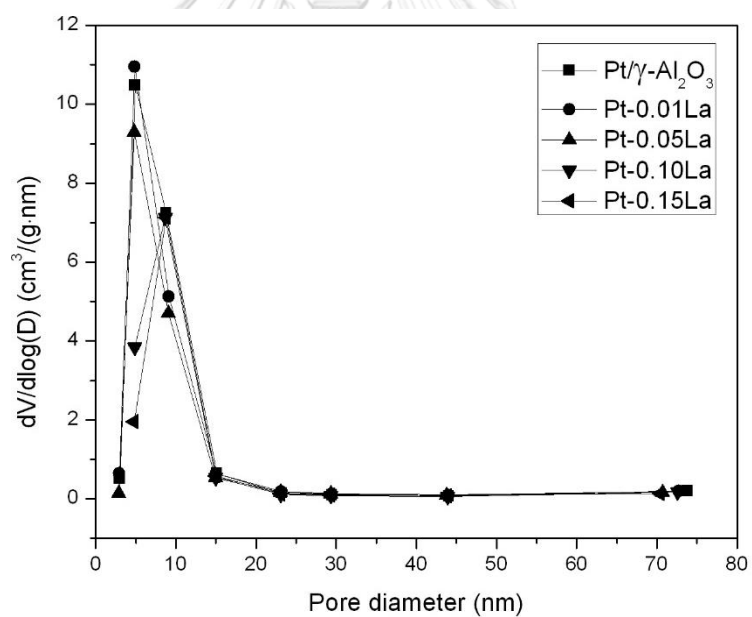


Figure 4.3 Pore size distribution of La modified Pt/ γ -Al₂O₃ catalysts

Table 4.1 Physical properties of La modified Pt/ γ -Al₂O₃ catalysts

Sample	Surface ^a area (m ² /g)	Pore volume ^b (cm ³ /g)	Average pore size ^b (nm)	Desorbed CO ₂ ^c (area/g)	Basicity ^c (mmol CO ₂ /g)	Active sites ^d (molecule COx10 ⁻¹⁸ /g.cat)
Pt/ γ - Al ₂ O ₃	210	0.48	6.2	1.17	0.41	7.20
Pt- 0.01La	203	0.47	5.8	1.76	0.62	8.87
Pt- 0.05La	162	0.40	5.9	4.21	1.48	7.55
Pt- 0.10La	107	0.30	7.4	7.48	2.63	6.02
Pt- 0.15La	75	0.25	8.1	8.22	2.89	5.00

^a calculated from BET method

^b calculated from BJH method (desorption branch)

^c calculated from CO₂ TPD method

^d calculated from CO chemisorption method

CO₂-TPD profiles and the amounts of desorbed CO₂ of the La modified Pt/ γ -Al₂O₃ catalysts were showed in Fig. 4.4 and Table 4.1, respectively. From Fig. 4.4, the results show that the peak of CO₂ desorption of Pt-0La and Pt-0.01La were clearly observed only at a low temperature about 100 °C. This peak could be attributed to the weak basic sites of Pt-0La and Pt-0.01La catalysts and was related to the desorption of undissociated CO₂ [56]. For the catalysts with higher loading of La: Pt-0.05La, Pt-0.10La and Pt-0.15La, another peak was observed at a high temperature about 300 °C. This peak could be attributed to the strong basic sites of Pt-0.05La, Pt-0.10La and Pt-0.15La catalysts and was related to the strong CO₂ interaction with La₂O₃ [56]. The amounts of basic sites of catalysts calculated from the peak area of CO₂ desorption

peak (Table 1) show that the amount of basicity of Pt-0La was 0.55 mmol CO₂/g and was increased to 0.99, 1.70, 2.87 and 3.14 mmol CO₂/g for Pt-0.01La, Pt-0.05La, Pt-0.10La and Pt-0.15La, respectively. The results suggest that the basicity of catalysts were increased with the increase of La loading. The La modified supports induced the construction of stronger base centers that could be correlated with free lanthanum highly dispersed on alumina surface [57, 58].

The amount of active sites of the catalysts from CO pulse chemisorption were shown in Table 4.1. The results show that the amount of active sites of Pt/ γ -Al₂O₃ was 7.20 molecule COx10⁻¹⁸/gcat and increased to 8.87 and 7.55 molecule COx10⁻¹⁸/gcat after loading La with molar ratio 0.01 and 0.05, respectively. The results suggest that the addition of a small amount of La can enhance the dispersion of Pt active metal on the catalysts compare with the unmodified catalyst [19, 52]. However, the high La loading catalysts were decreased the Pt active sites because of the high coverage of Al₂O₃ surface by La₂O₃ and resulted to more sintering of Pt metal [10].

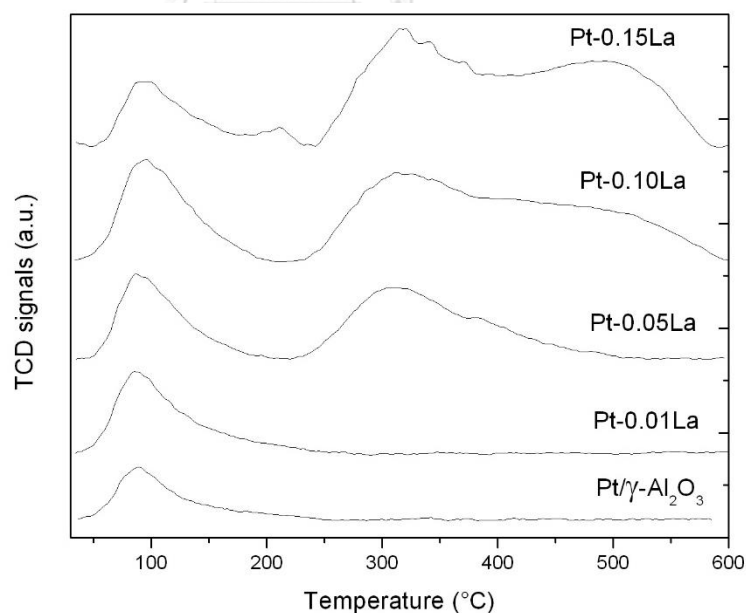


Figure 4.4 CO₂-TPD profiles of La modified Pt/ γ -Al₂O₃ catalysts

4.1.2 Catalytic performance and effect of oxygen mobility on CO oxidation over La modified Pt/ γ -Al₂O₃ catalysts

The CO conversion profiles as a function of reaction temperature were showed in Fig. 4.5A and The light off temperature (T_{50}) as a function of Pt active sites were showed in Fig 4.5B. The Pt-0.01La showed superior activity in CO oxidation with the lowest temperatures at 170°C for 50 % conversion. With increasing La content from 0.05 to 0.1 and 0.15 mole ratio, T_{50} increased from 170 to 173, 180 and 183°C. , respectively. Compared with the unmodified Pt/ γ -Al₂O₃ catalyst, La modified catalysts showed more catalytic activity than the unmodified catalyst because the addition of La can enhance the properties of Pt/ γ -Al₂O₃. For the Pt-0.05La and Pt/ γ -Al₂O₃ catalyst, T_{50} of Pt-0.05La was much higher than the Pt/ γ -Al₂O₃ despite closing amount of active sites (about 7.20 and 7.55 molecule CO $\times 10^{-18}$ /gcat). The differences in catalytic performances between two catalysts suggest that there might be some other effect besides the amount of Pt active sites involve in the CO oxidation on Pt/ γ -Al₂O₃ catalysts. According to N. Chotikrai et al. [10], the one of significant factor influencing CO oxidation activity is oxygen mobility. Therefore, the effect of La addition on oxygen mobility was investigated. According to D.Martin et al. [46], the rate of oxygen surface diffusion was practically linked to the amount of basic sites in which the higher basic sites exhibited higher oxygen mobility that correlated with CO₂-TPD result in Fig 4.4. The result show that the addition of La can increase the amount of basic sites of Pt/ γ -Al₂O₃ catalyst to result high catalytic activity because the Pt-O bond strength decreases as optical basicity increases [48], the O₂ movement on the surface is easier. The adsorbed oxygen can react with the adsorbed carbon monoxide easier.

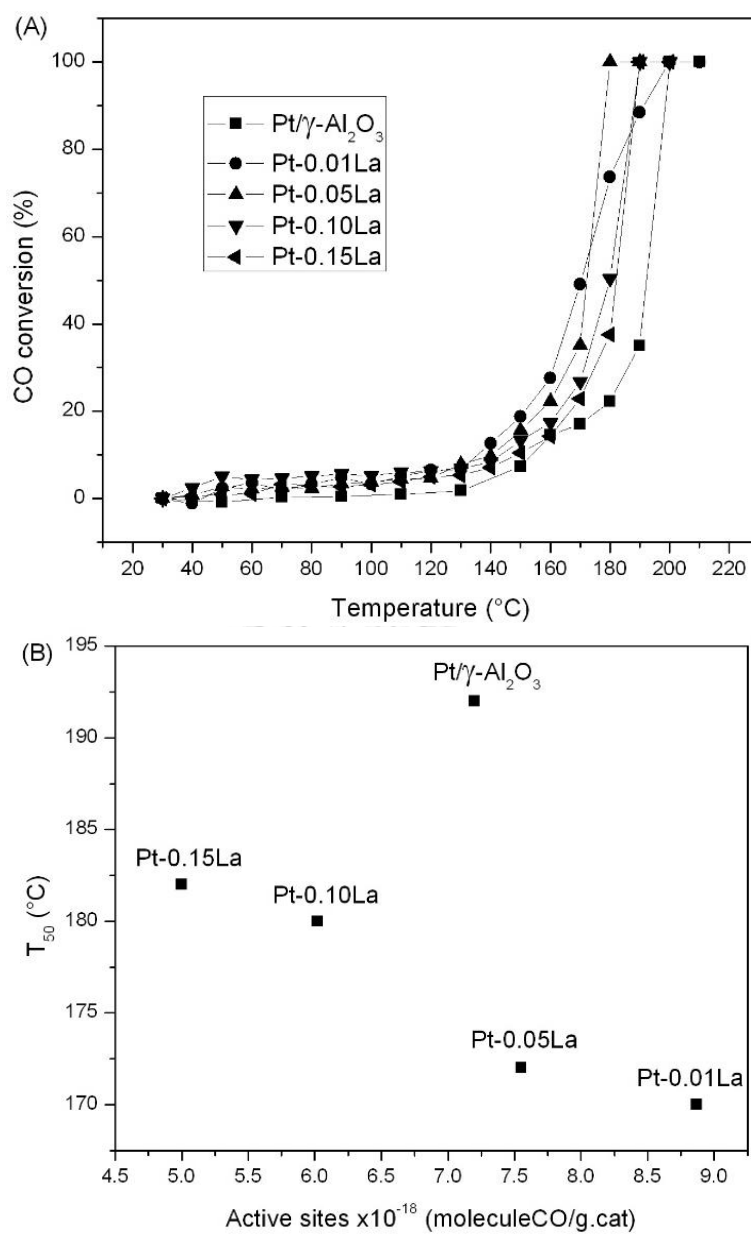


Figure 4.5 The CO oxidation results of La modified Pt/γ-Al₂O₃ catalysts: (A) conversion profiles, and (B) temperature at 50 % conversion versus Pt active sites

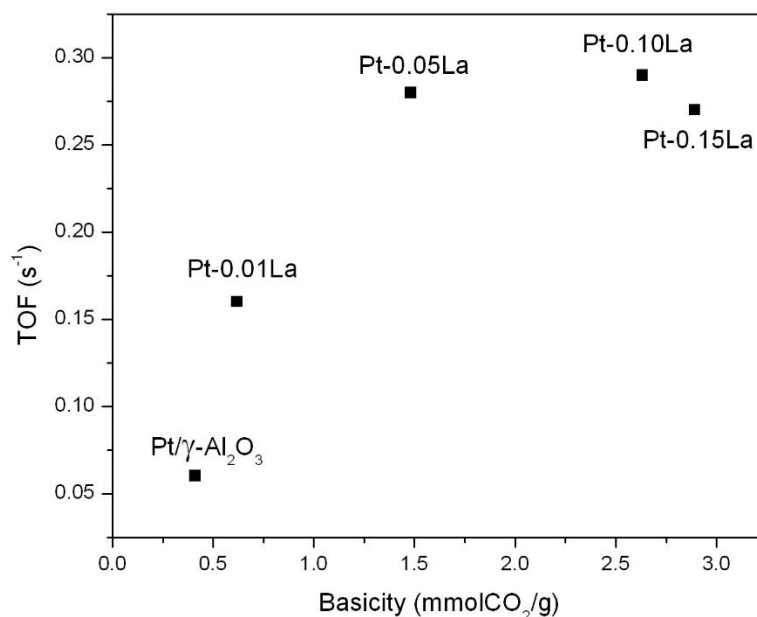


Figure 4.6 Relationship between TOF and Desorbed CO₂ of La modified Pt/γ-Al₂O₃ catalysts

In order to highlight the effect of oxygen mobility on CO oxidation besides the major influence of Pt active sites, the reaction rate per active site (TOF) is considered to be used for comparison as a function of basicity, for it is normally insensitive to the Pt particle size [59, 60]. Fig. 4.6 showed a relationship between TOF and basicity. It can be observed that the TOF increased as the amount of basicity increased (increasing La loading). This is highlight that the effect of oxygen on support basicity in oxidation reaction. However, the high addition of La decreased the Pt active sites and resulted to low TOF [61, 62]. As revealed by second metal dopants such as Si [10], the addition of La can improve oxygen mobility of Pt/γ-Al₂O₃ catalyst, which is opposite with adding Si that would decrease the oxygen mobility of catalyst. Therefore, La is suitable to the modified Pt/γ-Al₂O₃ catalyst more than Si.

4.2 Effects of Ce modified Pt/ γ -Al₂O₃ catalysts on Pt dispersion and oxygen mobility for CO oxidation

4.2.1 Effect of the modification on the physical and chemical properties of Pt/ γ -Al₂O₃ and Ce modified Pt/ γ -Al₂O₃ catalysts

The XRD patterns of the γ -Al₂O₃ supports and Ce modified Pt/ γ -Al₂O₃ catalysts at $2\theta = 20^\circ$ to 80° are shown in Fig. 4.7. The XRD of the γ -Al₂O₃ support showed the expected main peaks at $2\theta = 38^\circ$, 46° and 67° as mention above [49]. After Pt metal was loaded to γ -Al₂O₃, the characteristic peaks of Pt were not observed. This may be due to well dispersion of Pt on support or very low amount of Pt loading [50]. In the same way, the characteristic peaks of Ce were not observed in the XRD patterns of Pt-0.01Ce, Pt-0.05Ce probably due to the low amount of Ce loading. However, the characteristic peaks of Ce were observed in the XRD patterns of Pt-0.05Ce, Pt-0.10Ce, and Pt-0.15Ce at $2\theta = 29^\circ$, 33° , 49° and 57° . The results indicated that the characteristic peak were CeO₂ confirmed the formation of CeO₂ as the crystalline phase [63, 64].

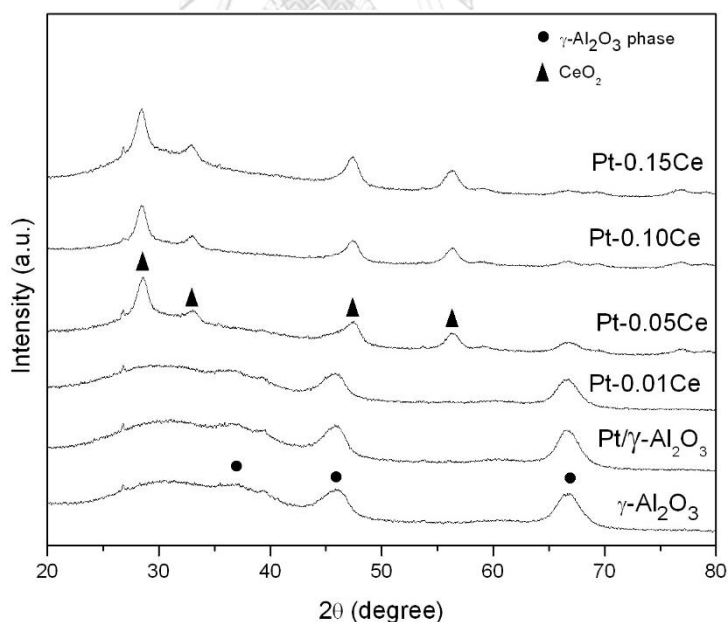


Figure 4.7 XRD patterns of the γ -Al₂O₃ support and Ce modified Pt/ γ -Al₂O₃ catalysts

The textural properties of the Ce modified catalysts were determined by N₂ physisorption methods and the results are shown in Table 4.2 and Figs. 4.8-4.9. Fig. 4.8 shows that all samples exhibited type IV isotherms, a characteristic of mesoporous materials [51]. The BET surface area of the Pt/ γ -Al₂O₃ catalyst was 210 m²/g. It was decreased to 188, 166, 149 and 114 m²/g with the increase of Ce loading to 0.01, 0.05, 0.10 and 0.15 molar ratio, respectively. The decreasing of surface area due to covering of the pores with cerium oxide species [30]. Similarly, the pore volume of the samples was decreased by increasing the Ce loading. After Ce addition, the pore size of Pt/ γ -Al₂O₃ catalyst was slightly increased from 6.2 nm to 6.4, afterward decreased to 6.0, 5.7, and 5.6 nm with increasing Ce 0.01, 0.05, 0.10, and 0.15 molar ratio, respectively. From Fig. 4.9, a shift of pore size distribution to the small pore size and the decreasing of the N₂ physisorption were owing to the accumulation of CeO₂ and pore blockages during the impregnation process [64].

Table 4.2 Physical properties of Ce modified Pt/ γ -Al₂O₃ catalysts

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Desorbed CO ₂ (area/g)	Basicity (mmol CO ₂ /g)	Active sites (molecule COx10 ⁻¹⁸ /g.cat)
Pt/ γ -Al ₂ O ₃	210	0.48	6.2	1.17	0.41	7.20
Pt-0.01Ce	188	0.46	6.4	1.32	0.46	8.89
Pt-0.05Ce	166	0.37	6.0	1.4	0.49	6.70
Pt-0.10Ce	149	0.32	5.7	1.52	0.54	5.51
Pt-0.15Ce	114	0.24	5.6	1.78	0.63	4.74

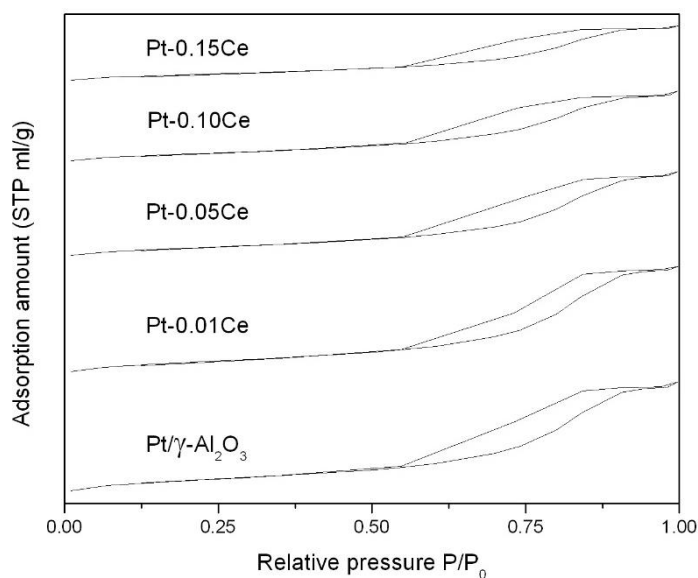


Figure 4.8 Nitrogen adsorption-desorption isotherms of Ce modified Pt/ γ -Al₂O₃ catalysts

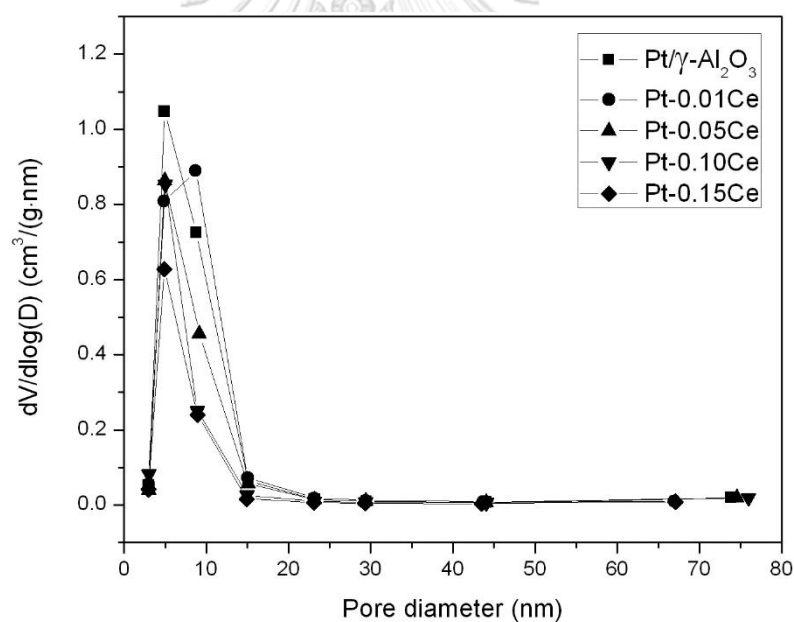


Figure 4.9 Pore size distribution of Ce modified Pt/ γ -Al₂O₃ catalysts

CO₂-TPD profiles and the amounts of desorbed CO₂ of the Ce modified Al₂O₃ catalysts are shown in Fig. 4.10 and Table 4.2, respectively. From Fig. 4.10, the results show that the peak of CO₂ desorption of Pt/ γ -Al₂O₃, Pt-0.01Ce Pt-0.05Ce were clearly observed only at a low temperature about 100 °C. This peak could be attributed to the weak basic sites. The weak basic sites were probably associated with Brønsted basicity and most likely with lattice-bound OH groups and physical adsorption of CO₂

[20]. For Pt-0.10Ce, and Pt-0.15Ce, a small peak was observed at a high temperature about 300 °C. This peak could be attributed to the strong basic sites. The strong basic sites were probably associated with Lewis basicity with the 3- and 4-fold-coordinated O_2^- anions, representing the strongest basicity among these sites [20]. The amounts of basic sites of catalysts calculated from the peak area of CO_2 desorption peak were showed in Table 2. The results showed that the amount of basicity was increased from 0.41 to 0.46, 0.49, 0.54 and 0.63 mmol CO_2/g for Pt/ γ - Al_2O_3 , Pt-0.01Ce, Pt-0.05Ce, Pt-0.10Ce and Pt-0.15Ce, respectively. The results suggest that the basicity of catalysts were slightly increased with the increasing of Ce loading. Compare with La modified catalysts, Ce modified catalysts showed slight increasing of basicity but La modified catalysts showed significant increasing of basicity due to very higher base properties of La more than Ce [21].

The amount of active sites of the Ce modified catalysts from CO-pulse chemisorption were showed in Table 4.2. For Pt-0.01Ce, the amount of active sites were increased from 7.20 to 8.89 molecule $CO \times 10^{-18}/g_{cat}$ compare with Pt/ γ - Al_2O_3 . The results indicated that the small addition of Ce inhibit the agglomeration of dispersed Pt, which has been attributed to a Pt-CeO₂ interaction. This interaction helps to maintain Pt in an oxidized state which is more difficult to sinter than metallic Pt [63]. However, high Ce loading lead to decrease the amount of active sites. The results suggest that P-Ce and/or Ce- Al_2O_3 interactions were formed which affected to the sintering of Pt metal during calcination that correlated with the decreasing of surface area in Table 4.2 [65, 66].

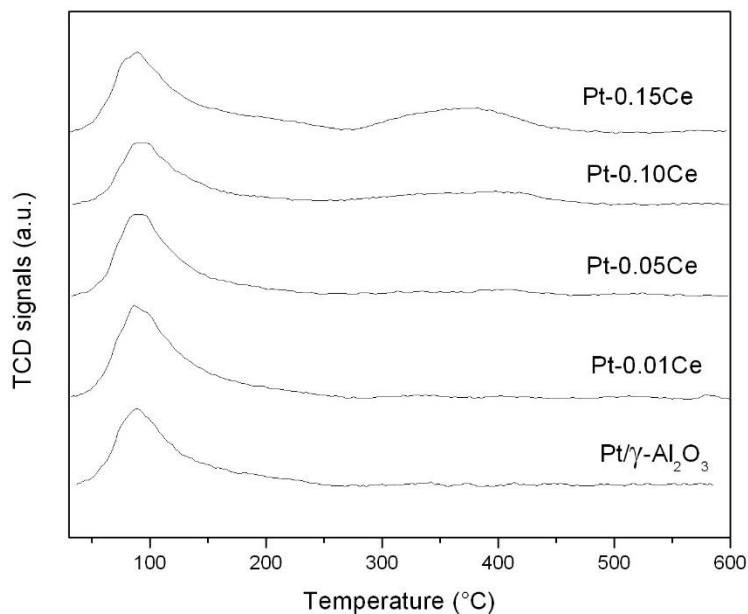


Figure 4.10 CO₂-TPD profiles of Ce modified Pt/ γ -Al₂O₃ catalysts

4.2.2 Catalytic performance and effect of oxygen mobility on CO oxidation over Ce modified Pt/ γ -Al₂O₃ catalysts

The CO conversion profiles as a function of reaction temperature were shown in Fig. 4.11A and The light off temperature (T_{50}) as a function of Pt active sites are shown in Fig 4.11B. The Pt-0.10Ce showed outstanding activity in CO oxidation with the lowest temperatures at 125°C for 50 % conversion. The results showed that the addition of Ce can increase the amount of basic sites of Pt/ γ -Al₂O₃ catalyst to result high catalytic activity due to the increasing of oxygen mobility [46]. Furthermore, the superior activity of Ce modified Pt/ γ -Al₂O₃ catalysts suggested that the O₂ storage properties affected to high O₂ vacancy in catalyst and easy movement of O₂ to active with CO adsorbed on surface [21]. However, the catalytic activity of Pt-0.15Ce was decreased due to the low amount of active sites.

To compare the activity between La and Ce modified catalysts in Fig. 4.12, the Ce modified catalysts showed higher activity than the La modified catalysts despite nearly active sites. The results suggest that were some factors affect to catalytic activity. This effect may be the O₂ storage property of Ce that modified on Pt/ γ -Al₂O₃ catalysts. The O₂ storage provide high O₂ vacancy of catalysts and improve mobility of

adsorbed O_2 [21, 67]. Furthermore, the O lattice in storage can react with CO adsorbed [68, 69].

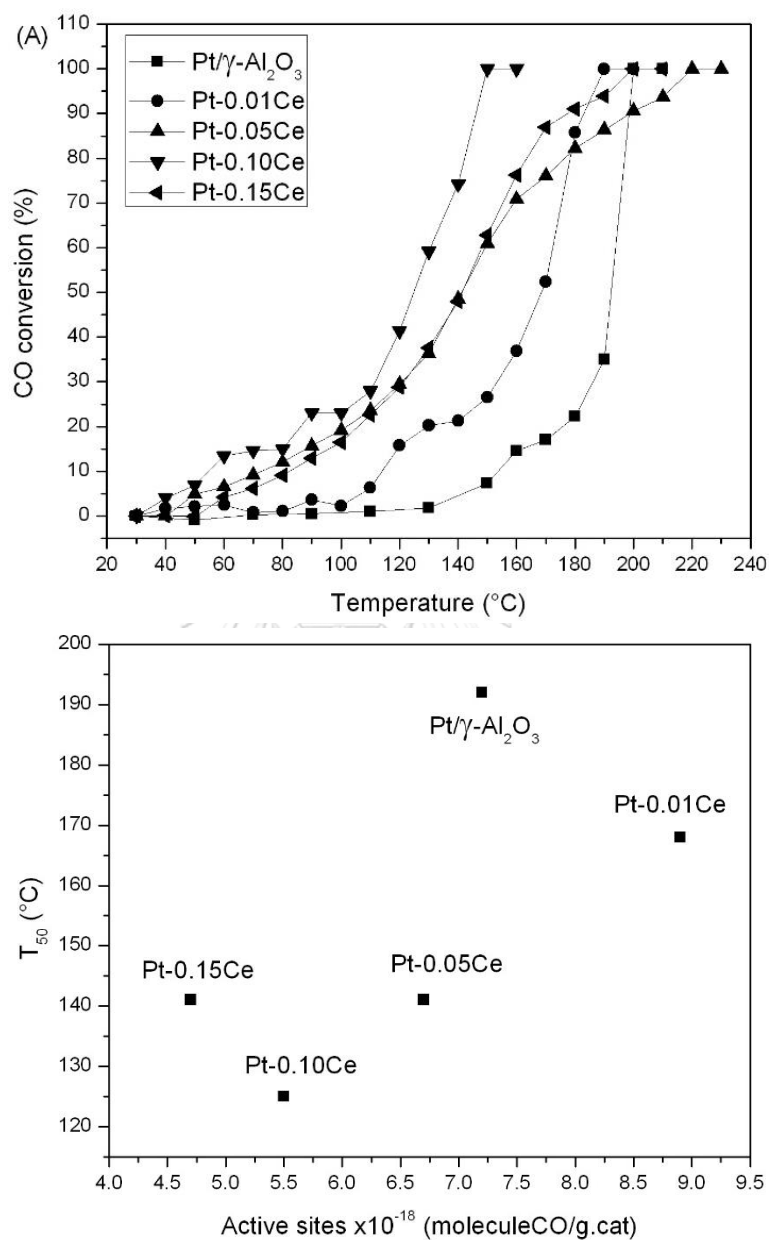


Figure 4.11 The CO oxidation results of Ce modified Pt/ γ -Al₂O₃ catalysts: (A) conversion profiles, and (B) temperature at 50 % conversion versus Pt active sites

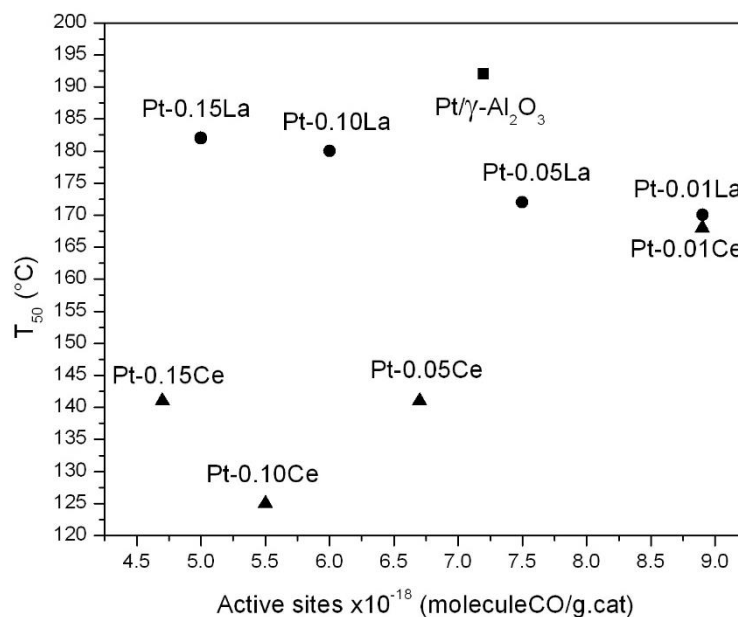


Figure 4.12 Light-off temperature (T_{50}) conversion versus Pt active sites of La and Ce modified Pt/ γ -Al₂O₃ catalysts

In order to highlight the effect of oxygen mobility on CO oxidation of Ce modified catalysts, the turnover frequency (TOF) is considered to be used for comparison as a function of basicity, Fig. 4.13 shows a relationship between TOF and basicity. It can be observed that the TOF increased as the amount of basicity increased with increasing of Ce loading. This is highlight the effect of oxygen on support basicity in oxidation reaction. However, the TOF of high addition of Ce (Pt-0.15Ce) was decreased due to the decreasing of Pt active sites [61, 62].

To compare the TOF between La and Ce modified catalysts in Fig. 4.14, both La and Ce modified catalysts was increased when the amount of basicity represented to oxygen mobility increased. Although, La modified catalysts showed higher oxygen mobility than Ce modified catalysts, Ce modified catalysts showed too much TOF than La modified catalysts. This results suggest that the catalytic activity of CO oxidation show different mechanism between La modified catalysts and Ce modified catalysts. The CO oxidation of La modified catalysts followed only the Langmuir Hinshelwood mechanism that related with reaction between adsorbed CO and O over metals sites at surface [2]. Nevertheless, the CO oxidation of Ce modified catalysts related with Langmuir Hinshelwood mechanism that involved the reaction between CO and O on

surface and Mars-van Krevelen mechanism that involved the reaction between CO and lattice O of catalyst [68-70]. Thus, the higher activity of Ce modified catalysts because of this reason.

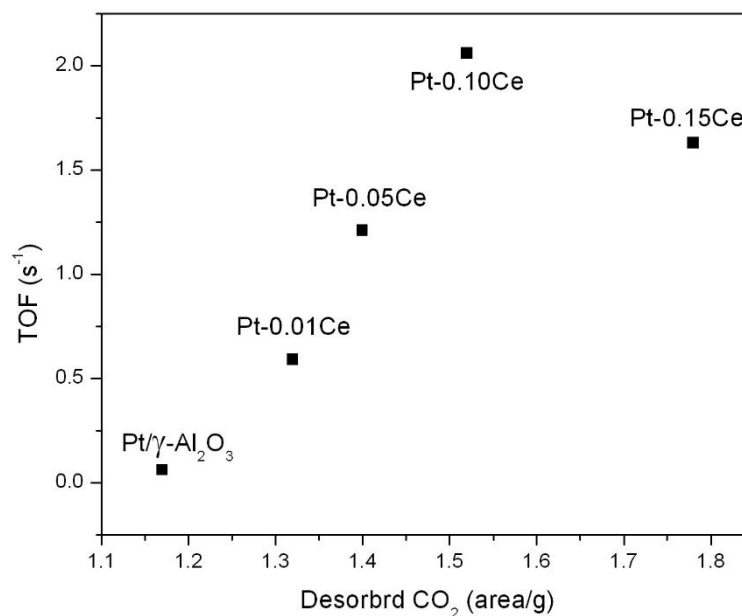


Figure 4.13 Relationship between TOF and Desorbed CO₂ of Ce modified Pt/γ-Al₂O₃ catalysts

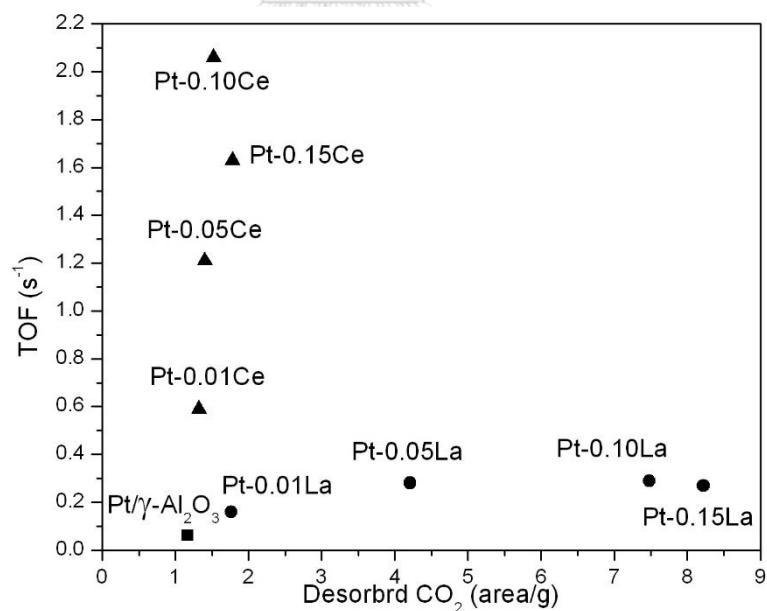


Figure 4.14 Relationship between TOF and Desorbed CO₂ of La and Ce modified Pt/γ-Al₂O₃ catalysts

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The results of CO oxidation over La modified catalysts suggested that the catalytic activity apparently depended not only on Pt dispersion but also oxygen mobility of the supports. The significant relationship between TOF and desorbed CO₂ also strengthened the effect of oxygen mobility relating to basicity of catalysts. The desorbed CO₂ as representative of oxygen mobility was extremely increased with increasing amount of La addition on the γ -Al₂O₃. Furthermore, Pt dispersion was highly improved on 0.01 and 0.05 mole ratio of La to supports and declined afterward due to the decreasing of active sites. The appropriate amount of La loading needs to be adjusted due to trading off effects between the dispersion of Pt sites and oxygen mobility. Among the various La modified Pt/ γ -Al₂O₃ catalyst catalysts prepared in this study, the Pt-0.05La showed the highest catalytic activity because it maximized Pt dispersion and the oxygen mobility.

In the same way, the Ce modified catalysts can improve the Pt dispersion and oxygen mobility. However, Ce modified catalysts showed superior activity than La modified catalysts because of the CO oxidation of Ce modified catalysts combine the O surface reaction and lattice O reaction that affect to higher activity than La modified catalysts. The addition of proper amount of La or Ce could adjust the Pt dispersion and oxygen mobility for high activity. Among of catalysts for CO oxidation in this work, Pt-0.10Ce was suitable used because of its highest activity.

5.2 Recommendations

5.2.1 To confirm the effect of oxygen mobility, other reaction without O₂ such as propane dehydrogenation should be investigated.

5.2.2 The oxygen vacancy of CeO₂ effect on mechanism of CO oxidation should be investigated.

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APPENDIX

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Appendix A

Calculation for catalyst preparation

A.1 Calculation for the preparation of La or Ce modified γ -Al₂O₃ support

Example calculation for the preparation of 0.01La-Al₂O₃ support

(molar ratio of La/Al = 0.01)

Data for calculation:

Mw. of Lanthanum nitrate hexahydrate = 433.01 g/mole

Mw. of Al₂O₃ = 101.96 g/mole

Base on 2g Al₂O₃ (La/Al ratio = 0.01)

Al₂O₃ 2g = 0.01962 mol Al₂O₃ = 0.03923 mol Al

La metal required = 0.0003923 mole

Lanthanum nitrate hexahydrate 1mole = 1mole La

$$\begin{aligned} \text{Weight of precursor required} &= \frac{\text{mole of precursor required} \times \text{Mw of precursor}}{\text{percent of purity}} \\ &= 0.0003923 \times 433.01 / 0.9999 \\ &= 0.16989 \text{ g} \end{aligned}$$

The 0.16989 g of Lanthanum nitrate hexahydrate is dissolved in 0.8 ml of de-ionized water to obtain a suitable amount of aqueous solution for 2 g of γ -Al₂O₃ support

A.2 Calculation for the preparation of metal loading catalyst (0.3 wt% Pt)

Example calculation for the preparation of Pt- γ -Al₂O₃

Data for calculation:

Mw. of Chloroplatinic acid hydrate (H₂Cl₆Pt • xH₂O) = 409.81 g/mole (38% Pt basis)

Mw. of Al₂O₃ = 101.96 g/mole

Mw of Platinum = 195.084 g/mole

Preparation platinum stock 20%wt/wt

1g of chloroplatinic acid hydrate was dissolved with 4ml of deionized water to design concentration stock.

Preparation 0.3%wt Pt- γ -Al₂O₃ catalyst

Based on 100 g of catalyst used, the composition of the catalyst is follow;

Platinum metal (Pt) = 0.3 g

Al₂O₃ = 100 - 0.3 = 99.7 g

For 1 g of Al₂O₃ support used

Platinum metal required = $1 \times (0.3/99.7)$ = 0.00301 g

Platinum metal 0.00301 g was acquired from H₂Cl₆Pt • xH₂O, which has 38% of Pt basis

H₂Cl₆Pt • xH₂O required = $0.00301/0.38$ = 0.007918 g

Thus, from the Pt stock solution with concentration 20%wt/wt

Pt stock solution required = $0.007918 \times (100/20)$ = 0.03959 g

The 0.03959 g of Pt stock solution is dissolved in 0.4 ml of de-ionized water to obtain a suitable amount of aqueous solution for 1 g of Al₂O₃ support

Appendix B

Calculation of total basic sites of catalysts

The surface basicity and strength of basic site for catalysts can be computed from the CO₂-TPD profiles by following these steps.

Definition - The area of the CO₂-TPD profiles of each sample = A

The mole of CO₂ was determined from the calibration curve of CO₂ desorbed as following formula:

The mole of CO₂ (mmol) = 0.017624 × A

Definition - Amount of each sample = B g.

The amount of basic sites of sample was determined in the range of temperature by this formula:

$$\begin{aligned} \text{The basicity of sample (mmol CO}_2\text{/g cat.)} &= \frac{\text{mmole of CO}_2\text{ of the sample}}{\text{Amount of dry catalysts}} \\ &= \frac{0.017624 \times A}{B} \end{aligned}$$

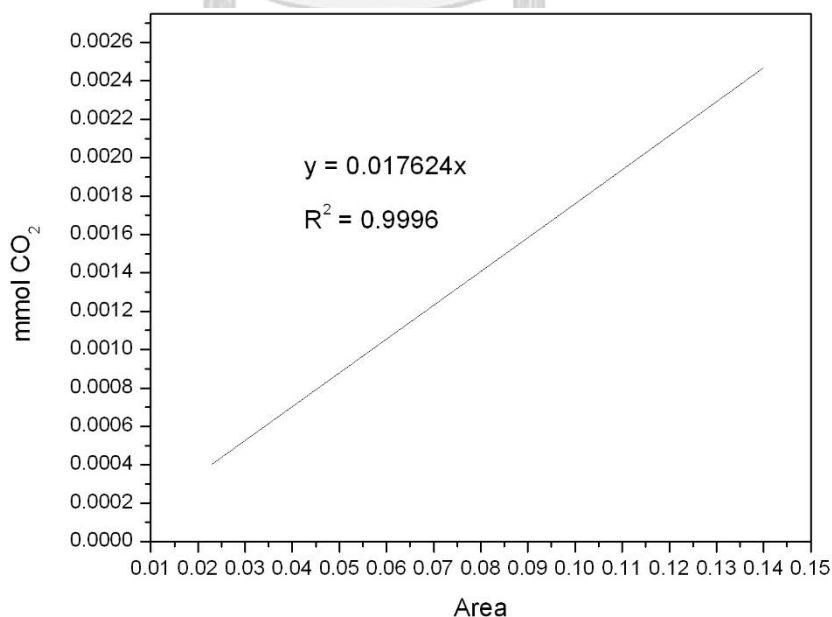


Figure B.1 The calibration curve of carbon dioxide obtained from CO₂-TPD profiles.

Appendix C

Calculation for CO chemisorption

CO pulse chemisorption was employed to determine the metal active sites on the Pt/ γ -Al₂O₃ catalyst.

The reaction stoichiometry of CO : Pt = 1 : 1

Let

Weight of catalyst used	= W	g
Peak area of CO per syringe	= A	unit
Integral adsorbed area of CO	= B	unit
Adsorbed ratio	= B/A	unit
Adsorbed quantity per 1 syringe	= 20 x B/A	μ L
Volume of CO 1mole of CO at 30°	= 24.85 x 10 ⁶	μ L
Mole of adsorbed CO on catalyst	= 20 x (B/A) / 24.85 x 10 ⁶	mmol
Molecule of adsorbed CO on catalyst	= [20 x (B/A) / 24.85 x 10 ⁶] x 6.02 x 10 ²³	molecule
Molecule of adsorbed CO per g-cat.	= [(B/A) x 4.845 x 10 ²³] / W	molecule/g-cat
Amount of metal active site	= Molecule of CO adsorbed per g-cat.	

Appendix D

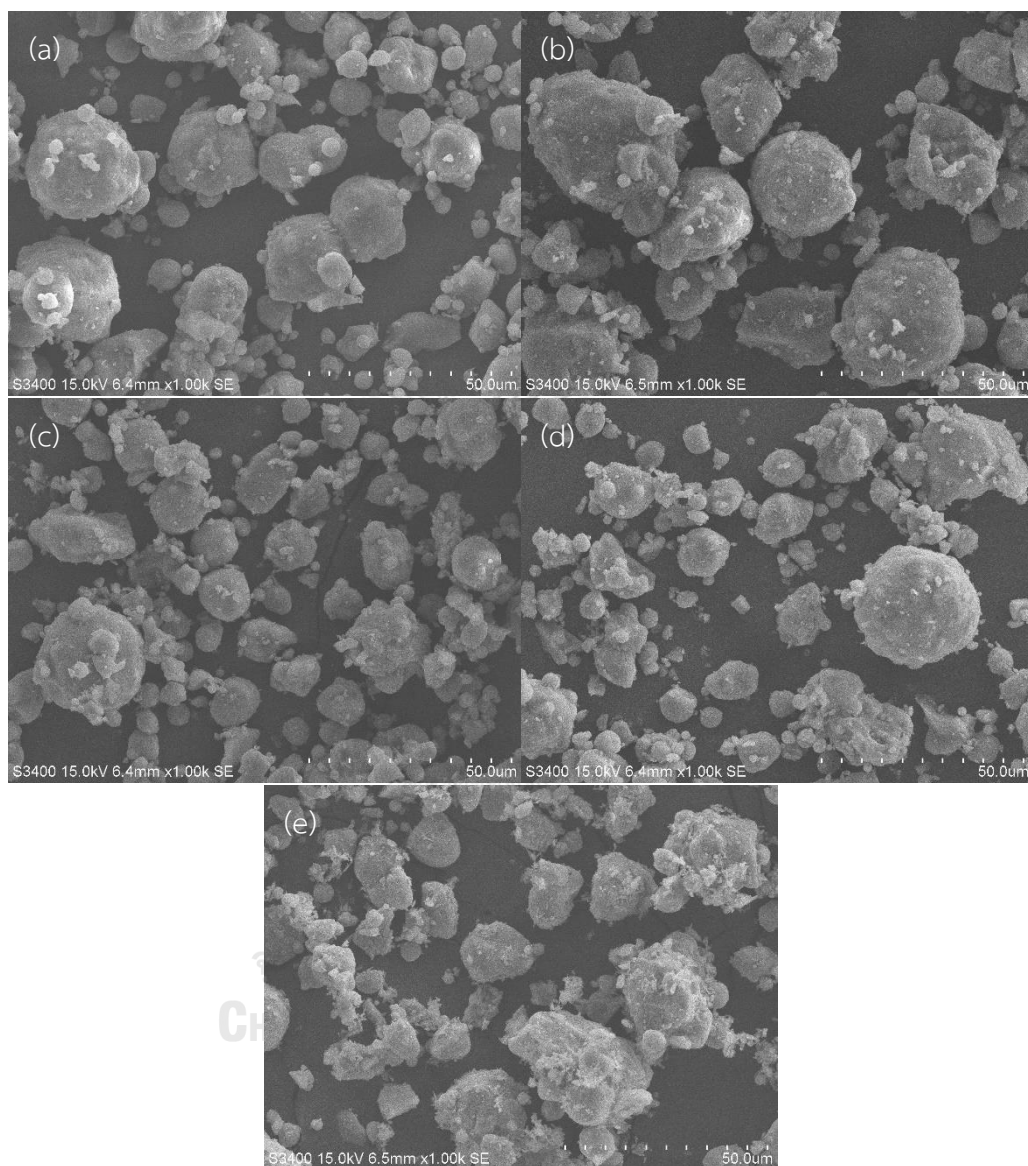
SEM Images and EDX Maps for La and Ce modified Pt/ γ -Al₂O₃ catalysts

Figure D.1 SEM images of the La modified Pt/ γ -Al₂O₃ catalyst at 1,000 magnification with molar ratio La/Al: (a) 0, (b) 0.01, (c) 0.05, (d) 0.10, and (e) 0.15

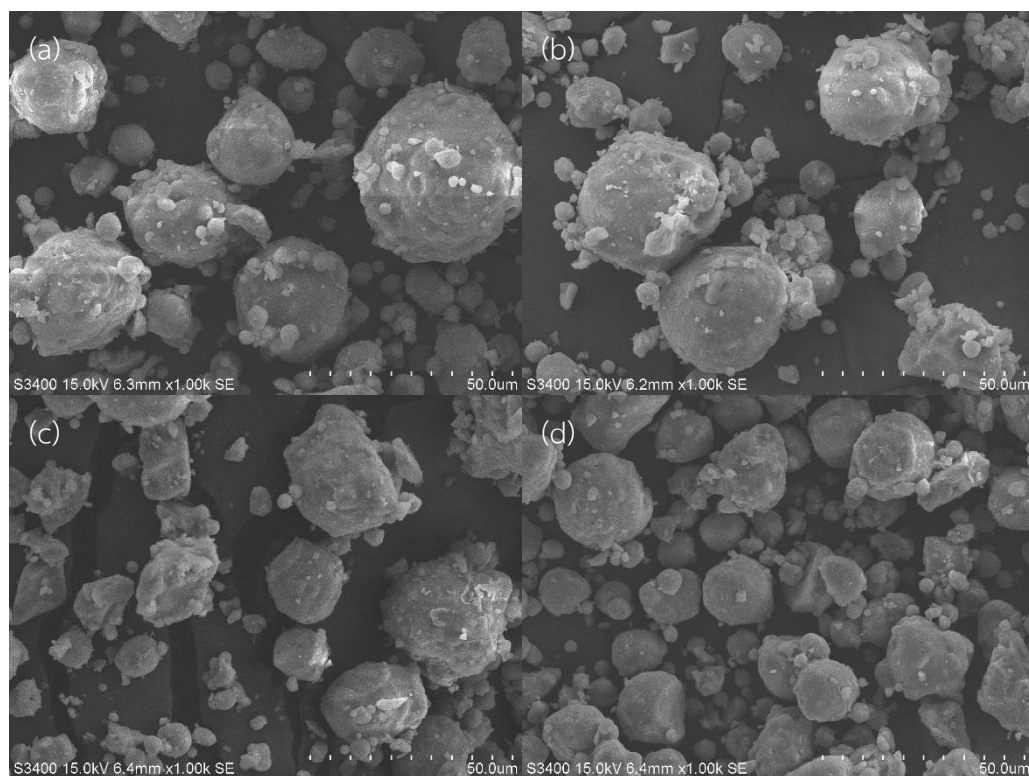


Figure D.2 SEM images of the Ce modified Pt/V-Al₂O₃ catalyst at 1,000 magnification with molar ratio Ce/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15

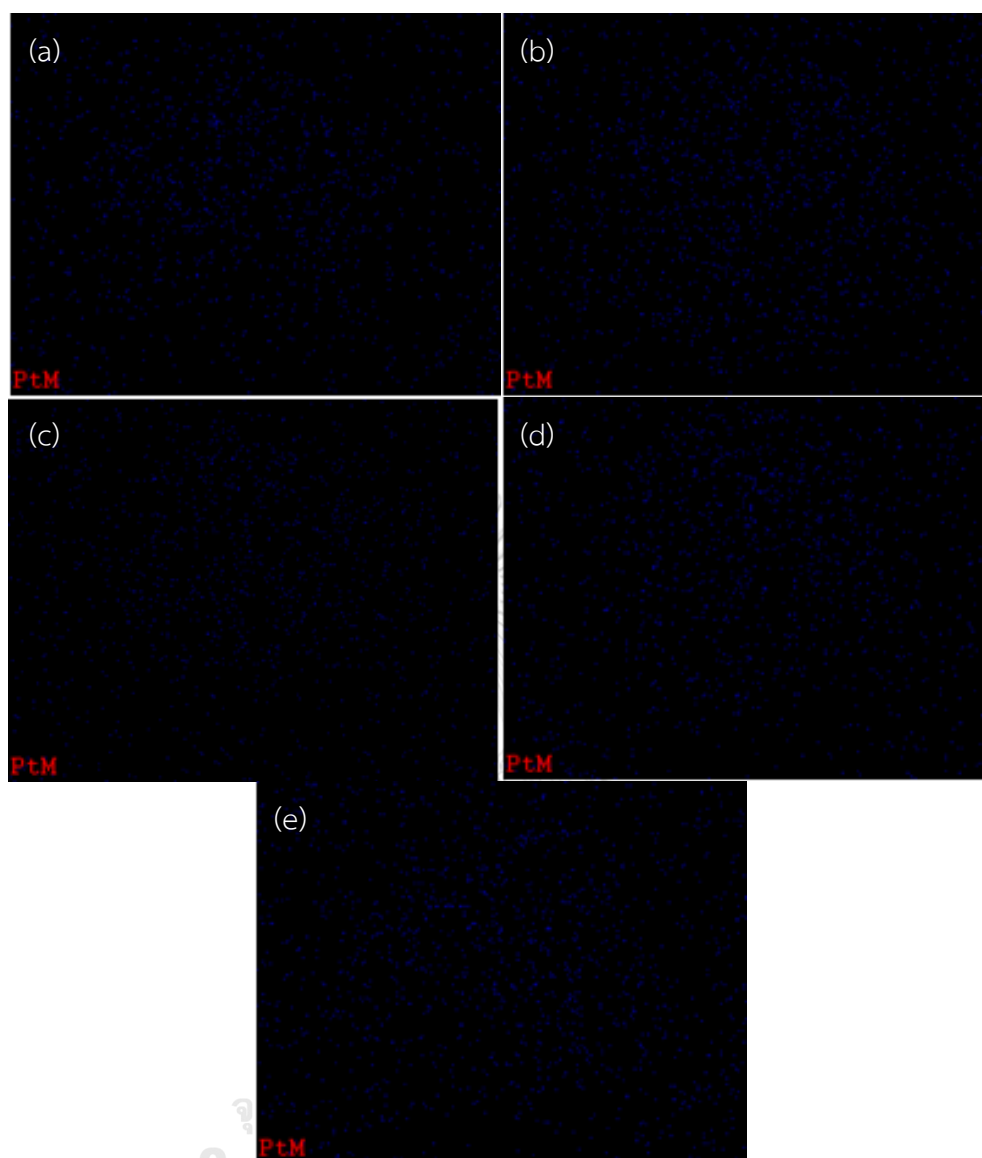


Figure D.3 EDX maps for Pt of the La modified Pt/ γ -Al₂O₃ catalyst at molar ratio La/Al: (a) 0, (b) 0.01, (c) 0.05, (d) 0.10, and (e) 0.15

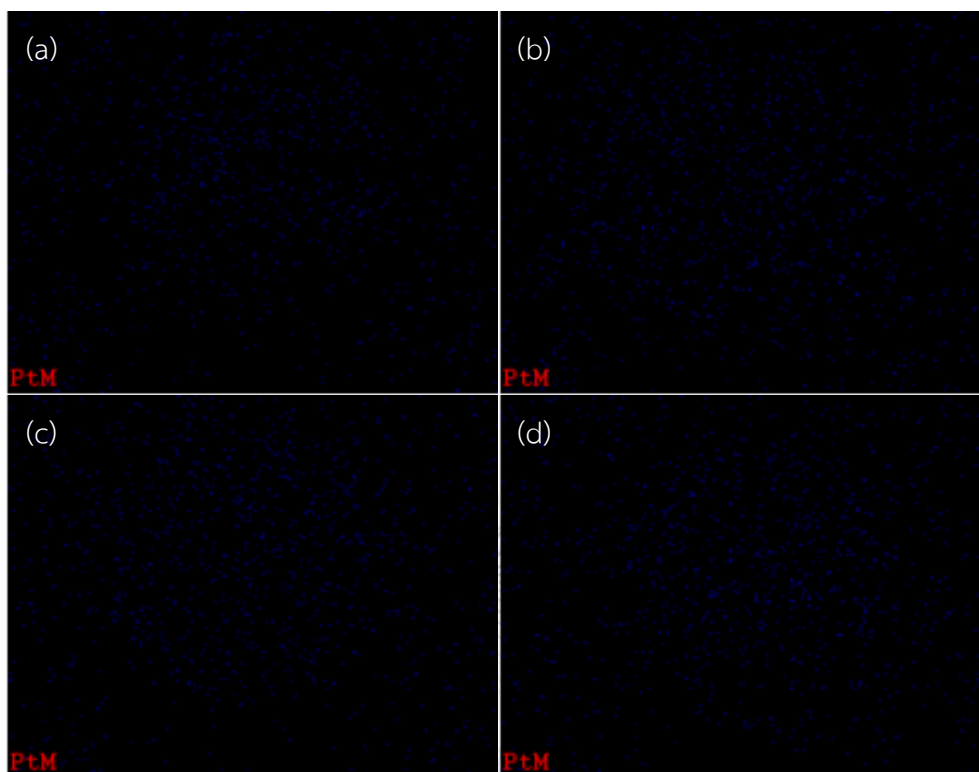


Figure D.4 EDX maps for Pt of the Ce modified Pt/ γ -Al₂O₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15

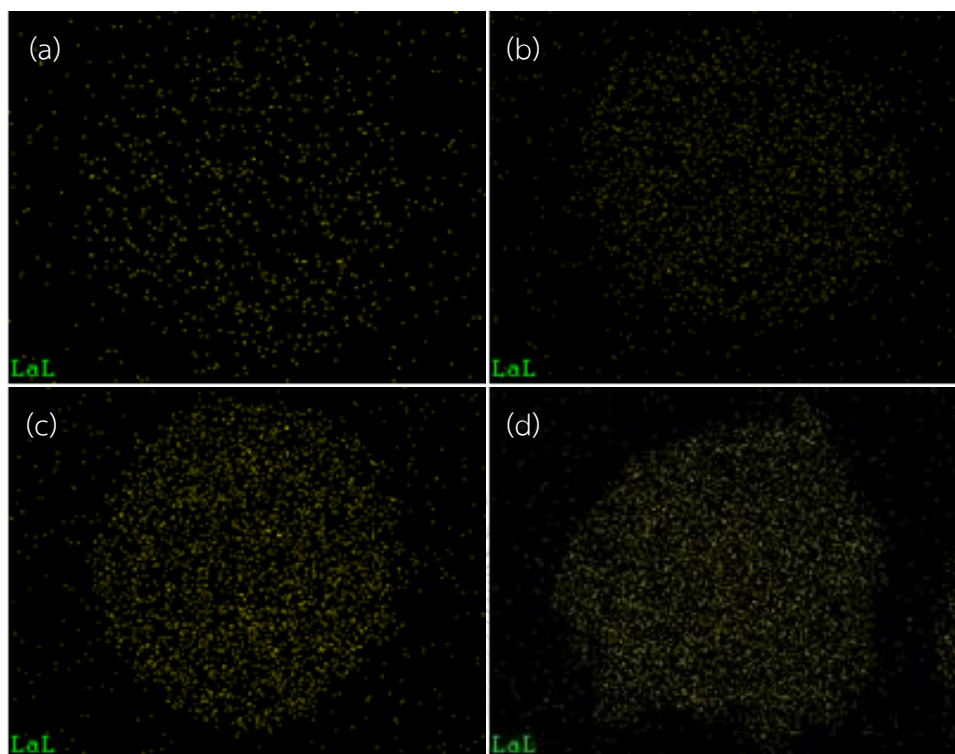


Figure D.5 EDX maps for La of the La modified Pt/ γ -Al₂O₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15

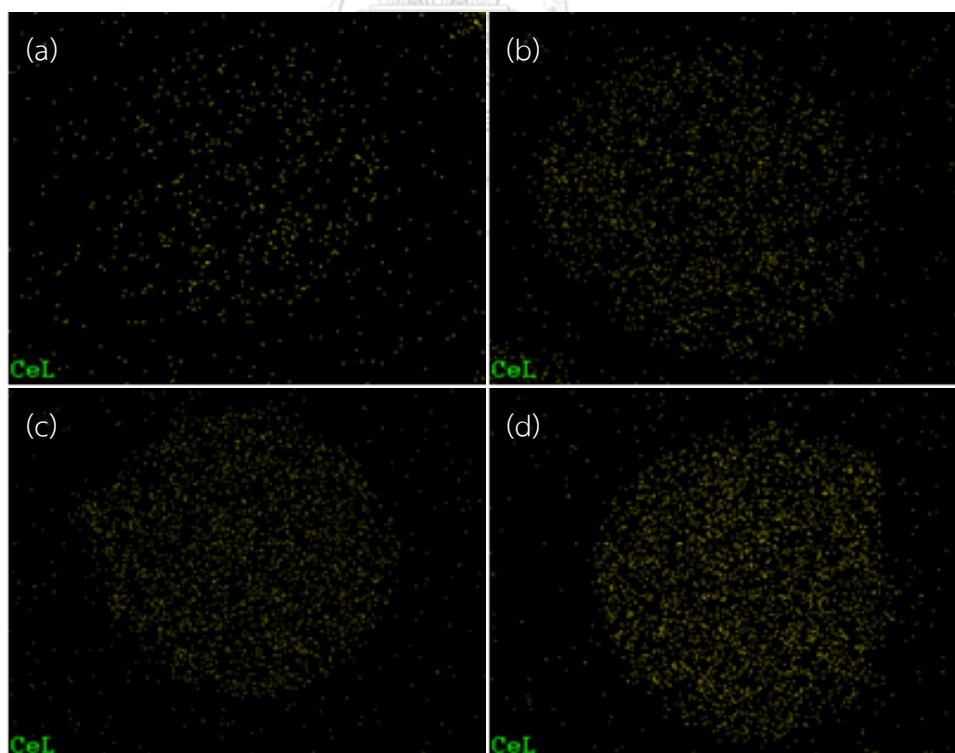


Figure D.6 EDX maps for Ce of the Ce modified Pt/ γ -Al₂O₃ catalyst at molar ratio La/Al: (a) 0.01, (b) 0.05, (c) 0.10, and (d) 0.15

VITA

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