ผลของการปรับสภาพอะลูมินาด้วยเหล็กและโคบอลต์ต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

นางสาวตติยา แสงคำ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550

EFFECT OF Fe- and Co-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION REACTION

Miss Tatiya Sangkhum

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2007

Thesis Title	EFFECT OF Fe- AND Co-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION REACTION
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ตติยา แสงคำ : ผลของการปรับสภาพอะลูมินาด้วยเหล็กและโคบอลต์ต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน (EFFECT OF Fe- and Co-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION REACTION) อ. ที่ปรึกษา: ผศ.ดร. จูงใจ ปั้นประณต, 93 หน้า.

งานวิจัยนี้ ศึกษาผลของอะลูมินาที่ปรับสภาพด้วยเหล็กและโคบอลต์ที่อัตราส่วนโดยโมลต่ออะลูมิเนียมต่างๆ (0 0.1 0.3 และ 0.5) ซึ่งเตรียมโดยวิธีโซล-เจลและวิธีโซลโวเทอร์มอลต่อสมรรถนะตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีนพบว่าสำหรับตัวเร่งปฏิกิริยาแพลเลเดียมที่ทำการปรับสภาพด้วยเหล็กทุกตัวซึ่งเตรียมโดยวิธีโซล-เจลแสดงความว่องไวและให้ค่าการเลือกเกิดเอทิลีนสูงกว่าตัวเร่งปฏิกิริยาแพลเลเดียมที่ไม่ทำการปรับสภาพ ในขณะที่วิธีโซลโวเทอร์มอลมีเพียงที่อัตราส่วนโดยโมลของเหล็กต่ออะลูมิเนียมเท่ากับ0.1เท่านั้นที่ทำการปรับสภาพแล้วประสิทธิภาพของตัวเร่งปฏิกิริยาสูงขึ้น ความว่องไวและการเลือกเกิดของเอทิลีนขึ้นอยู่กับขนาดอนุภาคของแพลเลเดียมของตัวเร่งปฏิกิริยาซึ่งสัมพันธ์กับขนาดผลึกของตัวรองรับ(ทั้งอัลฟา-อะลูมินาและเหล็กออกไซด์) จากการวิเคราะห์โดยการดูดซับแอมโมเนียแบบโปรแกรมอุณหภูมิแสดงให้เห็นว่าการปรับสภาพอะลูมินาด้วยเหล็กส่งผลต่อการลดความเป็นกรดของอะลูมินาทั้ง2 วิธีทำให้การเกิดโค้กลดลง ในอีกทางหนึ่งการปรับสภาพอะลูมินาด้วยโคบอลต์ของตัวเร่งปฏิกิริยาแพลเลเดียมซึ่งเตรียมโดยวิธีโซลโวเทอร์มอลจะทำให้เกิดโคบอลต์อะลูมิเนตที่อัตราส่วนโดยโมลโคบอลต์ต่ออะลูมินาต่ำกว่าวิธีโซลเจลเนื่องจากเกิดผลึกของแข็งได้ง่ายกว่า และการกระจายตัวของแพลเลเดียมลดลงเมื่อเกิดเป็นโคบอลต์อะลูมิเนตทั้งหมด ผลส่วนใหญ่แสดงว่าการปรับสภาพอะลูมินาด้วยโคบอลต์ทำให้ประสิทธิภาพของตัวเร่งปฏิกิริยาแพลเลเดียมดีขึ้น โดยเฉพาะอย่างยิ่งเมื่อค่าการแปลงของอะเซทิลีนเข้าใกล้100% แต่ไม่ส่งผลชัดเจนต่อการลดการเกิดโค้กบนตัวเร่งปฏิกิริยา

ภาควิชา..........วิศวกรรมเคมี.......... ลายมือชื่อนิสิต..........ตติยา แสงคำ..........
สาขาวิชา..........วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา....................
ปีการศึกษา..........2550..........

4970325421: MAJOR CHEMICAL ENGINEERING

KEYWORDS: IRON- AND COBALT-MODIFIED ALUMINA/IRON OXIDE/ COBALT ALUMINATE/ SOLVOTHERMAL METHOD/ SOL-GEL METHOD/ SUPPORTED PALLADIUM CATALYSTS/ SELECTIVE ACETYLENE HYDROGENATION

TATIYA SANGKHUM: EFFECT OF Fe- and Co-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION REACTION. THESIS ADVISOR: ASST. PROF. JOONGJAI PANPRANOT, Ph.D., 93 pp.

In this study, the effect of Fe- and Co-modified Al_2O_3 prepared by sol-gel and solvothermal methods with various Fe/Al and Co/Al molar ratios (0, 0.1, 0.3 and 0.5) on the catalytic performances of supported Pd catalysts for selective hydrogenation of acetylene have been studied. It was found that all the Pd catalysts supported on Fe-modified α-Al_2O_3 that were prepared by sol-gel method exhibited higher activity and ethylene selectivity than the unmodified while those prepared by solvothermal method, only the catalyst with Fe/Al=0.1 showed improvement. Acetylene conversion and ethylene selectivity depended on the average Pd particle size which itself was a function of crystallite size of the supports (both α-Al_2O_3 and α-Fe_2O_3). NH3-TPD results suggest that acidity of Fe-modified α-Al_2O_3 was lower than the unmodified supports so the modified catalysts exhibited lower coke formation. For Co-modified α-Al_2O_3 supported Pd catalysts, those prepared by solvothermal method resulted in $CoAl_2O_4$ formation at lower Co/Al ratio than sol-gel method because solid-solution occurred more easily by solvothermal method. However, for both techniques, dispersion of Pd decreased when $CoAl_2O_4$ was formed. In most cases, Pd catalysts on the Co-modified α-Al_2O_3 supports showed better performance than on the unmodified supports especially at nearly 100% conversion of acetylene. The effect of Co-modified Al_2O_3 on coke formation, however, was not clearly shown.

Department ...Chemical Engineering.....
Field of Study Chemical Engineering.......
Academic year ....2007..................

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Advisor's signature ....

ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude and appreciation to her advisor, Assistant Professor Joongjai Panpranot, Ph.D., for her invaluable suggestions, encouragement during her study, useful discussions throughout this research and especially, giving her the opportunity to present her research at 17th the Thai Institute of Chemical Engineering and Applied Chemistry conference in Chiangmai. In addition, the author would also be grateful to Associate Professor Supakanok Tongyai, as the chairman, Assistant Professor Bunjerd Jongsomjit, and Assistant Professor Okorn Mekasuwandurong as the members of the thesis committee.

She is indebted for financial supports of the Thailand Research Fund (TRF), TJTTP-JBIC, and the Graduate School of Chulalongkorn University are gratefully acknowledged.

Most of all, the author would like to express her highest gratitude to her parents who always pay attention to her all the times for suggestions and listen her complain. The most success of graduation is devoted to her parents.

The author would like to acknowledge with appreciation to Professor Piyasan Praserthdam for their kind suggestions on her research without hesitation

Finally, the author wishes to thank the members of the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for friendship and their assistance. To the many others, not specifically named, who have provided her with support and encouragement, please be assured that she thinks of you.

CONTENTS

Page

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Rationale

Petrochemical companies continuously strive to enhance the profitability of their ethylene plant operations as they face the ongoing challenges of an increasingly competitive industry. Growing competition from low-cost feedstock producers, tightening environmental regulations, and increasingly volatile feedstock and energy costs all contribute to the necessity of operating plants at maximum efficiency and reliability. The selective hydrogenation of acetylenes is a key unit operation within the ethylene process and can make a significant contribution to the efficiency gains demanded by this competitive operating environment.

The selective hydrogenation of acetylene is used in naphtha crackers in the manufacture of polymer-grade ethylene, which is required to contain less than 5–10 ppm of acetylene as an impurity. There have been two general approaches to reducing the amount of acetylene to 5 ppm: reaction and separation. Separation of acetylene from ethylene is very difficult and thus very costly. For this reason, the selective hydrogenation of this impurity to ethylene is the most attractive route.

Early work on the kinetics of the selective hydrogenation of acetylene began in Germany around the turn of the century. The use of palladium as the active metal was studied by Cremer et al. in a kinetic analysis. Work prior to 1963 has been summarized by Bond. He showed that Pd was the most selective metal for this reaction. Industries still rely on this formulation to prepare the traditional $Pd/\alpha\text{-}Al_2O_3$ catalyst, which is normally used for this reaction. It is usually prepared by either ion exchange or precipitation to produce a low-dispersion, low-metal content supported catalyst. The original idea was to prevent the re-adsorption of ethylene by using low metal content and to prevent the conjugation of adsorbed acetylene molecules to proceed towards either coke formation, C4 oligomers or C6's. The C4's are well known to industry as "green oil" [Matthew *et al.,* 2001].

Generally, the catalyst support must present a good stability to high temperature and a sufficiently large specific surface area. They can interact more or less with the active metal and can possess other functions, such as acidity or basicity [Guimon *et al.,* 2003]. Supported palladium catalysts are widely for selective hydrogenation of acetylene and modification of palladium with a second metal such as Si [Shin *et al.*, 1998], Au [Sárkány *et al.,* 2002], Co [Sárkány *et al.,* 1995] and Ag [Praserthdam *et al.,* 2002 and Ngamsom *et al.,* 2004] has been reported as an alternative way for selectivity enhancement for palladium catalysts. The commonly used supported are α-Al_2O_3 and silica.

It is interesting to study the effect of Fe-modified Al_2O_3 because it can form iron oxide (Fe_2O_3) in mixed oxide system (Al_2O_3-Fe_2O_3). The main characteristics of iron oxide are redox behavior, medium to low surface area, easy sintering. In principle, chemical mixing of Fe_2O_3 with Al_2O_3 could be beneficial, so as to produce oxidation catalysts with improved stability or mechanically and thermally stable powders with redox functionality [Ladavos *et al.,* 2001].

And it is interesting to study the effect of Co-modified Al_2O_3 because it can form Cobalt aluminate ($CoAl_2O_4$) which has a normal spinel structure in which Co^{2+} are accommodated in tetrahedral positions while Al^{3+} ions are in octahedral positions. $CoAl_2O_4$ has received special interest due to their technological applications as inorganic ceramics blue pigment [Zayat *et al.,* 2000 and Mimani *et al.,* 2001]. $CoAl_2O_4$ is also of great interest in the field of heterogeneous catalysis while it has been used for catalytic application [Chokkaram *et al.,* 1997 and Arean *et al.,* 1999].

The main purpose of this thesis is to investigate the characteristics and catalytic properties of Fe- or Co-modified Al_2O_3 supported Pd catalysts in selective hydrogenation of acetylene. In this investigation, the effects of preparation method such as sol-gel and solvothermal method as well as the Fe/Al ratio and Co/Al ratio on the properties of the final Pd/Al_2O_3 catalysts will be focused.

1.2 Objective

The objective of this research is to investigate the characteristics and catalytic properties of the Fe- or Co-modified Al_2O_3 supported Pd catalysts in selective acetylene hydrogenation in excess ethylene.

1.3 Research Scopes

(1) Preparation of using α-Al_2O_3 by sol- gel and solvothermal methods.

(2) Preparation of Fe- or Co-modified α-Al_2O_3 with various molar ratios of Fe or Co to Al (0, 0.1, 0.3 and 0.5) by sol-gel and solvothermal methods.

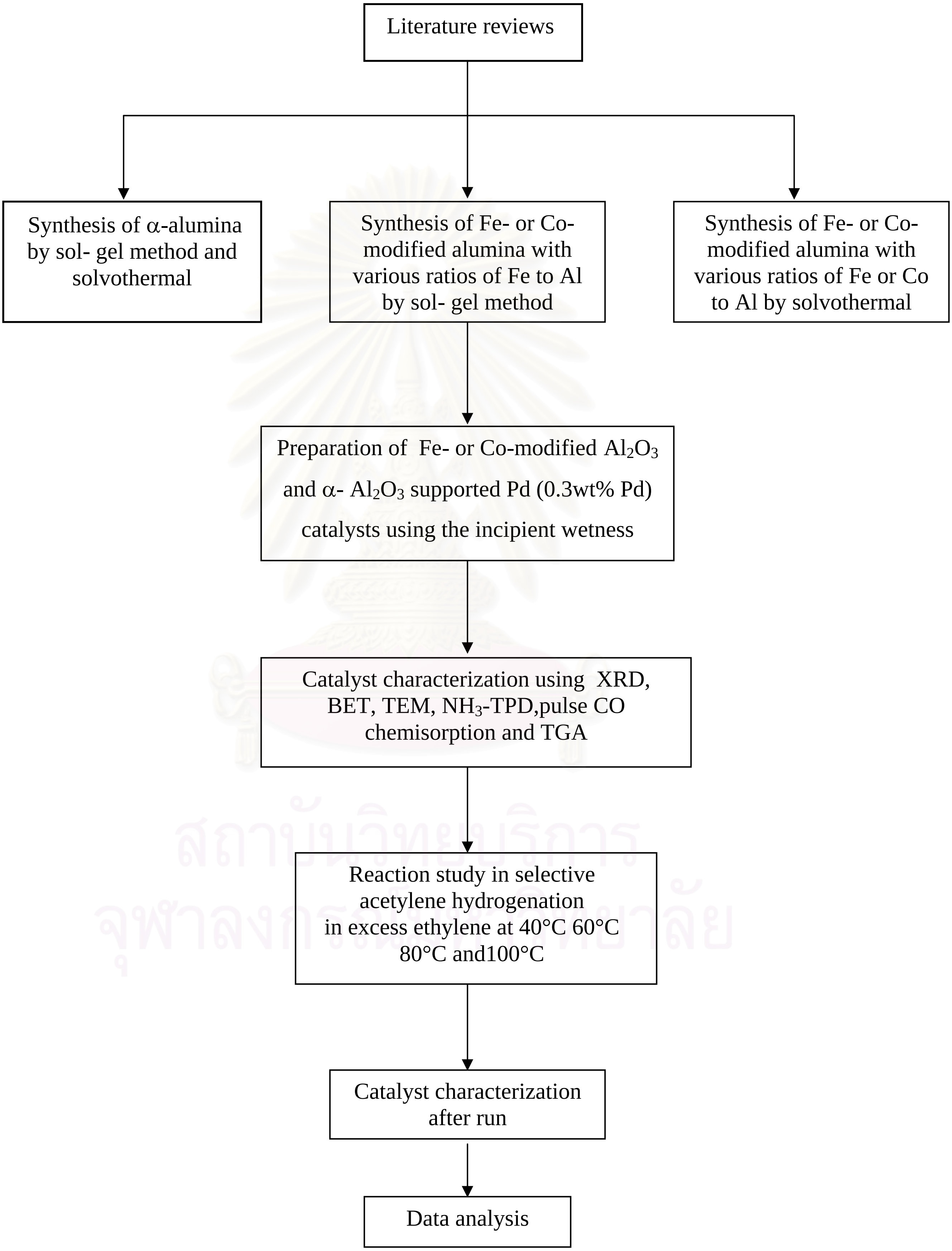
(3) Preparation of α-Al_2O_3 and Fe- or Co-modified α-Al_2O_3 supported Pd catalysts (0.3 wt% Pd) using the incipient wetness impregnation method.

(4) Characterization of the catalyst sample using X- ray diffraction (XRD), BET surface area, transmission electron microscopy (TEM), CO pulse chemisorption, NH_3-temperature programmed desorption and thermo gravimetric analysis (TGA),

(5) Study of catalyst performance in selective acetylene hydrogenation using a fixed-bed quartz reactor.

(6) Study of catalyst deactivation after performing acetylene hydrogenation using temperature program oxidation.

1.4 Research Methodology



CHAPTER II

LITERATURE REVIEWS

The present review is intended to collect and analyze the results of supported palladium catalysts in selective hydrogenation reaction as reported in recent years (2.1), Fe-Al_2O_3 (2.2), Co-Al_2O_3 (2.3) and comments on previous studies that have directly influenced the aims of this study are given (2.4).

2.1 Supported Pd Catalysts in Selective Hydrogenation Reaction

Sárkany and coworkers (1984) studied the hydrogenation of a mixture of 0.29 mole% C_2H_2, 0.44 mole% H_2 and C_2H_4 up to 100%, a so-call tail-end mixture, on palladium black and several Pd/Al_2O_3 catalysts. Hydrogenation of C_2H_4 increased with time on stream for all the Al_2O_3-supported catalysts; the opposite behaviour was noted with palladium black. Polymer formation was noted for all catalysts studied and also increased with time. It was recognized that a small number of C_2H_4 hydrogenation sites were located on the metal but the majority were on the polymer-covered support. The authors proposed that C_2H_4 adsorbed on the support and was hydrogenated there. Spill-over hydrogen was tentatively identified as the source of hydrogen. Because of the parallelism between polymer formation and ethylene hydrogenation, it was proposed that the surface polymer served as a hydrogen pool or facilitated diffusion of hydrogen from Pd to the support.

Jermim Noh *et al.* (1999) studied the characteristics of the Pd-only three-way catalysts prepared by sol–gel method. The catalysts were characterized with XRD, XPS, BET surface area and pore volume. The activity and thermal stability of the Pd–Al_2O_3 catalyst prepared at pH 10 were superior to those at pH 4 during hydrolysis and condensation, which could be explained by the anchoring effect. Zr and V were found to be good promoters for the enhancement of the thermal stability and SO_2 resistance, respectively. Optimally formulated catalyst, Pd(1)–V(2)–Zr(10)–Al_2O_3, was thermally stable up to 900°C and showed a much more improved low-temperature activity and excellent SO_2 resistance.

E. W. Shin *et al.* (2002) studied the origin of the selectivity improvement over the supported Pd catalyst modified with Si, which is deposited selectivity on Pd by silane decomposition and subsequently oxidized in oxygen, by observing the adsorption and desorption behavior of acetylene, ethylene, and hydrogen on the Pd surface. They reported that the adsorption strength of ethylene on Pd becomes weak and the amount of adsorbed hydrogen decreases when the Pd catalyst is modified with Si. The Si modification also reduces the amounts of surface hydrocarbons or carbonaceous species that are deposited on the catalyst either during the temperature programmed desorption (TPD) of ethylene or by surface reactions between co adsorbed acetylene and hydrogen. The hydrocarbon species deposited on the Si modified catalyst have a shorter chain length than those produced on the Pd-only catalyst. All these results are consistent with the improvement in ethylene selectivity on the Si-modified Pd catalyst, which has been explained based on the reaction mechanism of acetylene hydrogenation.

Tanaka *et al*. (2002) prepared Pd/SiO_2 catalysts by a complexing agent assisted sol-gel method and impregnation method using and organic complexing agent or water as the impregnation solvent. The Pd/SiO_2 were characterized by TG-DTA, FT-IRs, C-NMR, XRD, TM XPS and CO adsorption. The difference between the preparation method was discussed. The result showed that the palladium particles in the sol-gel catalysts were much smaller and more uniform in size than those in the corresponding impregnation catalysts.

Ming-Yen Wey *et al*. (2006) studied the effects of various precursors and different fabricating procedures of Pd/Al_2O_3–CeO_2 catalysts by the sol–gel method. The physicochemical properties and structures of catalyst were characterized with BET surface area, X-ray powder diffraction (XRPD), and scanning electron microscopy (SEM). The performance of the Pd/Al_2O_3–CeO_2 catalyst was also evaluated by CO oxidation tests with a continuous quartz reactor. The results indicated that the catalyst prepared with inorganometallic precursors showed a high dispersion of Pd, large surface area and pore volume, and a high activity in CO oxidation.

Nitikorn studied the effect of Ni-modified Al_2O_3 prepared by sol-gel and solvothermal methods with varying Ni/Al molar ratios on catalytic performances of supported Pd catalysts for selective hydrogenation of acetylene. It was found that catalytic performances of the Pd catalyst supported on Ni-modified Al_2O_3 were superior compared to those of Pd-supported on commercial α-Al_2O_3. For Ni-modified α-Al_2O_3 prepared by sol-gel method, an appropriate amount of Ni/Al that gave the best properties when used as a support for Pd catalyst was 1 while for those obtained from solvothermal method, Ni/Al = 0.3 yielded the best catalytic performance.

2.2 Fe-Al_2O_3

Ladavos *et al.* (2001) studied the Al_2O_3-Fe_2O_3 mixed oxidic system in catalytic decomposition of N_2O with composition ranging from 0 to 100% of Fe_2O_3 were prepared. The XRD diagrams showed peak of α- Al_2O_3 and hematite phase. The specific surface area of the mixture decreased by the addition of iron and depended on the crystal phases of the mixture. In the addition of iron in to alumina increased the catalytic activity up to Y=2 (Y=atomic ratio of Fe). Thereafter it remained almost constant up to Y=25 and the decreased.

Shakawy *et al.* (2000) studied the effect of Fe_2O_3 content and thermal treatment on the various properties of the Fe_2O_3-Al_2O_3 system were used $Al(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ as precursors of Al_2O_3 and Fe_2O_3 containing 10 20 30 50 and 80 wt.% Fe_2O_3 were prepared by coprecipitation method. The XRD patterns shown that the increased of iron content in the coprecipitated samples is associated with the increased of the α-Fe_2O_3 diffraction band intensities and therefore, increasing the crystallinity of this phase. The increase of the amount of Fe_2O_3 as well as the thermal treatments resulted in a decrease of the total pore volume and the surface area. The DTA curves had shown the presence of a solid solution of α-Fe_2O_3

in α-Al_2O_3, or α-Al_2O_3 in α-Fe_2O_3 at 1073 K, depending on the amount of both oxides. The dehydration and dehydrogenation activities of the three alcohols (ethanol, 1-propanal and 2-propanol), it was found that both dehydration and dehydrogenation activities rises with increases of iron content up to 50 wt.% and activities decrease for 80 wt.%. The decrease in selectivity for dehydration and the increase in selectivity for dehydrogenation depend on the concentration of surface acidic and basic sites, respectively.

Young-Woo Rhee *et al*. (2003) studied the diffusion induced grain-boundary migration and mechanical property improvement in Fe-doped alumina. When 1 wt.%-Fe_2O_3-doped Al_2O_3 samples were sintered at 1600 °C in a reducing atmosphere, the additive remained as Fe precipitates at the triple grain-junctions. On annealing the sintered samples in an oxidizing atmosphere, however, the Fe precipitates dissolved into the Al_2O_3 grains at the surface region and induced grain-boundary migration. This diffusion induced grain-boundary migration (DIGM) resulted in the corrugation of grain boundaries and the formation of misfit dislocations in the migration region. The mechanical properties of the samples were evaluated by the Hertizian indentation technique under static and cyclic loading.

Y.L. Huang *et al*. (2003) studied about the reduction process showed that $FeAl_2O_4$ is present as the intermediate phase between α-Fe_2O_3 and α-Fe below 700 °C. The relative weight of metallic iron increases with the reduction temperature up to 900 °C. The α-Fe-Al_2O_3 nanocomposites are resistant to oxidation at 300 °C. In the present sol- gel process, the solution temperature and its pH value are strictly controlled in order to get clear sols and transparent gels, i.e. to avoid the hydrolysis precipitation. Excellent composite homogeneity and dispersion are achieved. The structural and magnetic properties of the obtained nanocomposites are characterized by XRD and TEM. $FeAl_2O_4$ was observed as an intermediate phase between α-Fe_2O_3 and α-Fe, occurring during the reduction treatment.

P.M. Botta *et al*. (2003) studied the physicochemical and structural changes induced by mechanical activation of Al–Fe_3O_4 mixtures. The formation of an Fe–

$FeAl_2O_4$–Al_2O_3 metal–ceramic complex powder of variable composition. The evolution of the system can be described as a three-step reaction. Towards this formulation, the sensitivity of Mossbauer spectroscopy was essential because the emergence of the reaction products, like hercynite and iron, could be detected ahead of XRD. DTA analyses indicate that the resultant α-Fe phase is in fact a solid solution, which contains from 3 to 8 wt.% of Al. The hercynite formed by thermal treatment of S30 (3 h at 1200 °C under Ar atmosphere) is indeed a solid solution $Fe[Al_{2-x}Fe_x]O_4$, with $0{:}13 < x < 0{:}29$. This fact might have important effects on the magnetic properties of the spinel. For this reason, further studies would be needed to determine the influence of these mechanochemically thermally induced changes on the functional properties of the synthesized material.

2.3 Co-Al_2O_3

C. Otero Areán *et al*. (1999) studied the sol–gel method for preparing high surface area $CoAl_2O_4$ and Al_2O_3–$CoAl_2O_4$ spinels. The sol–gel method described here leads to spinel-type $CoAl_2O_4$ and Al_2O_3–$CoAl_2O_4$ solid solutions having very high surface area, which is not achieved when these materials are prepared by more conventional methods. Most of this surface should be accessible to molecules from a gas phase, since pore diameters are sufficiently large. These are relevant features for potential applications, e.g., in heterogeneous catalysis or in gas sensing. A further advantage of the sol–gel method is the high purity with which metal alkoxides can be prepared; since only hydrolysis and calcination steps are involved in transforming alkoxides into oxides, this route should lead to very pure metal oxide products.

Marcos and coworker (2000) studied the blue $CoAl_2O_4$ particles prepared by the Sol-Gel and Citrate-Gel methods using aluminum *sec*-butoxide, cobalt salts, and citric acid as oxides precursors. Both methods start from sols of the precursor alkoxides and salts, and involve formation of homogeneous solid intermediates, reducing atomic diffusion processes during thermal treatment. This important feature results in a substantial lowering of the time and temperature needed for the formation of the desired compounds. The stages of the formation of $CoAl_2O_4$, as well as the characterization of the resulting compounds were done using XRD, FTIR, UV-VIS, SEM, and TGA/DTA techniques. The structure, coloration, particle size, and temperature of formation of the resulting $CoAl_2O_4$ phases were found to depend on the precursors and methods used for preparation and the calcination temperature. The lowest temperature for preparation of the blue cobalt aluminate of about 700 °C was obtained using the citrate-gel method. This temperature is much lower than that needed for preparation of the compound through traditional solid-state reactions (above 1000 °C).

A. Kanyanucharat *et al*. (2002) studied the synthesis of spinel type mixed oxide ($CoAl_2O_4$, $ZnAl_2O_4$ and $NiAl_2O_4$) by solvothermal method using toluene as a solvent at various reaction temperatures for 2 hours with the molar ratio 0.5. It was found that the reaction temperature in the synthesis and the calcination temperature affected the thermal stability of each metal aluminate spinels that results in the change of crystallite size and BET surface area. The varying of divalent ions (Co^{2+}, Zn^{2+} and Ni^{2+}) in tetrahedral sites of metal aluminate spinels affected the thermal stability in the order of $NiAl_2O_4 > CoAl_2O_4 > ZnAl_2O_4$. That was the results of the difference in bond dissociation energy of metal oxides and cation distribution over sites with tetrahedral coordination in the spinel-type structure.

Weidong Li *et al*. (2003) studied the synthesis and characterization of nanocrystalline $CoAl_2O_4$ spinel powder by low temperature combustion. Pure and homogeneous nanocrystalline $CoAl_2O_4$ spinel powders have been directly prepared by the autoignited combustion of citric acid-nitrates gel precursors. The combustion products are in the form of loose agglomerates which are easily ground to fine powders. The powder characteristics are strongly dependent on the amount of heat, or the flame temperature generated by the redox reaction, which is a function of the fuel-tooxidant ratio used in the starting composition. It is suggested that a mild reaction between fuel and oxidants is necessary to produce finer crystallites at lower temperature. The $CoAl_2O_4$ spinel particle size increases with the enhancement of calcination temperature, and has a drastic lifting from 30 to 40 nm to 110 nm when calcined at 1100 °C instead of 900 °C.

S. Cava *et al*. (2006) studied the Structural and spectroscopic analysis of γ-Al_2O_3 to α-Al_2O_3-$CoAl_2O_4$ phase transition. Alumina and Co-added alumina powders were synthesized by means of the polymeric precursors method. γ-Al_2O_3 is crystallized at temperatures higher than 700 °C, remaining as single phase until about 1000 °C in spite of the added cobalt percentage. From this, α-Al_2O_3 begins its formation together with $CoAl_2O_4$ spinel. A phase diagram was proposed demonstrating these phase transitions and the effect of cobalt addition. An abrupt increase in the crystallite size is noticed close to temperature of phase transition due to large grain sizes and well-defined long-range order in corundum. UV–vis results show Co^{2+} in tetrahedral sites in γ-Al_2O_3. An additional band assigned to octahedral sites appears with the phase transition to α-Al_2O_3 + $CoAl_2O_4$. The wavelength position of the band with maximum intensity was plotted against the calcining temperature demonstrating that there is a relationship between the phase transition and the spectroscopic bands shift. Colorimetric data show that a bluer color is attained with single phase γ-Al_2O_3 at 950 °C.

2.4 Comments on the previous studies

From literature reviews, Pd is the one of the most useful catalysts used in selective hydrogenation reaction. The commonly used support for palladium is α-Al_2O_3. The use of a second metallic component has proven to be a suitable method to improve the desired properties of metallic deposits in a variety of different applications. Admixture of a second metallic component has also proven to be an interesting approach to tune the magnetic properties of the systems. It has been shown that Pd catalysts can be improved towards different catalytic reactions by the addition of a second metal such as Ag. Sol–gel procedures are currently under study as a practical means to prepare high surface area spinels. High surface area $CoAl_2O_4$ spinels are versatile materials which find a wide range of technical applications, for example as chemical sensors, ion conductors or heterogeneous catalysts.

There is no report study of Fe and Co on the catalytic performance selective hydrogenation of acetylene. Thus, it is interesting to study the properties of Fe- or Co-modified alumina supported Pd catalysts in selective hydrogenation of acetylene.

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CHAPTER III

THEORY

This chapter focuses on the fundamental theory of the selective hydrogenation of acetylene over supported palladium catalyst based on the real industrial conditions. The chapter consists of seven main sections. Reactions proceeding during acetylene hydrogenation as well as influencing parameters on such reactions are discussed in section 3.1. Palladium used for acetylene hydrogenation is detailed in section 3.2. Details of catalyst supports (alumina, iron oxide and cobalt aluminate) used for the selective hydrogenation of acetylene are detailed in section 3.3, 3.4 and 3.5, respectively. Finally the preparation methods (solvothermal and sol-gel) are detailed in section 3.6 and 3.7.

3.1 Acetylene Hydrogenation Reaction

Generally, there are two primary reactions proceeding during acetylene hydrogenation:

$$C_2H_2 + H_2 \xrightarrow{k_1} C_2H_4 \qquad \Delta H = -42{,}000 \text{ kg-cal/kg-mol} \qquad (3.1)$$

$$C_2H_4 + H_2 \xrightarrow{k_2} C_2H_6 \qquad \Delta H = -32{,}900 \text{ kg-cal/kg-mol} \qquad (3.2)$$

The first reaction (3.1) is the desired reaction whereas the second reaction (3.2) is an undesired side reaction due to the consumption of ethylene product. There is also a third reaction occurring during normal operation, which adversely affects the catalyst performance, i.e., the polymerization reaction of C_2H_2 with itself to form a longer chain molecule, commonly called “green oil”.

$$C_2H_2 + (n)\, C_2H_2 \xrightarrow{k_3} C_xH_x \text{ (polymer/green oil)} \qquad (3.3)$$

According to the above reactions involving acetylene hydrogenation, two influencing parameters on the desired reaction can be assigned. The first parameter is reaction temperature, which has a direct relationship with the kinetics of the system. However, it affects not only the reaction rate of the desired reaction (k_1), but also the rate of ethylene hydrogenation (k_2). The rate of polymerisation (k_3) also increases with temperature and the resulting green oil can affect catalyst activity by occupying active sites. When the catalyst is new or has just been regenerated, it has high activity. With time on stream, activity declines as the catalyst becomes fouled with green oil and other contaminants. By the end-of-run (EOR), the inlet temperature must be increased (25-40^oC) over start-of-run (SOR) inlet temperature in order to maintain enough activity for complete acetylene removal. In order to selectively hydrogenate acetylene to ethylene, it is critical to maintain the differential between the activation energies of reaction (eq. 3.1) and (eq. 3.2). However, it is desirable that the ethylene remains intact during hydrogenation. Once energy is supplied to the system over a given catalyst by increasing the temperature, the differential between the activation energies disappears and complete removal of acetylene, which generally has the lower partial pressure, becomes virtually impossible. In other words, higher temperature reduces selectivity; more hydrogen is used to convert ethylene to ethane, thereby increasing ethylene loss. The inlet temperature should therefore be kept as low as possible while still removing acetylene to specification requirements. Low temperatures minimise the two undesirable side reactions and help optimise the converter operation.

Another crucial parameter affecting the selectivity of the system is the ratio between hydrogen and acetylene (H_2:C_2H_2). Theoretically, the H_2:C_2H_2 ratio would be 1:1, which would mean that no hydrogen would remain for the side reaction (eq. 3.2) after acetylene hydrogenation (eq. 3.1). However, in practice, the catalyst is not 100% selective and the H_2:C_2H_2 ratio is usually higher than 1:1 to get complete conversion of the acetylene. As hydrogen is one of the reactants, the overall acetylene conversion will increase with increasing hydrogen concentration. Increasing the H_2:C_2H_2 ratio from SOR to EOR can help offset the decline in catalyst activity with time on stream. However, this increased acetylene conversion with a higher H_2:C_2H_2

ratio can have a cost in selectivity which leads to ethylene loss. Typically, the H_2:C_2H_2 ratio is between 1.1 and 2.5 [Derrien *et al*., 1986 and Molnár *et al*., 2001].

The mechanism of acetylene hydrogenation involves four major paths as shown in Fig. 3.1. Path I is the partial hydrogenation of acetylene to ethylene, which is either desorbed as a gaseous product or further hydrogenated to ethane via Path II. It previously was proposed that Path I proceeds mostly on Pd sites, which are covered to a great extent with acetylene under typical industrial reaction conditions, and Path II occurs on support sites, particularly those covered with polymer species.

Consequently, selectivity may be improved by reducing both the strength of ethylene adsorption on Pd and the amount of polymer, which accumulates on the catalyst. One of the methods for improving selectivity is to maintain a low H_2/acetylene ratio in the reactant stream such that the low hydrogen concentration on Pd retards the full hydrogenation of the ethylenic species on the Pd surface. However, this method has the drawback of accelerating the polymer formation and therefore the H_2/acetylene ratio must be managed deliberately or sometimes controlled in two steps. Path III, which allows for the direct full hydrogenation of acetylene, becomes negligible at high acetylene coverage and low hydrogen partial pressures. Ethylidyne was suggested as an intermediate in Path III but was later verified to be a simple spectator of surface reactions. Path IV, which allows for the dimerization of the C_2 species, eventually leads to the production of green oil and the subsequent deactivation of the catalyst. Polymer formation lowers ethylene selectivity because it consumes acetylene without producing ethylene and, in addition, the polymer species, which is usually located on the support, acts as a hydrogen pool, thus promoting ethane formation [Kang *et al*., 2002].

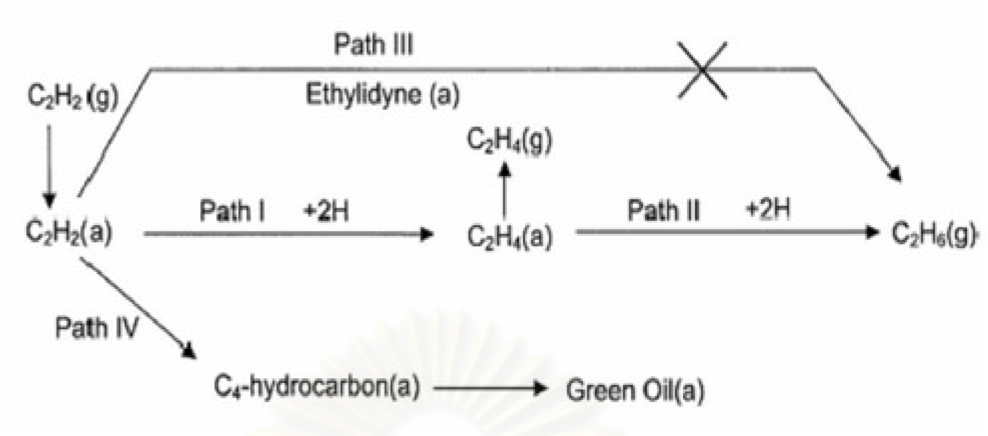


Figure 3.1 Major reaction path of acetylene hydrogenation [Kang *et al.*, 2002]

Considering the mechanism of acetylene hydrogenation described above, it was found that ethylene selectivity is improved when the C_2 species produced by Path I is readily desorbed from the catalyst surface and the other paths are simultaneously retarded.

In this study, The Catalytic performance for selective hydrogenation of acetylene was evaluated in terms of activity for acetylene conversion and ethylene gain based on the following equation (3.1) and (3.2).

Activity of the catalyst for acetylene conversion is defined as moles of acetylene converted with respect to acetylene in the feed:

$$C_2H_2 \text{ conversion (\%)} = 100 \times \frac{\text{acetylene in feed} - \text{acetylene in product}}{\text{acetylene in feed}} \qquad \text{(i)}$$

Ethylene gain is defined as the ratio of those parts of acetylene that are hydrogenated to ethylene to the amount of totally hydrogenated acetylene:

$$C_2H_4 \text{ gain (\%)} = 100 \times \frac{C_2H_2 \text{ hydrogenated to } C_2H_4}{\text{totally hydrogenated } C_2H_2} \qquad \text{(ii)}$$

Where total hydrogenated acetylene is the difference between moles of acetylene in the product with respect to those in the feed (dC_2H_2). In other words, acetylene hydrogenated to ethylene is the difference between the total hydrogenated acetylene (dC_2H_2) and the ethylene being loss by hydrogenation to ethane (equation 3.2). Regarding the difficulty in precise measurement of the ethylene change in the feed and product, the indirect calculation using the difference in the hydrogen amount (hydrogen consumed: dH_2) was used.

The ethylene being hydrogenated to ethane is the difference between all the hydrogen consumed and all the acetylene totally hydrogenated.

$$C_2H_4 \text{ gain } (\%) = 100 \times \frac{[dC_2H_2 - (dH_2 - dC_2H_2)]}{dC_2H_2} \qquad \text{(iii)}$$

As shown in equation (3.1) and (3.2), 2 moles of hydrogen were consumed for the acetylene lost to ethane, but only 1 mole of hydrogen for the acetylene gained as ethylene. The overall gain can also be written as:

$$C_2H_4 \text{ gain } (\%) = 100 \times \left[2 - \frac{dH_2}{dC_2H_2}\right] \qquad \text{(iv)}$$

Equation (iii) and (iv) are, of course the same, and ethylene gain discussed in this research is then calculated based on equation (iii). This value is the percentage of the theoretically possible ethylene gain which has been achieved in the operation. A positive value represents net production of ethylene. When the negative value refers to ethylene loss. However, it should be noted that these calculations can not provide a measure of acetylene polymerization reaction that forms green oil.

Typically, the normal operating temperature in an acetylene converter lies in the range 65-85^{o}C [Derrien *et al.*, 1986 and Molnár *et al.*, 2001]. During start-up, the reaction can proceed at as low as 45^{o}C. After a short period during which the catalyst has stabilized, the reactor temperature would reach the normal operating range and remain constant throughout its life-time. According to the literature, acetylene hydrogenation usually exhibits three distinct phases [Bond *et al.*, 1958; Al-Ammar *et al.*, 1978 and McGown *et al.*, 1978]. In a brief initial period (0-2 min on stream), the reaction is rapid, forming both ethylene and ethane. In the second phase (2-60 min on stream), the rates of acetylene consumption, and ethylene and ethane production are all constant. During this period, hydrogenation of acetylene is the primary reaction. The selectivity is usually high, and is the characteristic of changes occurring in the catalyst. The third phase begins when acetylene hydrogenation is nearly complete and in this region approximates to the industrial situation.

3.2 Palladium

Palladium as a group VIII noble metal has unique catalytic properties in homogeneous and in heterogeneous reactions. In heterogeneous catalysis palladium is used for oxidation and hydrogenation reactions. One of the most remarkable properties of palladium is the ability to dissociate and dissolve hydrogen. Atomic hydrogen occupies the octahedral interstices between the Pd atoms of the cubic-closed packed metal. Palladium can absorb up to 935 times of its own volume of hydrogen. Depending on hydrogen partial pressure and temperature a so-called α- and β-hydride is formed.

Some physical properties of palladium.

atomic number	46
atomic weight	106.42atomic
diameter	275.2 pm
melting point	1827 K
crystal structure	cubic closed packed
electron configuration	[Kr] $4d^{10}$
electron negativity (Allred & Rochow)	1.4

Like other group VIII metals, palladium can be used for hydrogenation of unsaturated hydrocarbons. Palladium shows the highest selectivity of these metals in heterogeneously catalyzed semi-hydrogenation of alkynes and dienes to the corresponding alkenes [H.Amold *et al.*, 1997]. Activity of palladium for hydrocarbon hydrogenation is based on the ability for the dissociative adsorption of hydrogen and chemisorption of unsaturated hydrocarbons. The chemisorption of alkenes and alkynes is based on the interaction of the d-band of the Pd metal with the π-bonding system of the unsaturated hydrocarbons [V.Pallassana *et al.*, 2000 and F.Mittendorfer *et al.*, 2003]. Industrially used catalysts for acetylene hydrogenation contain relatively low Pd content (< 0.1 wt%) and are supported on metal oxides like alumina. Palladium shows high activity but only limited selectivity and long-term stability for hydrogenation of acetylene. The limited selectivity is mainly due to enhanced ethane formation and the formation of by-products like C4 and higher hydrocarbons. Palladium shows a strong deactivation behavior because of hydrocarbon and carbon deposits. Catalyst deactivation by hydrocarbon and carbon deposits requires a frequent exchange or regeneration of the catalyst in the hydrogenation reactor. Moreover, fresh or regenerated catalysts show high activity and consequently lead to increased ethylene consumption and reduced selectivity. Furthermore, high activity of fresh or regenerated catalysts can lead to overheating (“thermal run away”) of the reactor because of the exothermic hydrogenation reaction.

The limited selectivity of Pd catalysts in acetylene hydrogenation can be attributed to the presence of ensembles of active sites on the catalyst surface [E.G.Derouane et al., 1984, B.Coq et al., 2001 and L.Guczi et al., 2003]. Selectivity can be increased by active-site isolation (“geometric effect”), modification of the electronic structure by alloying or promoting of Pd catalysts (electronic effect”) or by suppressing hydride formation (“kinetic effect”).

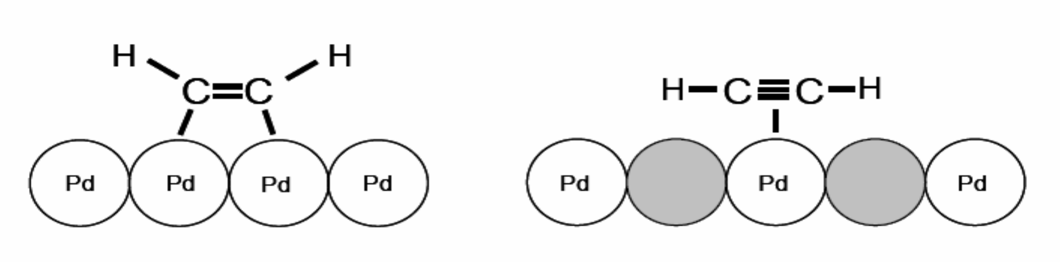


Figure 3.2 Di-σ bonded acetylene molecule to two neighbouring Pd atoms (left) and a weakly π-bonded acetylene molecule to an isolated Pd atom (right). Only the π-bonded acetylene is hydrogenated in high selectivity to ethylene.

3.3 Aluminium oxides or Alumina (Al_2O_3)

The structure of α-alumina consists of close packed planes of the large oxygen ions stacking in A-B-A-B sequence, thus forming hexagonal close packed array of anions. The aluminium cations are located at octahedral sites of this basic array and from another type of close packed planes between the oxygen layer. To maintain neutral charge, however, only two third of the available octahedral sites are filled with cation. Figure 3.3 illustrates the packing of Al and O atom in the basal plane. Since the vacant octahedral sites also from regular hexagonal array, three different types of cation layer can be defined, namely a, b, and c layer, depending on the position of the vacant cation site within the layer These layer are stacked in a-b-c-a-b-c sequence in the structure of alumina

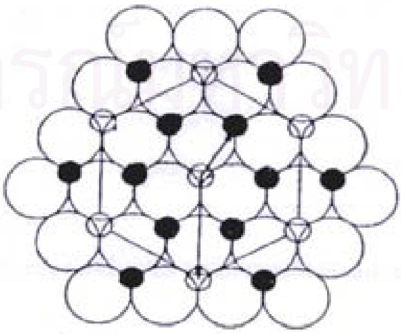


Figure 3.3 Illustration of Al and O atom packing in the basal plan

Alumina can exist in many metastable phase before transforming to the stable α-alumina (corundum from). There are six principle phase designated by The Greek letters Chi, kappa, eta, theta, delta and gamma. The nature of the product obtained by calcinations depends on the starting hydroxide (Gibbsite,boehmite and others) and on the calcinations conditions. Normally, transition alumina start to lose their surface area even at temperature below 800 ^{o}C due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000 ^{o}C when the crystallization to the thermodynamically stable α- alumina occurs.

3.4 Iron

Atomic Number:	26	Atomic Radius:	124.1 pm
Atomic Symbol:	Fe	Melting Point:	1538 °C
Atomic Weight:	55.847	Boiling Point:	2861 °C
Electron Configuration:	$[Ar]4s^{2}3d^{6}$	Oxidation States:	3, 2

Iron is hard, brittle, fairly fusible, and is used to produce other alloys, including steel. Wrought iron contains only a few tenths of a percent of carbon, is tough, malleable, less fusible, and usually has a "fibrous" structure. The pure metal is very reactive chemically and rapidly corrodes, especially in moist air or at elevated temperatures. It has four allotropic forms or ferrites, known as alpha, beta, gamma, and omega, with transition points at 700, 928, and 1530 °C. The alpha form is magnetic, but when transformed into the beta form, the magnetism disappears although the lattice remains unchanged. The relations of these forms are peculiar. Pig iron is an alloy containing about 3 percent carbon with varying amounts of sulfur, silicon, manganese, and phosphorus.

Carbon steel is an alloy of iron with small amounts of Mn, S, P, and Si. Alloy steels are carbon steels with other additives such as nickel, chromium, vanadium, etc. Iron is a cheap, abundant, useful, and important metal.

- **Iron(III) oxide**

Iron oxides, including oxyhydroxides, are a kind of natural minerals and geocatalysts, naturally existing in the earth's crust with great content. Since these iron oxides are very reactive, a number of secondary iron oxides such as maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), lepidocrocite (γ-FeOOH), goethite (α-FeOOH), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), and magnetite (Fe_3O_4) were found in aqueous streams as suspended materials with a significant amount. Hence, the iron oxides in aquatic ecosystems play a vital role in a variety of chemical and biological processes relevant to the transformation of organic compounds.

Iron(III) oxide is often used in magnetic storage, for example in the magnetic layer of floppy disks. These consist of a thin sheet of PET film, coated with iron(III) oxide. The particles can be magnetised to represent binary data. MICR (Magnetic Ink Character Recognition) also uses iron(III) oxide compounds, suspended in an ink which can be read by special scanning hardware.

Iron(III) oxide is used in the production of pure iron in a blast furnace. Iron(III) oxide is also used in an extremely exothermic reaction called a thermite reaction.

$$2\ Al + Fe_2O_3 \rightarrow 2\ Fe + Al_2O_3$$

Iron(III) oxide is also used as a pigment, under names Pigment Black 11, Pigment Brown 6, Pigment Brown 7, and Pigment Red 101 (also Iron Oxide Red). Some of them, eg. Pigment Red 101 and Pigment Brown 6, are Food and Drug Administration (FDA)-approved for use in cosmetics.

3.5 Cobalt

Atomic Number:	27	**Atomic Radius:**	124.3 pm
Atomic Symbol:	Co	**Melting Point:**	1495 ^{o}C
Atomic Weight:	58.9332	**Boiling Point:**	2927 ^{o}C
Electron Configuration:	[Ar]$4s^2 3d^7$	**Oxidation States:**	3, 2

Cobalt is a brittle, hard metal, resembling iron and nickel in appearance. It has a metallic permeability of about two thirds that of iron. Cobalt tends to exist as a mixture of two allotropes over a wide temperature range. The transformation is sluggish and accounts in part for the wide variation in reported data on physical properties of cobalt.

- Cobalt aluminate ($CoAl_2O_4$)

$CoAl_2O_4$ is a binary oxide consisting of cobalt oxides and aluminum oxides that crystallize in spinel structure. The unit cell of spinels is represented by formula of AB_2O_4. The Co^{2+} ions occupy the tetrahedrally coordinated A site and Al^{3+} ions occupy the octahedrally coordinated B site. The structure of cobalt aluminate is shown in Figure 3.4

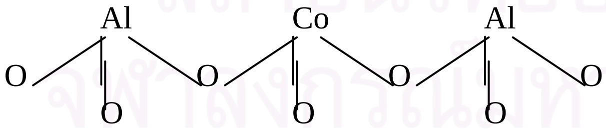


Figure 3.4 Structure of cobalt aluminate

3.6 Solvothermal method

Solvothermal synthesis is improved from the hydrothermal synthesis by using organic solvent as the reaction medium instead of water. This method is based on the decomposition of metal alkoxide at elevated temperature (200-300^{o}C) under autogeneous pressure. It is particularly suited for the synthesis of alumina in phase that is unstable at high temperature. It is also a useful technique for growing single crystals. In this method, parts or all of the reactants can dissolve in the organic solvent under high pressure. This feature enables the reaction to take place at lower temperature.

Alumina can also be synthesize inorganic materials by using organic media at elevated temperature (200-300^{o}C) under autogeneous pressure of organic for many years (1988-2002). It has been found that many oxides and mixed oxides can be crystallized in organic media at temperature lower than that required by the hydrothermal reaction. In 1988, they have reported that the glycothermal treatment (the use of glycol instead of water for hydrothermal treatment) of gibbsite at 250^{o}C yielded glycol derivative of boehmite. In 1992, they have found that the reaction of aluminum isopropoxide (AIP) in toluene at 300^{o}C resulted in λ-alumina. Mekasuwandumrong, et al., (2003) have reported that thermal decomposition of aluminum isopropoxide in ineral oil at 250-300^{o}C over 2 h resulted in λ-alumina powder having high thermal stability and clued be transformed directly to α-alumina at temperature higher than 1000^{o}C.

3.7 Sol-gel method

Basically, the sol-gel process means the synthesis of an inorganic network by chemical reactions in solution at low temperature. The most obvious feature of this reaction is the transition from liquid (solution or colloidal solution) into solid (di-ormultiplasic gel) leading to the expression “sol-gel process”. Nevertheless, this type of reaction is not necessarily restricted to an aqueous system, although reactions in aqueous solution have been know for a very long time. Any precursor, which is able to form reactive “inorganic” monomers or oligomers can be used for sol-gel techniques. It is very difficult to foresight type of precursor to be used for a specific aim. The reactivity of the precursor does not only depend on its chemical nature but also on the applied reaction conditions. Even finely divided silica particles can be peptisized and used for preparation of sols. However, it is necessary to generate appropriate surface charges in order to prevent coagulation and precipitation. Most work in the sol-gel has been done by using alkoxides as precursors. Alkoxide provide a convenient source for “inorganic” monomers which in most cases are soluble in common solvents. Another advantage of the alkoxide route is possibility to control rate by cotrolling hydrolysis and condensation by chemical means, not by surface or colloid chemisistry. In the case of a few metals, it might not be convenient to use alkoxides due to theire unavailability and/or difficulties in synthesis, alternative precursors may have to be employed. Metal salts provide a viable alterative, because of the advantage in theire solubity in organic solvents from the initial stage or during the sol-gel processing. However, care has to be exercised to choose such precursors since they can be converted easily to oxide by thermal or oxidative decomposition. Among the inorganic salts, metal nitrates are probably the best candidates as other salts such as sulfate or chloride are more thermally stable and therefore, it may be difficult to remove the anionic portion effectively from the final ceramic product.

Sol-gel preparation is widely used in glass and ceramic industries as well as in catalyst preparation. There are many routes of sol-gel preparation starting with different precursors such as inorganic salt or metal alkoxide. Sol, which is suspension of nanosized or micron-sized solid particles in liguid, can be obtained by hydrolysis and partial condensation of the precursor. Further condensation of sol particles result in three-dimensional network called gel, which is a diphasic material with solids encapsulating solvent. Alternatively, gel can be produced by destabilizing the solution of preformed sols. Therefore, control of the gelation condition is important. Operation at low temperature is the major advantage of this method. Furthermore, the obtained products are uniform. Sol-gel derived alumina offers a number of advantages such as high purity, high degree of homogeneity, well-define nanostructure, large surface area and superior mechanical properties.

The most often cited process for making alumina gel, developed by Yoldas, is to hydrolyze aluminum isopropoxide or sec-butoxide in large excess of water, with an acid catalyst in the ratio of 0.07 mole acid/mole Al. If the reaction is carried out at room temperature, the product is an amorphous gel that can be converted to bayerite [$Al(OH)_3$] over a period of 24 h. At 80^{o}C, the reaction produces boehmite [$AlO(OH)$]. If the process is starts at room temperature and continue heating to 80^{o}C, the product obtained is bayerite.

Chapter IV

Experimental

This chapter describes the experimental systems and the experimental procedures used in this study. The chapter is divided into four sections, i.e., chemicals using in this experiment are shown in section 4.1. Details of catalyst preparation are explained in section 4.2. Properties of the catalyst characterized by various techniques are discussed in section 4.3. Finally, the reaction study in acetylene hydrogenation is explained in section 4.4.

4.1 Chemicals

The chemicals used in this experiment are specified as follows:

1. Aluminium Isopropoxide (AIP, $[(CH_3)_2CHO]_3Al$) available from Aldrich, 98%+
2. Aluminium nitrate (98%) ($Al(NO_3)_3.9H_2O$) available from Aldrich Chemical Company, USA.
3. Ethyl alcohol absolute anhydrous available from Mallinckrodt Baker Co., Ltd.
4. Ferric nitrate nonahydrate ($FeN_3O_9{\cdot}9H_2O$) available from Aldrich, 98%
5. Iron (II) acetylacetonate $(C_5H_8O_2)_3Fe$ available from Aldrich, 97%
6. Cobalt (II) nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$ available from Aldrich, 98%
7. Cobalt (II) acetylacetonate $[CH_3COCH{=}C(O^-)CH_3]_2Co$ available from Aldrich, 97%
8. Palladium (II) nitrate hydrate from Aldrich.
9. Toluene ($C_6H_5CH_3$) available from Carlo Erba Reagenti, 99.5%
10. Urea (99.5%) available from Univar, Australia.

4.2 Catalyst Preparation

4.2.1 Preparation of α-Al_2O_3 by Solvothermal Method

α-Al_2O_3 was prepared by mixture of aluminum isopropoxide 15.0 grams. The starting materials were suspended in 100 mL of toluene in beaker, and then set up in 300 mL autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely purged with nitrogen, the suspension was heated to 300°C at the rate of 2.5°C/min and held at that temperature for 2 h. The diagram of the reaction equipment for the catalyst preparation is shown in Figure 4.1. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the thus-obtained product carried out in a furnace. The product was heated at a rate of 10°C/min to a desired temperature 1150°C and held at that temperature for 1 h.

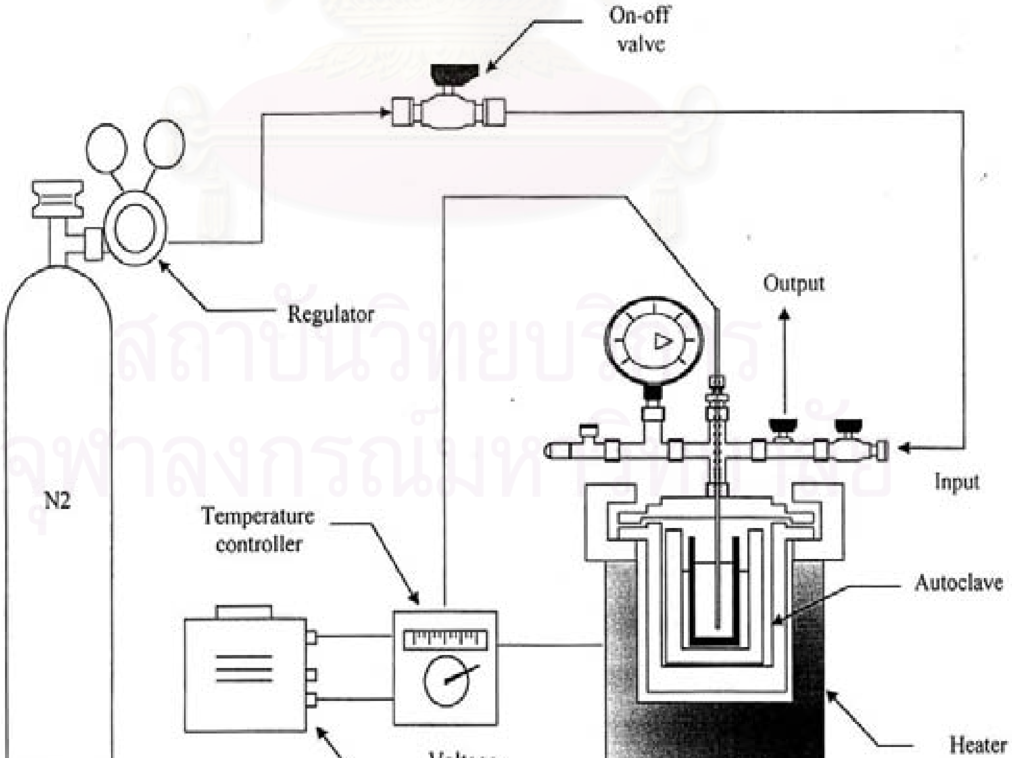


Figure 4.1 Diagram of the reaction equipment for the catalyst preparation.

4.2.2 Preparation of Fe-modified alumina by Solvothermal Method

Fe-modified alumina was prepared by mixture of aluminum isopropoxide 15.0 grams and appropriate amount of Iron (II) acetylacetonate $(C_5H_8O_2)_3Fe$ (Fe/Al molar ratio = 0.1, 0.3 and 0.5). The starting materials were suspended in 100 mL of toluene in beaker, and then set up in 300 mL autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely purged with nitrogen, the suspension was heated to $300^{o}C$ at the rate of $2.5^{o}C/min$ and held at that temperature for 2 h. However, the same synthesis method is performed at various holding temperature. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the thus-obtained product carried out in a furnace. The product was heated at a rate of $10^{o}C/min$ to a desired temperature $1150^{o}C$ and held at that temperature for 1 h.

4.2.3 Preparation of Co-modified alumina by Solvothermal Method

Fe-modified alumina was prepared by mixture of aluminum isopropoxide 15.0 grams and appropriate amount of Cobalt (II) acetylacetonate $[CH_3COCH=C(O^-)CH_3]_2Co$ (Co/Al molar ratio = 0.1, 0.3 and 0.5). The starting materials were suspended in 100 mL of toluene in beaker, and then set up in 300 mL autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely purged with nitrogen, the suspension was heated to $300^{o}C$ at the rate of $2.5^{o}C/min$ and held at that temperature for 2 h. However, the same synthesis method is performed at various holding temperature. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the thus-obtained product carried out in a furnace. The product was heated at a rate of 10°C/min to a desired temperature 1150°C and held at that temperature for 1 h.

4.2.4 Preparation of α-Al_2O_3 by Sol-gel Method

A mixture of aluminium nitrate nonahydrate and ethanol used as starting solution was prepared by dissolving 24 g of aluminium nitrate in 50 cc of ethanol at room temperature. A homogeneous solution was obtained after mixing for approximately 10 minutes using magnetic stirrer. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80°C for 18 h. Then, urea solution, which consist of 60 g of urea and 50 ml of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition.

The obtained product was calcined with 2 steps heating rate to avoid overflowing of gel during calcinations, i.e. 3°C/min from room temperature to 500°C and continue heating at 5°C/min to 1150°C. Then, temperature was hold for 3 h.

4.2.5 Preparation of Fe-modified alumina by Sol-gel Method

A mixture of aluminium nitrate nonahydrate and ethanol used as starting solution was prepared by dissolving 24 g of aluminium nitrate nonahydrate and Ferric nitrate nonahydrate ($FeN_3O_9 \cdot 9H_2O$) was added to the starting solution at the Fe/Al molar ratio = 0.1, 0.3 and 0.5 in 50 cc of ethanol at room temperature. A homogeneous solution was obtained after mixing for approximately 10 minutes using magnetic stirrer. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80°C for 18 h. Then, urea solution, which consist of 60 grams of urea and 50 ml of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition.

The obtained product was calcined with 2 steps heating rate to avoid overflowing of gel during calcinations, i.e. 3^{o}C/min from room temperature to 500^{o}C and continue heating at 5^{o}C/min to 1150^{o}C. Then, temperature was hold for 3 h.

4.2.6 Preparation of Co-modified alumina by Sol-gel Method

A mixture of aluminium nitrate nonahydrate and ethanol used as starting solution was prepared by dissolving 24 g of aluminium nitrate nonahydrate and Cobalt (II) nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ was added to the starting solution at the Co/Al molar ratio = 0.1, 0.3 and 0.5 in 50 cc of ethanol at room temperature. A homogeneous solution was obtained after mixing for approximately 10 minutes using magnetic stirrer. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80^{o}C for 18 h. Then, urea solution, which consist of 60 grams of urea and 50 ml of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition.

The obtained product was calcined with 2 steps heating rate to avoid overflowing of gel during calcinations, i.e. 3^{o}C/min from room temperature to 500^{o}C and continue heating at 5^{o}C/min to 1150^{o}C. Then, temperature was hold for 3 h.

4.2.7 Palladium loading

0.3 wt% Pd over α-Al_2O_3 and Fe- and Co-modified Al_2O_3 supports were prepared by the sequential impregnation technique detailed as follow:

1. α-Al_2O_3 and Fe- and Co-modified Al_2O_3 supports were impregnated with a solution of palladium by the incipient wetness technique. Using the water capacity measurement obtained previously for α-Al_2O_3 and Fe- and Co-modified Al_2O_3 particles, a sufficient amount of the palladium salt was added to obtain a 0.3% weight of palladium.

2. The impregnated support was left to stand for 6 hours to assure adequate distribution of metal complex. The support was subsequently dried at 110°C in air overnight.

3. The dried impregnated support was calcined under 60 mL/min nitrogen with the heating rate of 10°C/min until the temperature reached 500°C. A 100 mL/min of flowing air was then switched into the reactor to replace nitrogen and the temperature was held at 500°C for 2 hours.

4. The calcined sample was finally cooled down and stored in a glass bottle in a desicator for later use.

4.3 Catalyst Characterization

4.3.1 X-ray diffraction (XRD)

XRD was used to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using CuKα radiation with Ni filter in the 2θ range of 10-80 degrees resolution 0.04^o. The crystallite size was estimated from line broadening according to the Scherrer's equation.

4.3.2 BET Surface Area Analysis

BET was used to surface area, pore volume, average pore diameter, and pore size distribution of catalysts, with nitrogen as the adsorbate using a micrometritics model ASAP 2000 at liquid-nitrogen point temperature (-196° C).

4.3.3 Transmission Electron Microscopy (TEM)

The particle size and distribution of palladium on catalyst supports were observed using AJEM-200CX transmission electron microscope operated at 160 kV at the Scienctific and Technological Researh Equipment Center, Chulalongkorn University (STREC).

4.3.4 Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) study was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. The amount of NH_3 adsorbed on the surface was determined by temperature programmed desorption. The thermal conductivity detector was used to measure the amount of NH_3

Approximately 0.1 gram of sample was placed in a quartz tube in a temperature-controlled oven. Helium gas with flow rate at 15 ml/min was released to flow through our sample. The sample was heated from room temperature to 200^{o}C with a heating rate of 10^{o}C/min and hold for 1 hour. Then, the sample was cooled down to 40^{o}C. In the next step, 15 vol% ammonium gas with flow rate at 20 ml/min flowed through sample instead of helium, and hold for 30 minutes. Adsorption of 15 vol% ammonium on the catalyst surface occurred in this step. Consequently, helium gas at the same flow rate flowed through our sample instead of ammonium and also holds for another hour. In the final step which was the desorption step; our sample was heated from 40^{o}C to 650^{o}C with a heating rate of 10^{o}C/min. The signal from this step was recorded every second and reported on a microcomputer.

4.3.5 Metal active site measurement

Metal active sites were measure using CO chemisorption technique performed in a Micromeritic Chemisorb 2750 automated system. The known amount of CO was pulsed into the catalyst bed at room temperature. Carbon monoxide that was not adsorbed was measured using thermal conductivity detector. Pulsing was continued until catalyst surface was saturated with CO. The number of metal active sites was calculated in the basic assumption that only one CO molecule adsorbed on one metal active site [Vannice *et al.*, 1981: Anderson *et al.*, 1995: Ali *et al.*, 1998 and Mahata *et al.*, 2000].

4.3.6 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) thermograms were performed using a SDT Analyzer Model Q600 from TA Instruments, USA. The samples were determined by using TGA-DTA analysis. The analysis was performed as follow:

The gel of Ni-modified alumina prepared by sol-gel was heated with 2 steps heating rate. 3°C/min from room temperature to 500°C and continue heating at 5°C/min to 1150 °C. Then, temperature was hold for 3 h.

The catalyst supports before calcined of Ni-modified alumina prepared by solvothermal were heated at a rate of 10°C/min to a desired temperature 1150°C and held at that temperature for 1 h.

Finally, coke deposits on catalysts were carried out from room temperature to 1000°C at a heating rate of 5°C/min in oxygen.

4.4 Reaction study in acetylene hydrogenation

Catalytic performance of the catalysts was studied in selective hydrogenation of acetylene. The experiment was performed in a quartz tube reactor (i.d. 10.1 mm). Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.), a GHSV of 16901 h^{-1} was used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). The operating conditions for each instrument are summarized in Table 4.1

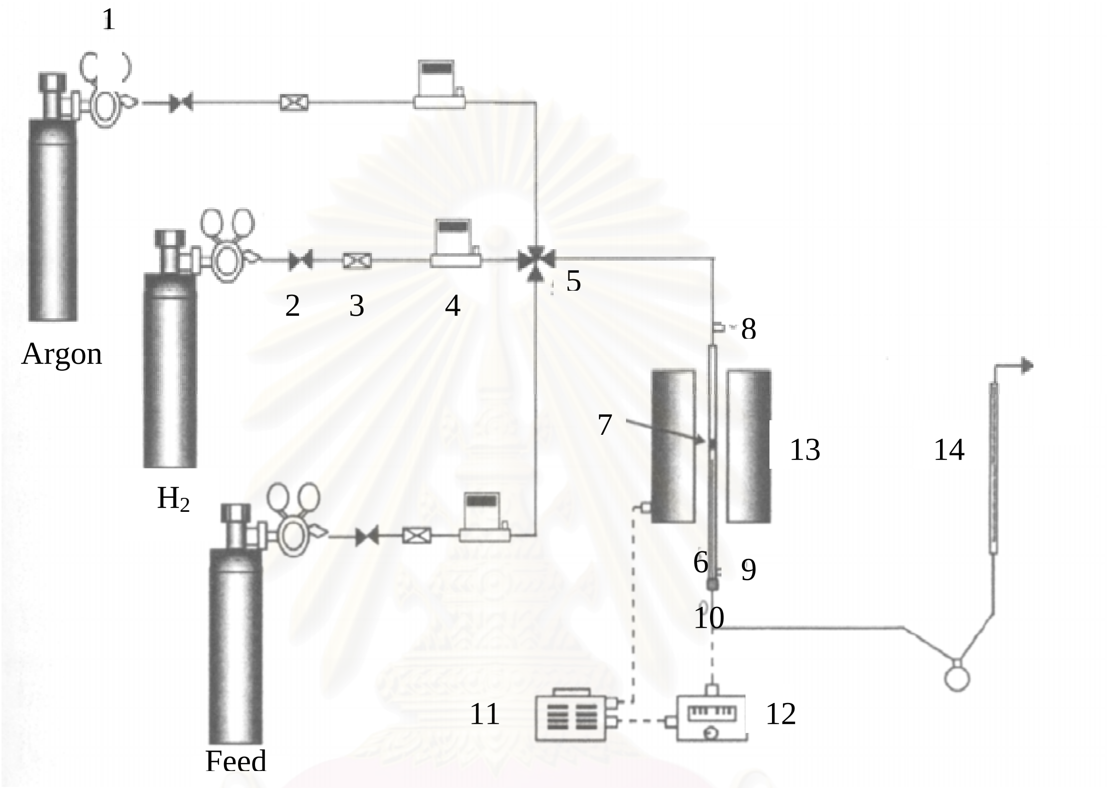
Table 4.1 Operating conditions of gas chromatograph for selective hydrogenation of acetylene

Gas Chromatograph	SHIMADZU FID GC 9A	SHIMADZU TCD GC 8A
Detector	FID	TCD
Packed column	Carbosieve column S-II	Molecular sieve 5A
Carrier gas	Ultra high purity N_2	Ultra high purity Ar
Carrier gas flow rate (ml/min)	30	30
Injector temperature (ºC)	180	80
Initial column temperature (ºC)	100	50
Initial holding time (min)	50	-
Programmed rate (ºC/min)	10	-
Final column temperature (ºC)	160	50
Final holding time (min)	160	-
Current (mA)	-	70
Analyzed gas	CH_4, C_2H_2, C_2H_4, C_2H_6	H_2

Approximately, 0.15 g of catalyst was packed in a quartz tubular down flow reactor. The catalyst bed length was about 0.3 cm. The reactor was placed into the furnace and argon was introduced into the reactor in order to remove remaining air. Prior to reaction, the catalyst was reduced with 100 ml/min hydrogen flow at a temperature of 150°C and held at that temperature for 2 h. Afterwards, argon was switched in to replace hydrogen and held at that temperature for 15 min in order to remove the remaining hydrogen.

The reactant was introduced at elevated temperature from 40 ºC to 100 °C, 1 atm, sampling was undertaken when the steady state of the system was reached, which was approximately within 2 h. Effluent gases were sampled to analyze the concentration of CH_4, C_2H_2, C_2H_4 and C_2H_6 using GC-9A equipped with a carbosieve

S-II column, whereas H_2 concentration was analyzed by GC-8A equipped with a molecular sieve 5A column. System of acetylene hydrogenation is shown in Figure 4.2.



1. pressure regular
2. on-off valve
3. filter
4. mass flow controller
5. 4-ways fitting
6. reactor
7. catalyst bed
8. sampling point (feed)
9. sampling point (product)
10. thermocouple
11. variable voltage transformer
12. Temperature controller
13. electric furnace
14. bubble flow meter

Figure 4.2 A schematic of acetylene hydrogenation system

CHAPTER V

RESULTS AND DISCUSSION

The main topic of this thesis involves an attempt to clarify effects of Fe- and Co-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts in selective hydrogenation of acetylene reaction. The results and discussions are divided into two main sections. The effect of Fe-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts is described in section 5.1. The effect of Co-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts is described in section 5.2.

5.1 Fe-modified Al_2O_3 and Al_2O_3 Supported Pd Catalysts

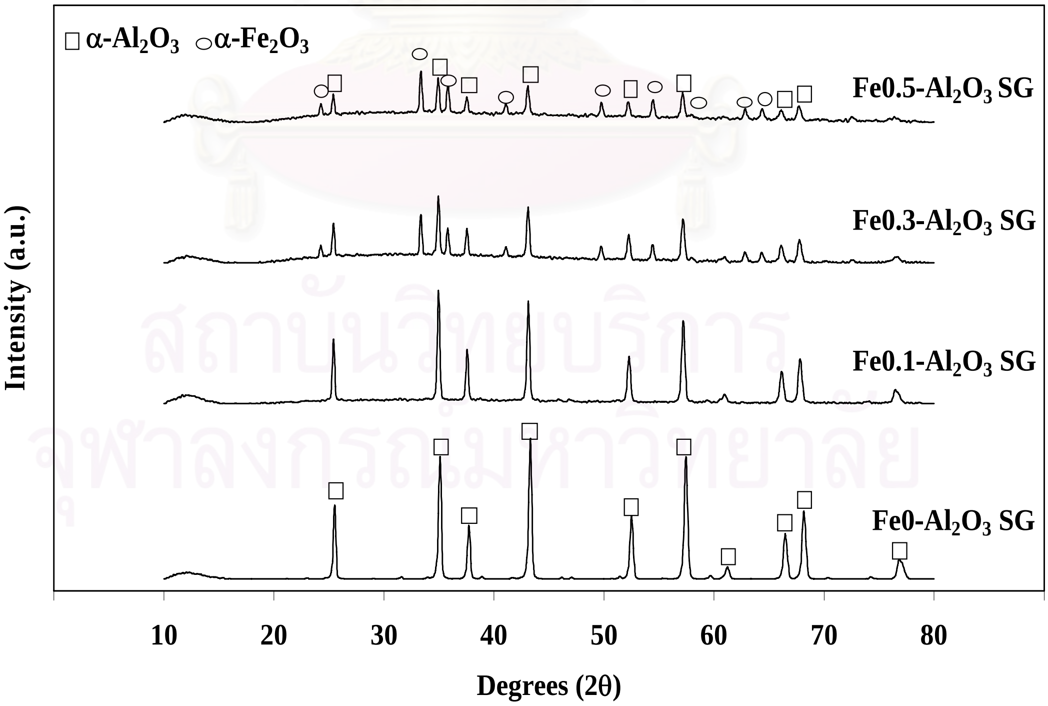
The samples of Fe-modified Al_2O_3 with various molar ratios of Fe to Al (0, 0.1, 0.3 and 0.5) synthesized by sol-gel method were named as Fe0-Al_2O_3SG, Fe0.1-Al_2O_3SG, Fe0.3-Al_2O_3SG, and Fe0.5-Al_2O_3SG, respectively. The samples prepared by solvothermal method were name as Fe0-Al_2O_3SV, Fe0.1-Al_2O_3SV, Fe0.3-Al_2O_3SV, and Fe0.5-Al_2O_3SV, respectively. Pd catalysts supported on the corresponding Fe-modified Al_2O_3 prepared by sol-gel and solvothermal were called Pd/Fe0-Al_2O_3SG, Pd/Fe0.1-Al_2O_3SG, Pd/Fe0.3-Al_2O_3SG, Pd/Fe0.5-Al_2O_3SG, Pd/Fe0-Al_2O_3SV, Pd/Fe0.1-Al_2O_3SV, Pd/Fe0.3-Al_2O_3SV, and Pd/Fe0.5-Al_2O_3SV, respectively.

5.1.1 Characterization of the Catalysts

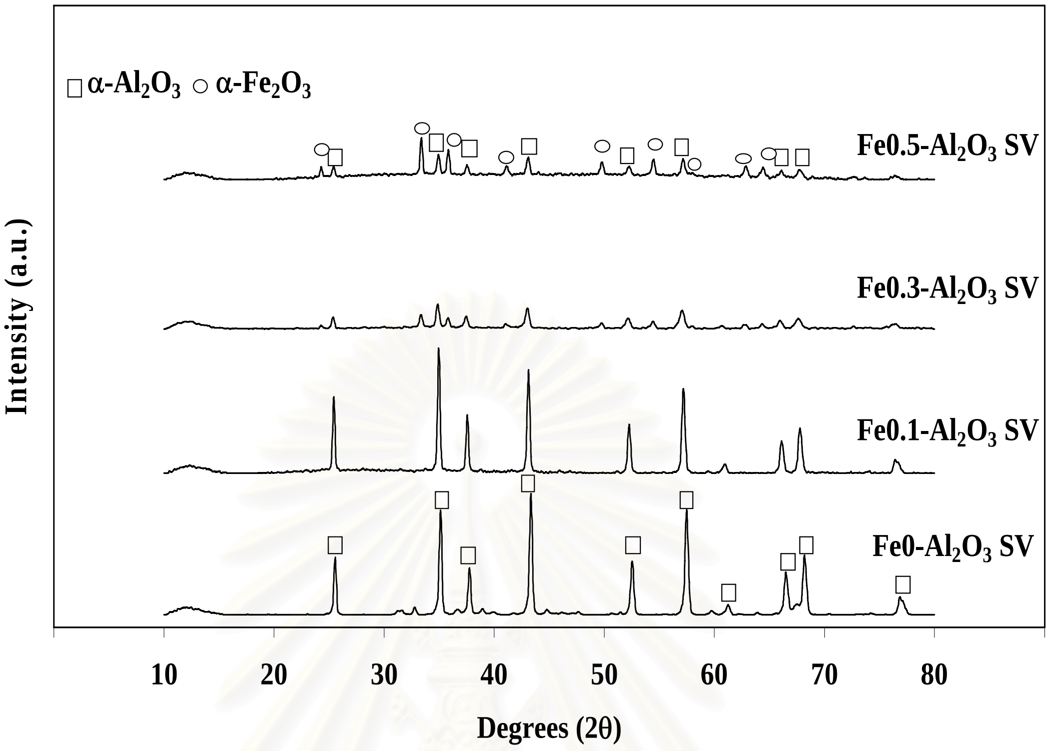
It is well known that catalyst characteristics such as BET surface area, surface morphology, crystallite size, etc. have crucial effects on their catalytic properties. Various analytical techniques have been performed including X-ray diffraction (XRD), specific surface area measurements (BET), CO chemisorption, transmission electron microscopy (TEM), NH_3 temperature programmed desorption (NH_3-TPD) and thermal gravimetric analysis (TGA) and were detailed as follows:

5.1.1.1 X-ray Diffraction (XRD)

The XRD patterns of non-modified Fe on Al_2O_3 (Fe0-Al_2O_3SG and Fe0-Al_2O_3SV and Fe-modified Al_2O_3 with various molar ratios of Fe to Al were carried out at the diffraction angles (2θ) between 10^o and 80^o. The results are shown in Figure 5.1. Fe0-Al_2O_3SG and Fe0-Al_2O_3SV showed the same patterns of only α-Al_2O_3 peaks at 25.52°, 35.10°, 37.74°, 43.32°, 52.52°, 57.46°, 61.22°, 66.50°, 68.18° and 77.86° 2θ [Prasitwuttisak *et al.*, 2004]. In the case of Fe-modified Al_2O_3, Fe0.1-Al_2O_3SG and Fe0.1-Al_2O_3SV showed only α-Al_2O_3 peaks whereas Fe0.3-Al_2O_3SG, Fe0.3-Al_2O_3SV, Fe0.5-Al_2O_3SG and Fe0.5-Al_2O_3SV exhibited XRD characteristic peaks of both α-Al_2O_3 and α-Fe_2O_3 (hematite). The XRD peaks for Fe_2O_3 appeared at 24.48, 35.56, 35.96, 41.83, 50.4, 53.56, 60.4 and 63.2° [Gang *et al.*, 2007]. The increase of iron content in the samples was associated with the increase of the hematite diffraction band intensities, therefore increasing the crystallinity of this phase [Sharkawy *et al.*, 2000].



(A)



(B)

Figure 5.1 The XRD patterns of Fe-modified Al_2O_3 supports with various molar ratios of Fe to Al prepared by (A) sol-gel and (B) solvothermal methods.

5.1.1.2 Average Crystallite Size

The average crystallite size of each crystal phase was calculated from the Scherrer equation. The crystallite size of the Fe-modified Al_2O_3 supports with various molar ratios of Fe to Al prepared by sol-gel and solvothermal methods are shown in Table5.1.

Table 5.1 Crystallite size of Fe-modified Al_2O_3 supports with various molar ratios of Fe to Al prepared by sol-gel and solvothermal methods.

Sample	Crystallite size (nm)
Fe0-Al_2O_3SG	45.5^{α}
Fe0.1-Al_2O_3SG	61.7^{α}
Fe0.3-Al_2O_3SG	47.0^{α} , 41.8^{FO}
Fe0.5-Al_2O_3SG	37.1^{α}, 44.6^{FO}
Fe0-Al_2O_3 SV	52.2^{α}
Fe0.1-Al_2O_3 SV	63.1^{α}
Fe0.3-Al_2O_3 SV	28.9^{α} , 26.3^{FO}
Fe0.5-Al_2O_3 SV	28.6^{α} , 53.4^{FO}

$^{\alpha}$ α-Al_2O_3

^{FO} α-Fe_2O_3

For the supports prepared by sol-gel method, the average crystallite size of Fe0-Al_2O_3SG was 45.5 nm. Fe0.1-Al_2O_3SG, the crystallite size of α-Al_2O_3 was 61.7 nm. Fe0.3-Al_2O_3SG, the crystallite size of α-Al_2O_3 and α-Fe_2O_3 were 47.0 and 41.8 nm, respectively, and Fe0.5-Al_2O_3SG, the crystallite size of α-Al_2O_3 and α-Fe_2O_3 were 37.1 and 44.6 nm, respectively.

And for the supports prepared by solvothermal method, the average crystallite size of Fe0-Al_2O_3SV was 52.2 nm. Fe0.1-Al_2O_3SV, the crystallite size of α-Al_2O_3 was 63.1 nm. Fe0.3-Al_2O_3SV, the crystallite size of α-Al_2O_3 and α-Fe_2O_3 were 28.9 and 26.3 nm, respectively, and Fe0.5-Al_2O_3SV, the crystallite size of α-Al_2O_3 and α-Fe_2O_3 were 28.6 and 53.4 nm, respectively.

There were no significant differences between crystal phase and crystal size of α-Al_2O_3 and α-Fe_2O_3 formed by the two different techniques.

5.1.1.3 BET Surface Areas

The most common procedure for determining surface area of a solid is based on adsorption and condensation of nitrogen at liquid nitrogen temperature using static vacuum procedure. This method is also called BET (Brunauer Emmett Teller) method. The BET surface areas of the Fe-modified Al_2O_3 supports are shown in Table 5.2.

Table 5.2 BET Surface Areas of Fe-modified Al_2O_3 with various molar ratios of Fe to Al

Sample	BET S.A. (m^2/g)
Fe0-Al_2O_3 SG	1.0
Fe0.1-Al_2O_3 SG	1.4
Fe0.3-Al_2O_3 SG	0.7
Fe0.5-Al_2O_3 SG	1.1
Fe0-Al_2O_3 SV	5.1
Fe0.1-Al_2O_3 SV	3.9
Fe0.3-Al_2O_3 SV	4.9
Fe0.5-Al_2O_3 SV	1.2

The BET surface areas of the supports prepared by sol-gel method were ranged from 0.7-1.4 m^2/g. which was quite low but typical for the α-Al_2O_3 supports. While the supports prepared by solvothermal method were range 1.2-5.1 m^2/g. All the supports were no significantly differences in the BET surface area of the Fe-modified Al_2O_3 with various Fe/Al ratios, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature [Prasitwuttisak T. *et al.*, 2004].

5.1.1.4 Metal Active Sites

The metal active sites measurement is based on CO chemisorption technique on the assumption that one CO molecule adsorbs on one palladium site [Anderson *et.al.*, 1985 and N. Mahata *et.al.*, 2000]. The amounts of CO chemisorption on the catalysts reduced at 150ºC and the percentages of palladium dispersion are given in Table 5.3. The details for calculation of Pd dispersion and average Pd^0 particle size are given in Appendix C.

Table 5.3 Results from CO chemisorption of Pd supported on Fe-modified Al_2O_3 with various molar ratios of Fe to Al by sol-gel and solvothermal methods.

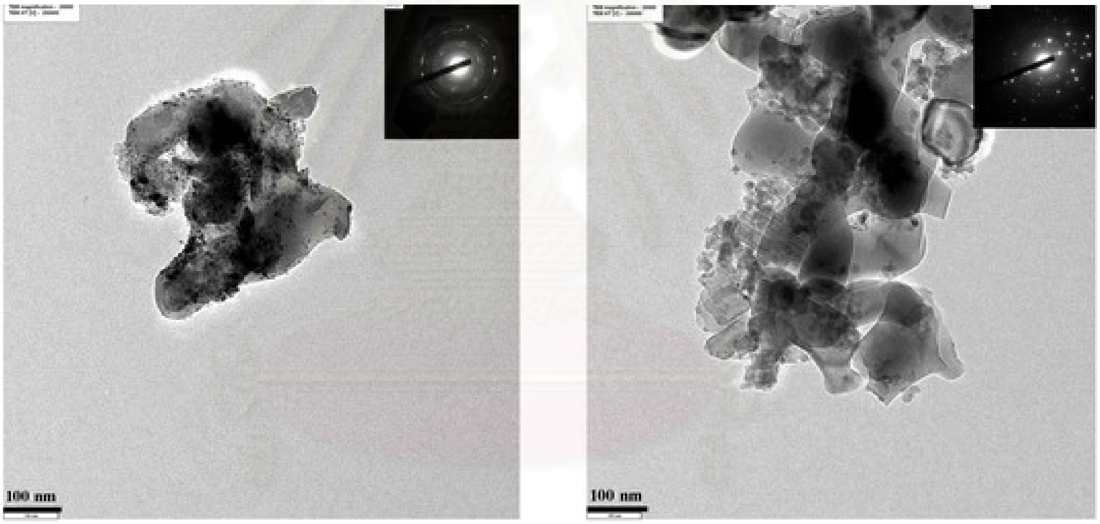
Sample	CO chemisorption ($\times10^{17}$ site/g cat.)	% Dispersion	d_p Pd^0 (nm)
Pd/Fe0-Al_2O_3 SG	10.0	8.4	13
Pd/Fe0.1-Al_2O_3 SG	4.1	2.7	42
Pd/Fe0.3-Al_2O_3 SG	4.2	2.8	41
Pd/Fe0.5-Al_2O_3 SG	6.4	4.2	27
Pd/Fe0-Al_2O_3 SV	11.0	7.2	16
Pd/Fe0.1-Al_2O_3 SV	7.8	5.1	22
Pd/Fe0.3-Al_2O_3 SV	31.6	20.7	5
Pd/Fe0.5-Al_2O_3 SV	11.4	7.4	15

For the catalysts prepared by sol-gel method, the amounts of CO chemisorption decreased when the all catalysts were supported on Fe-modified Al_2O_3 corresponding to the decreasing in the percentage of Pd dispersion. The average Pd^0 particle sizes were ranged from 13-42 nm. For the catalysts prepared by solvothermal method, the amounts of CO chemisorption decreased for Pd/Fe0.1-Al_2O_3SV corresponding to the decreasing in the percentage of Pd dispersion. A large increase in the amounts of CO chemisorption was found for Pd/Fe0.3-Al_2O_3SV. The average Pd^0 particle sizes were ranged from 5-22 nm.

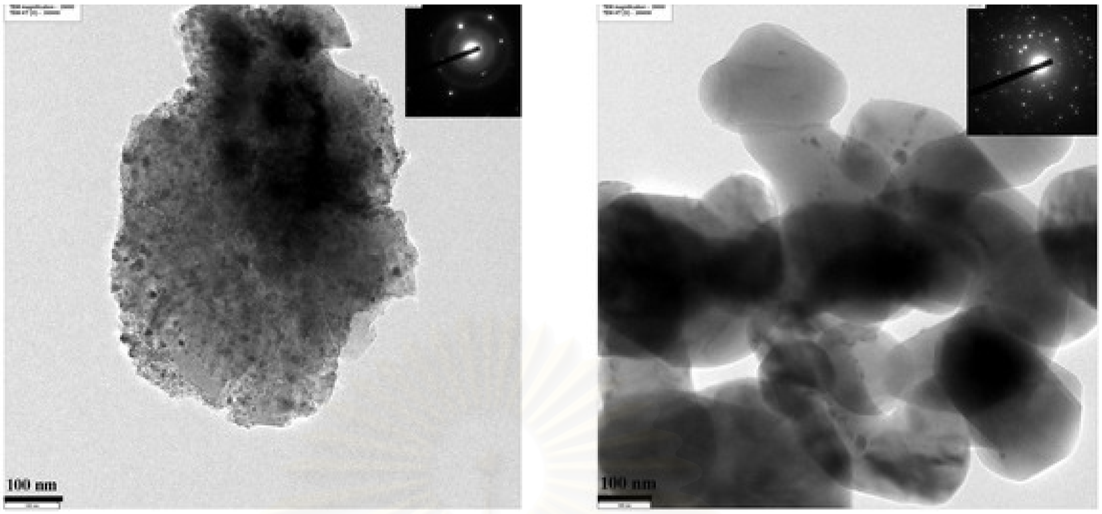
For both preparation methods, when the crystallite size α-Al_2O_3 increased, Pd^0 particle sizes also increased as seem for Pd/Fe0.1-Al_2O_3SG and Pd/Fe0.3-Al_2O_3SV.

5.1.1.5 Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)

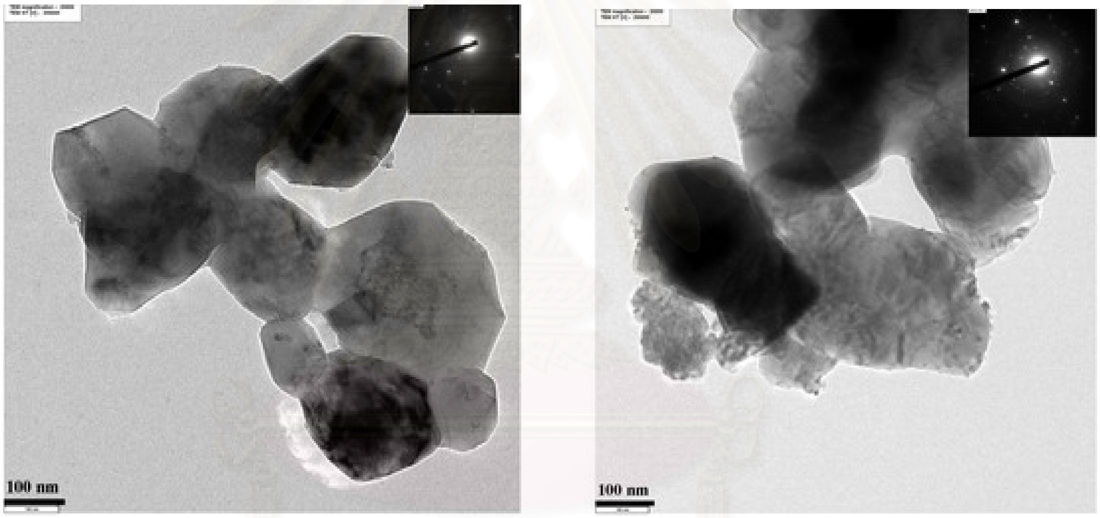
TEM is a useful tool for determining particle size and particle size distribution of supported metals. Transmission electron micrographs and the corresponding selected area electron diffraction patterns of the Pd catalysts supported on Fe-modified Al_2O_3 with molar ratios of Fe to Al 0, 0.1 and 0.5 prepared by sol-gel and solvothermal methods are shown in Figure 5.2.



(A) Pd/Fe0-Al_2O_3 SG (B) Pd/Fe0-Al_2O_3 SV



(C) Pd/Fe0.1-Al_2O_3 SG (D) Pd/Fe0.1-Al_2O_3 SV



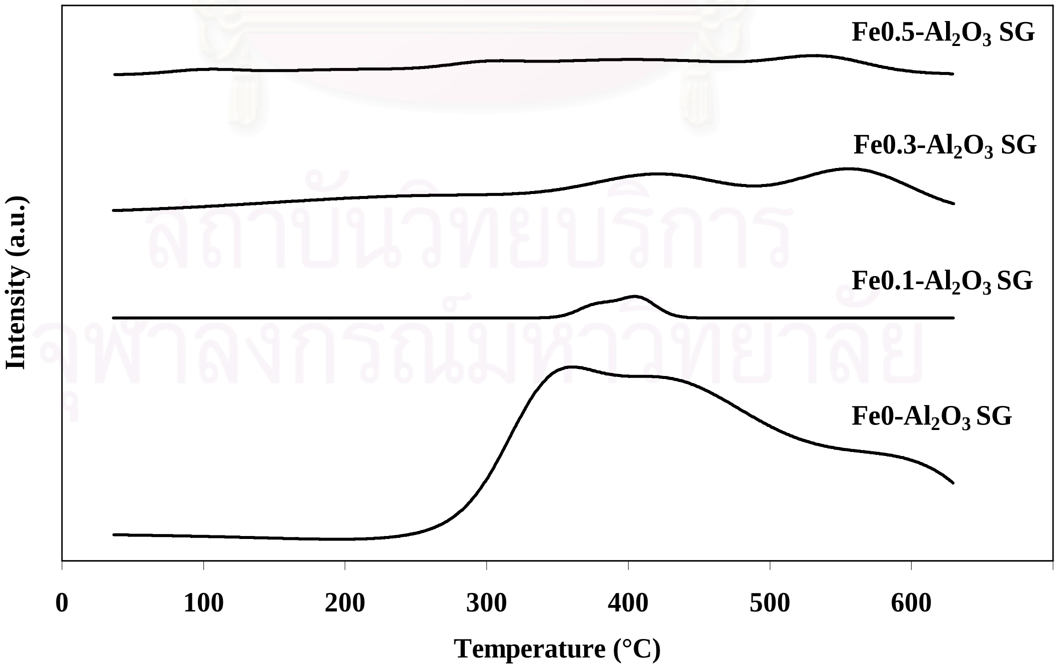
(E) Pd/Fe0.5-Al_2O_3 SG (F) Pd/Fe0.5-Al_2O_3 SV

Figure 5.2 TEM micrographs with SADE pattern of Pd supported on Fe-modified Al_2O_3 with various molar ratios of Fe to Al prepared by sol-gel and solvothermal methods.

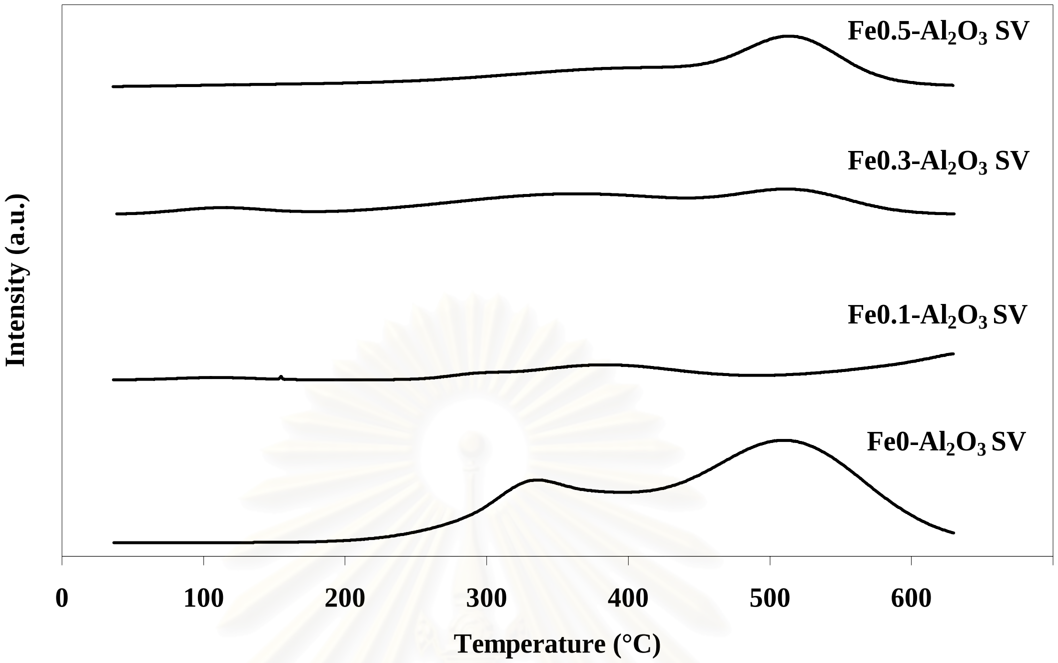
It can be seen that the sol-gel made catalysts (Pd/Fe0-Al_2O_3SG, Pd/Fe0.1-Al_2O_3SG and Pd/Fe0.5-Al_2O_3SG) were consisted of agglomerated particles with primarily irregular shape structure. In case of the solvothermal made catalysts (Pd/Fe0-Al_2O_3SV, Pd/Fe0.1-Al_2O_3SV and Pd/Fe0.5-Al_2O_3SV) had no significantly difference in the TEM images with and without Fe modification. However, agglomeration of finger-like particles was observed for the Pd/α-Al_2O_3 (Pd/Fe0-Al_2O_3SV) whereas spherical-shape particles were found for the Pd/Fe-modified Al_2O_3 catalyst. The finger-like α-Al_2O_3 particles are normally obtained by calaination of the solvothermal-made α-Al_2O_3 powder at high temperature [Mekasuwandumrong and Pavarajarn, 2006]. Based on TEM analysis, palladium particles/clusters with average paticle size ca. 5-10 nm were found to be deposited on the catalyst supports. The selected area electron diffraction patterns shown in Fe-modified consisted of diffraction spots/rings that were indexed in correspondence to the rhombohedral hematite structure.

5.1.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

NH_3-TPD is used for determining acid properties of the catalyst supports. The amount of NH_3 adsorbed on the surface was determined by temperature programmed desorption using a thermal conductivity detector and the Micromeritics Chemisorb 2750 analyzer. The profiled of NH_3 temperature programmed desorption of the catalysts are shown in Figure 5.3.



(A)



(B)

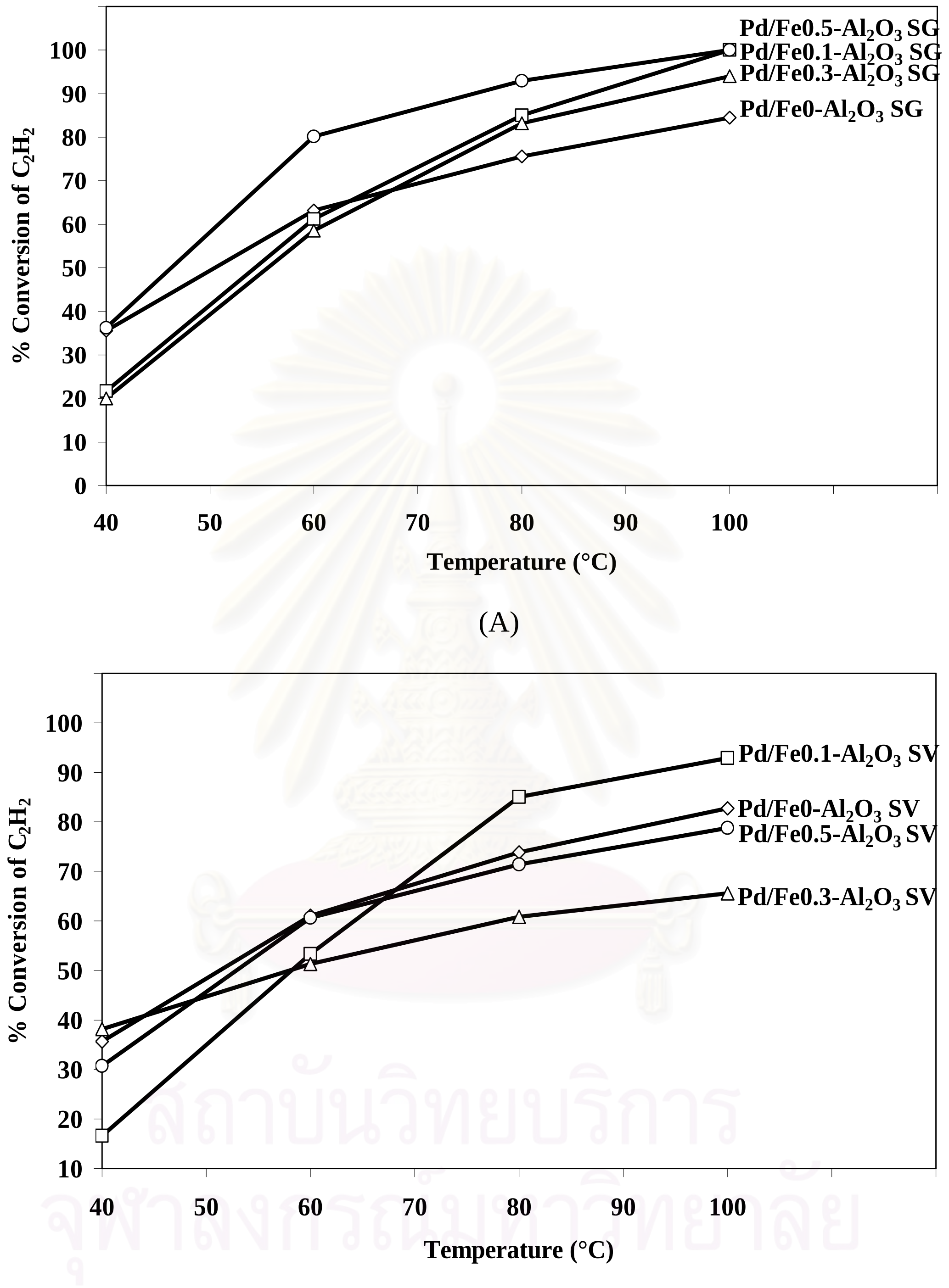
Figure 5.3 NH_3 temperature programmed desorption of Fe-modified Al_2O_3 supports with various molar ratios of Fe to Al by (A) sol-gel and (B) solvothermal methods.

Figure 5.3 (A) shows NH_3 temperature programmed desorption profiles for the sol-gel made α-Al_2O_3 and the Fe-modified α-Al_2O_3 supports. The peak areas of all the Fe-modified α-Al_2O_3 supports (Fe0.1-Al_2O_3SG, Fe0.3-Al_2O_3SG and Fe0.5-Al_2O_3SG) showed lower acidity than unmodified (Fe0-Al_2O_3SG). Fe0.5-Al_2O_3SG had lower acidity than Fe0.3-Al_2O_3SG because α-Fe_2O_3 content increased. Similarly, In the case of solvothermal made α-Al_2O_3 and the Fe-modified α-Al_2O_3 supports, the peak areas of all the Fe-modified α-Al_2O_3 supports (Fe0.1-Al_2O_3SV, Fe0.3-Al_2O_3SV and Fe0.5-Al_2O_3SV) also showed lower acidity than the unmodified Fe0-Al_2O_3SV.

5.1.2 Catalytic Performance of 0.3%Pd/Fe-modified Al_2O_3

The performance of a catalyst for the selective hydrogenation of acetylene is evaluated in terms of acetylene conversion and selectivity towards ethylene. Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in the feed. Selectivity is the ratio of the amount of acetylene converted to ethylene and total amount of acetylene converted. Ideally, there should be one acetylene molecule converted to ethylene for every hydrogen molecule consumed, or 100% selectivity, since all of the acetylene is converted into ethylene. In actual practice, some hydrogen will always be consumed in the side reaction of ethylene conversion to ethane. The selectivity in term of ethylene gain could also be measured by looking at the hydrogen consumed in the converter and the amount of acetylene converted. The performances of the catalysts in this study were therefore reported in terms of acetylene conversion and ethylene gain observed from hydrogen and acetylene concentrations.

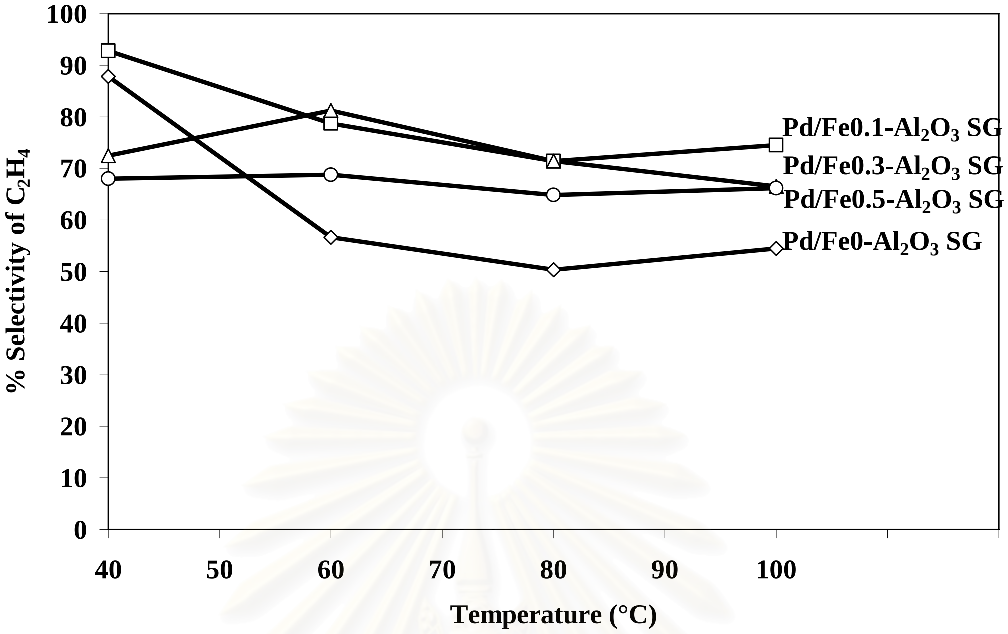
In this study, the performance of 0.3%Pd catalysts supported on Fe-modified Al_2O_3 with various Fe/Al ratios in acetylene hydrogenation was evaluated at the temperature 40-100 °C. Feed gas composed of 1.5% C_2H_2, 1.7% H_2 and balanced C_2H_4 (TIG Co., Ltd.), a GSHV of 16901 h^{-1} were used. Figure 5.4 and 5.5 show catalytic performance for the catalysts prepared by sol-gel and solvothermal methods.



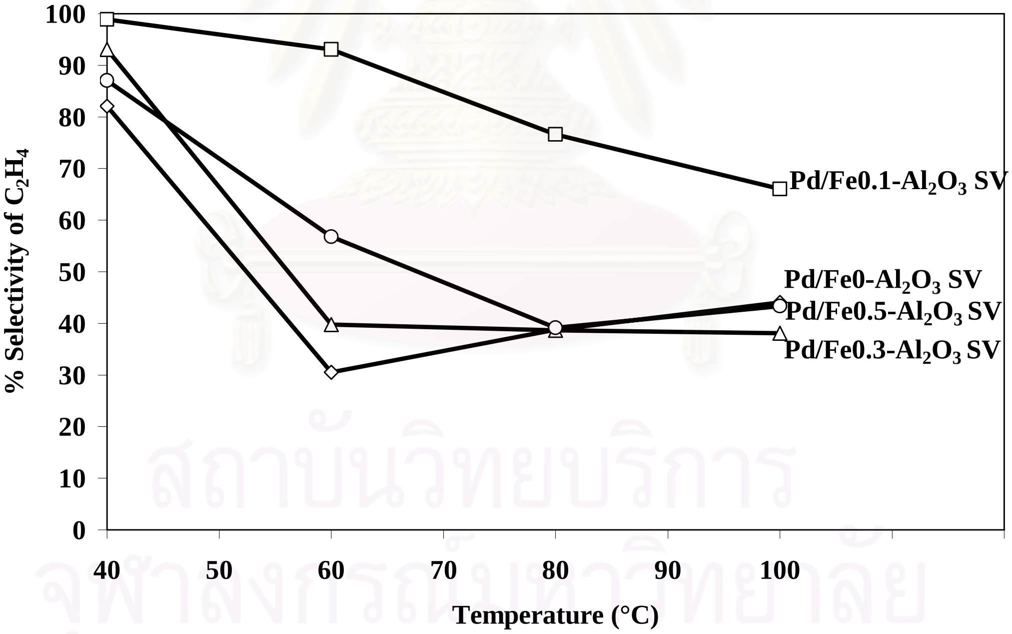
(A)

(B)

Figure 5.4 Temperature dependence of the catalytic performance (% conversion of C_2H_2) of Pd/Fe-modified Al_2O_3 catalysts with various molar ratios of Fe to Al prepared by (A) sol-gel and (B) solvothermal methods.



(A)



(B)

Figure 5.5 Temperature dependence of the catalytic performance (% selectivity of C_2H_4) of Pd/Fe-modified Al_2O_3 catalysts with various molar ratios of Fe to Al prepared by (A) sol-gel and (B) solvothermal methods.

As shown in Figure 5.4, acetylene conversion of all catalysts increases with increasing temperature. The Pd catalysts supported on Fe-modified α-Al_2O_3 prepared by sol-gel method exhibited higher activity than Pd/Fe0-Al_2O_3SG at high reaction temperatures (80-100°C). The effect was not seen at lower reaction temperatures. For the catalysts prepared by solvothermal method, only Pd/Fe0.1-Al_2O_3SV exhibited higher activity than the unmodified α-Al_2O_3 supported on Pd catalyst. It is likely that hydrogenation activity may depend on the average Pd particle size in which larger Pd particle size show higher activity than small Pd particle size.

Ethylene selectivity, Figure 5.5, observed over all the samples, declines when temperature was increased. However, it is clearly seen that for the Pd catalysts supported on Fe-modified α-Al_2O_3 that prepared by sol-gel method, ethylene selectivities were quite constant under the reaction conditions. Modifcation of α-Al_2O_3 with Fe by sol-gel can improve the catalyst stability due probably to less acidity of the supports compared to the unmodified one. On the other hand, for all the catalysts on solvothermal-derived supports, ethylene selectivities declined with increasing temperature. Except Pd/Fe0.1-Al_2O_3SV, the Pd catalysts on Fe-modified supports that prepared by solvothermal method exhibited lower ethylene selectivities than the unmodified ones.

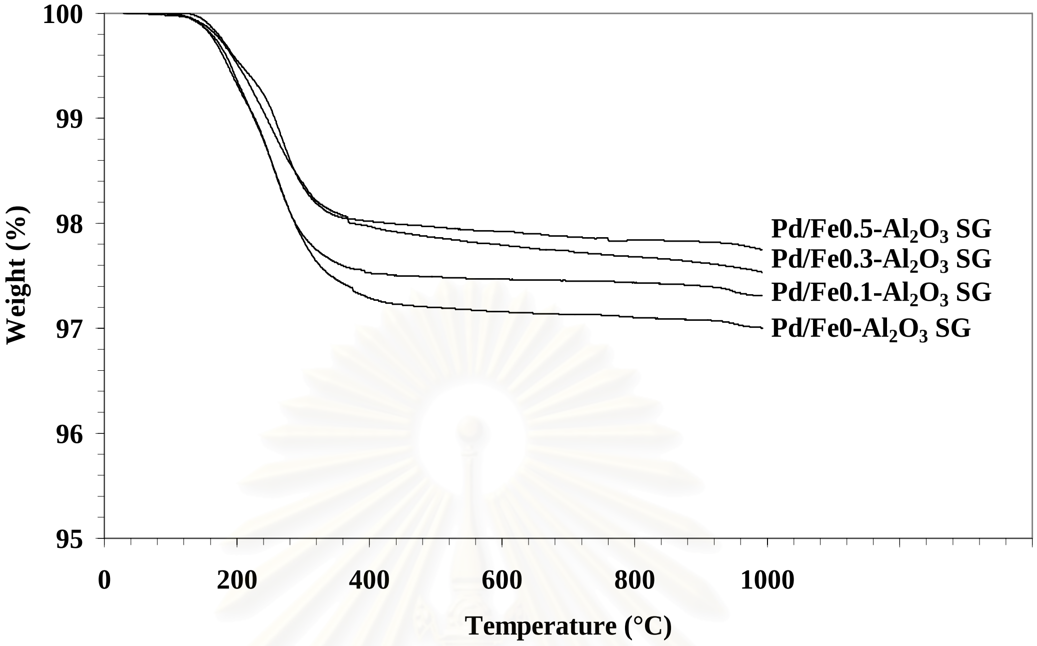
The improvement of ethylene selectivity for Pd/Fe0.1-Al_2O_3SG and Pd/Fe0.1-Al_2O_3SV may be due to larger α-Al_2O_3 crystallite size obtained and as a consequence larger Pd particles size was formed resulting in better catalytic performance of Pd/Al_2O_3. The differences performances for the Pd catalysts supported on Fe-modified α-Al_2O_3 with higher Fe loading (0.3 and 0.5 Fe/Al molar ratios) that were prepared by sol-gel and solvothermal method suggest that formation of mixed α-Al_2O_3 and α-Fe_2O_3 oxides by the two different techniques was not similar. The mixed oxides formed by sol-gel technique may result in more homogeneous mixed oxides that those formed by solvothermal method as seen from TEM images.

Ethylene selectivity was improved in the order: Pd/Fe0.1-Al_2O_3SG ≈ Pd/Fe0.3-Al_2O_3SG ≈ Pd/Fe0.5-Al_2O_3SG > Pd/Fe0.1-Al_2O_3SV > Pd/Fe0-Al_2O_3SV ≈ Pd/Fe0.5-Al_2O_3SV ≈ Pd/Fe0-Al_2O_3SG > Pd/Fe0.3-Al_2O_3SV.

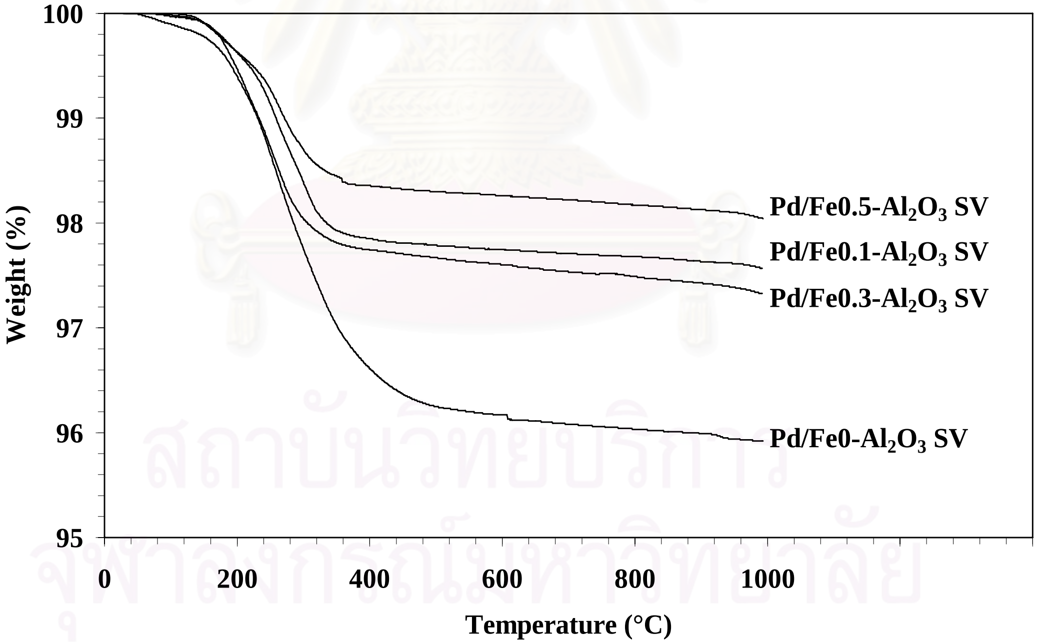
5.1.3 Characterization of the Spent Catalysts

After reaction, the amount of carbonaceous deposits on the catalyst samples in selective hydrogenation of acetylene were measured by thermal gravimetric analysis and are shown in Figure 5.6 and 5.7.

For the catalysts prepared by sol-gel method, the weight loss of all the Pd/Fe-modified Al_2O_3 were ranged from 2.2-2.7 wt. % which were lower than unmodified (Pd/Fe0-Al_2O_3SG) (3.0 wt. %). The weight loss of the catalysts prepared by solvothermal method was also lower than the unmodified supported one (Pd/Fe0-Al_2O_3SV). The results of coke formation were consistent with the amount of acidity observed from NH_3-TPD technique. The exothermic peaks observed in temperature difference profiles of all catalysts corresponding to the oxidation of one type of coke ‘‘soft-type’’ [Xiangjing *et al.*,2006].

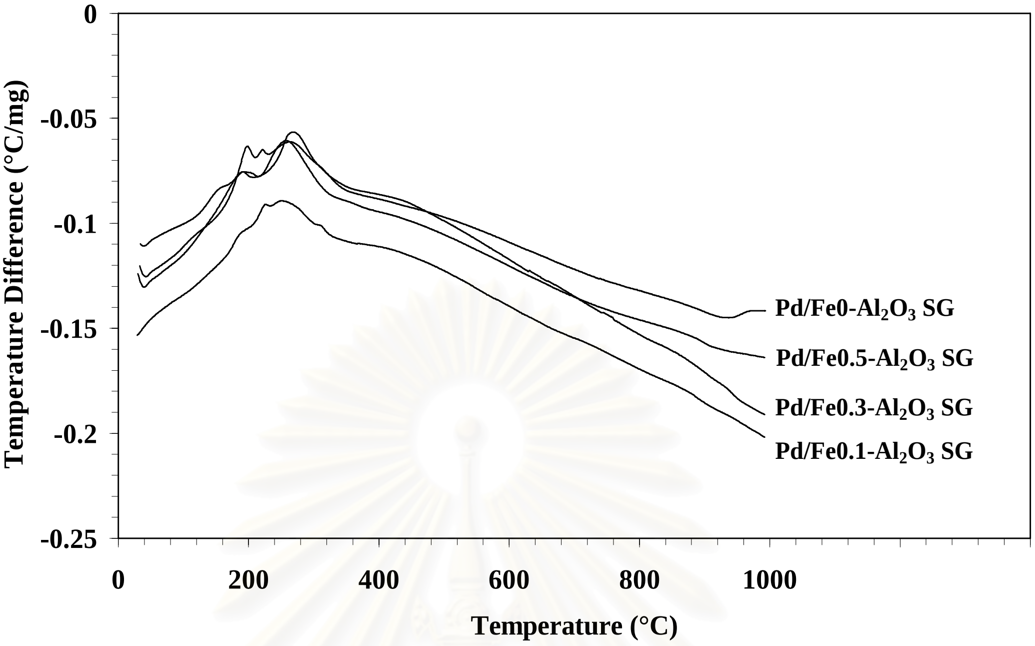


(A)

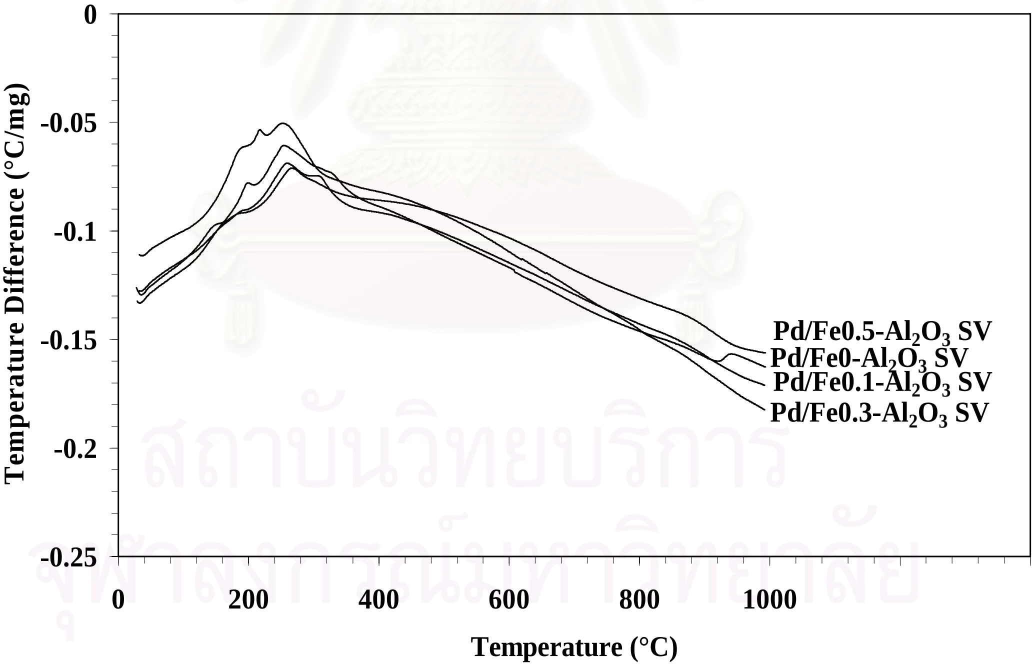


(B)

Figure 5.6 TGA profiles of Pd/Fe-modified Al_2O_3 catalysts after reaction with various molar ratios of Fe to Al prepared by (A) sol-gel and (B) solvothermal methods.



(A)



(B)

Figure 5.7 DTA profiles of Pd/Fe-modified Al_2O_3 catalysts after reaction with various molar ratios of Fe to Al prepared by (A) sol-gel and (B) solvothermal methods.

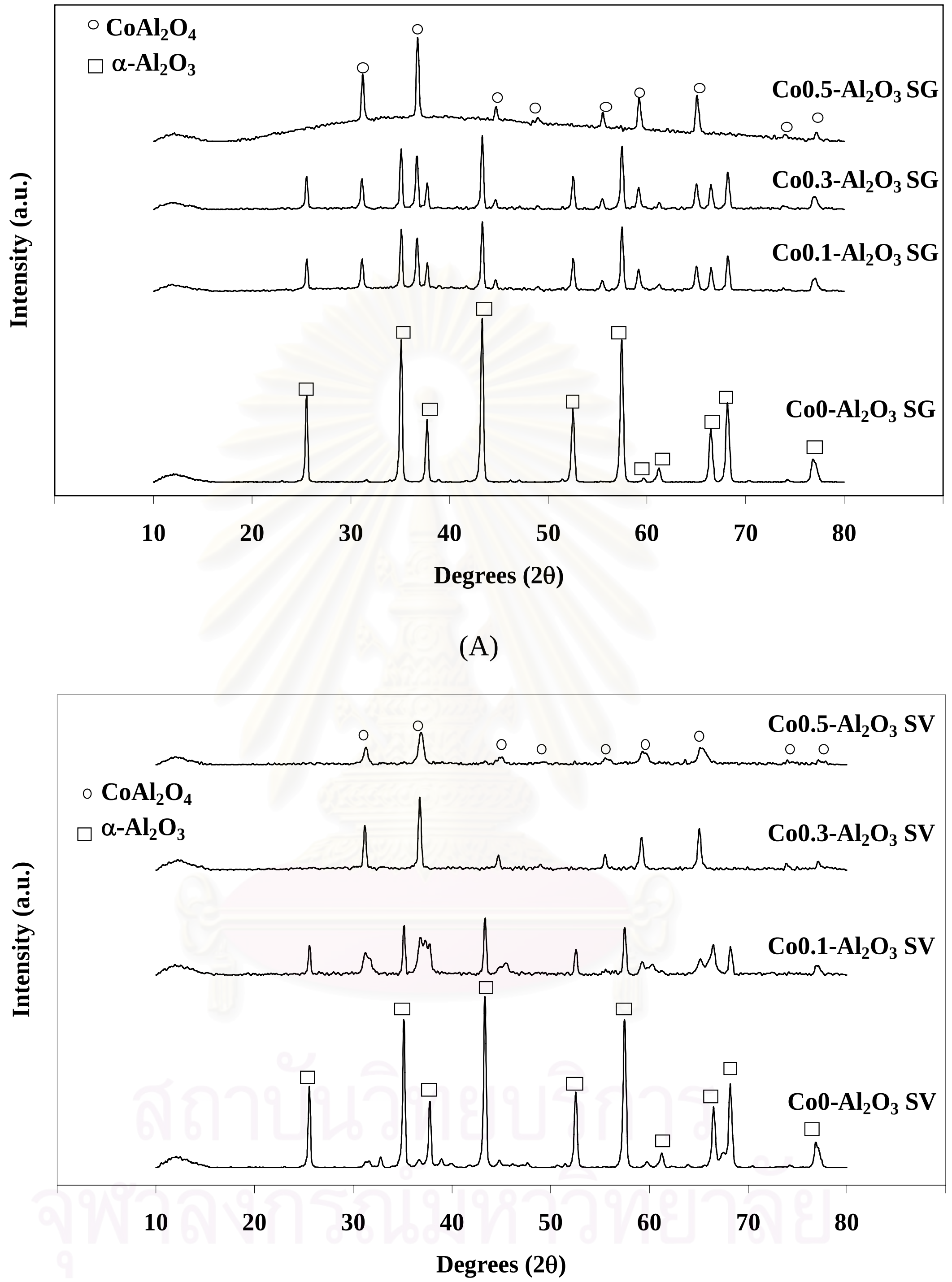
5.2 Co-modified Al_2O_3 and Al_2O_3 Supported Pd Catalysts

The samples of Co-modified Al_2O_3 with various molar ratios of Co to Al (0, 0.1, 0.3 and 0.5) synthesized by sol-gel method were named as Co0-Al_2O_3SG, Co0.1-Al_2O_3SG, Co0.3-Al_2O_3SG, and Co0.5-Al_2O_3SG, respectively. The samples prepared by solvothermal method were name as Co0-Al_2O_3SV, Co0.1-Al_2O_3SV, Co0.3-Al_2O_3SV, and Co0.5-Al_2O_3SV, respectively. Pd catalysts supported on the corresponding Co-modified Al_2O_3 prepared by sol-gel and solvothermal were called Pd/Co0-Al_2O_3SG, Pd/Co0.1-Al_2O_3SG, Pd/Co0.3-Al_2O_3SG, Pd/Co0.5-Al_2O_3SG, Pd/Co0-Al_2O_3SV, Pd/Co0.1-Al_2O_3SV, Pd/Co0.3-Al_2O_3SV, and Pd/Co0.5-Al_2O_3SV, respectively.

5.2.1 Characterization of the Catalysts

5.2.1.1 X-ray Diffraction (XRD)

The XRD patterns of the Al2O3 and Co-modified Al2O3 supports with various molar ratios of Co to Al prepared by sol-gel and solvothermal methods are shown in Figure 5.8.



(A)

(B)

Figure 5.8 The XRD patterns of Co-modified Al_2O_3 supports with various molar ratios of Co to Al synthesized by (A) sol-gel and (B) solvothermal methods.

They were found that without Co modification (Co0-Al_2O_3SG and Co0-Al_2O_3SV), only peaks of α-Al_2O_3 at 25.52º, 35.10º, 37.74º, 43.32º, 52.52º, 57.46º, 61.22º, 66.50º, 68.18º and 77.86º 2θ [Prasitwuttisak T. et al., 2004]. In case of sol-gel method, Co0.1-Al_2O_3SG and Co0.3-Al_2O_3SG resulted in the mixed α-Al_2O_3 and $CoAl_2O_4$ while Co0.5-Al_2O_3SG showed only peaks of $CoAl_2O_4$ spinel at 31.2º, 36.72º, 44.8º, 49.16º, 55.64º, 59.24º, 65.08º, 74.24º and 77.32º 2θ [Kanyanucharat A. et al., 2001]. For those prepared by solvothermal method, Co0.1-Al_2O_3SV resulted in the mixed α-Al_2O_3 and $CoAl_2O_4$ while Co0.3-Al_2O_3SV and Co0.5-Al_2O_3SV showed only peaks of $CoAl_2O_4$ spinel.

Such results suggesting that crystallization mechanism for both α-Al_2O_3 and $CoAl_2O_4$ were different for the different preparation technique. $CoAl_2O_4$ spinel may form easier by solvothermal technique than by sol-gel method and occur at Co/Al ratio less than its stoichiometric ratio (0.5).

5.2.1.2 Average Crystallite Size

The average crystallite size of each crystal phase was calculated from the Scherrer equation. The crystallite size of the Co-modified Al_2O_3 supports with various molar ratios of Co to Al prepared by sol-gel and solvothermal methods are shown in Table5.4.

Table 5.4 Crystallite size of Co-modified Al_2O_3 supports with various molar ratios of Co to Al prepared by sol-gel and solvothermal methods.

Sample	Crystallite size (nm)
Co0-Al_2O_3 SG	45.5^{α}
Co0.1-Al_2O_3 SG	48.6^{α} , 36.1^{CA}
Co0.3-Al_2O_3 SG	52.3^{α} , 38.9^{CA}
Co0.5-Al_2O_3 SG	29.3^{CA}
Co0-Al_2O_3 SV	52.2^{α}
Co0.1-Al_2O_3 SV	48.9^{α}, 6.2^{CA}
Co0.3-Al_2O_3 SV	35.6^{CA}
Co0.5-Al_2O_3 SV	15.2^{CA}

$^{\alpha}$ α-Al_2O_3

^{CA} $CoAl_2O_4$

Addition of Co during the synthesis of α-Al_2O_3 by sol-gel technique did not alter with the crystallite size of α-Al_2O_3 formed except Co0.5-Al_2O_3SG where only $CoAl_2O_4$ was formed. The crystallite size of α-Al_2O_3 was increased from 45.5 to 52.3 nm as the Co/Al changed from 0 to 0.3. On the other hand, addition of Co during the synthesis of α-Al_2O_3 by solvothermal method resulted in a slight decrease of crystallite size of α-Al_2O_3 from 52.2 to 48.9 nm. The crystallite size of $CoAl_2O_4$ formed by solvothermal was also smaller than those obtained from sol-gel technique.

5.2.1.3 BET Surface Areas

The BET surface areas of catalyst supports prepared sol-gel and solvothermal methods measured by N_2 physisorption measurement are shown in Table 5.5.

Table 5.5 BET Surface Areas of Co-modified Al_2O_3 with various molar ratios of Fe to Al

Sample	BET S.A. (m2/g)
Co0-Al_2O_3 SG	1.0
Co0.1-Al_2O_3 SG	0.6
Co0.3-Al_2O_3 SG	0.3
Co0.5-Al_2O_3 SG	2.4
Co0-Al_2O_3 SV	5.1
Co0.1-Al_2O_3 SV	3.8
Co0.3-Al_2O_3 SV	0.8
Co0.5-Al_2O_3 SV	4.3

The BET surface areas of the supports prepared by sol-gel method were ranged from 0.3-2.4 m^2/g. which was quite low but typical for the α-Al_2O_3 supports. While the supports prepared by solvothermal method were range 0.8-5.1 m^2/g. There were no significantly different and still quite low, which due probably to high agglomeration of pqrticles by calcinations at high temperature [Kanyanucharat A. *et al.*, 2001].

Comparing both techniques, the supports that were prepared by solvothermal method had higher BET surface areas than those obtained by sol-gel method because sintering of Al2O3 particles during calcinations for both techniques were different.

5.2.1.4 Metal Active Sites

CO chemisorption technique provides the information on the number of palladium active sites and the percentages of palladium dispersion. The total CO uptakes and the percentages of palladium metal dispersion are reported in Table 5.6.

Table 5.6 Results from CO chemisorption of Pd supported on Co-modified Al_2O_3 with various molar ratios of Co to Al by sol-gel and solvothermal methods.

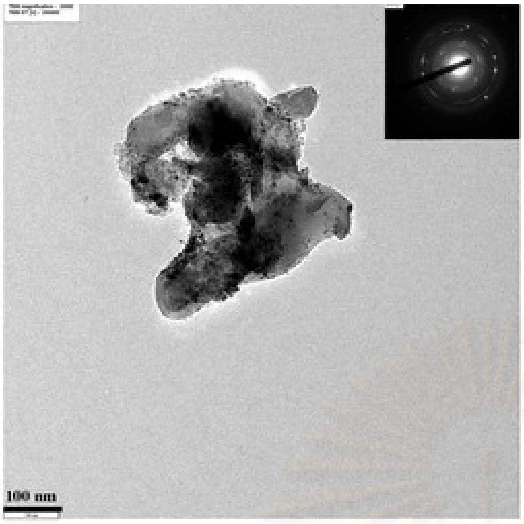
Sample	CO chemisorption ($\times 10^{17}$ site/g cat.)	% Dispersion	d_p Pd^0 (nm)
Pd/Co0-Al_2O_3SG	10.0	8.4	13
Pd/Co0.1-Al_2O_3SG	6.9	4.5	25
Pd/Co0.3-Al_2O_3SG	9.0	6.7	17
Pd/Co0.5-Al_2O_3SG	3.9	2.5	44
Pd/Co0-Al_2O_3 SV	11.0	7.2	16
Pd/Co0.1-Al_2O_3SV	7.9	5.2	22
Pd/Co0.3-Al_2O_3SV	4.3	2.9	40
Pd/Co0.5-Al_2O_3SV	5.5	3.6	31

The metal active sites measurement is based on CO chemisorption technique on the assumption that one CO molecule adsorbs on one palladium site [Anderson *et.al.*, 1985 and N. Mahata *et.al.*, 2000].

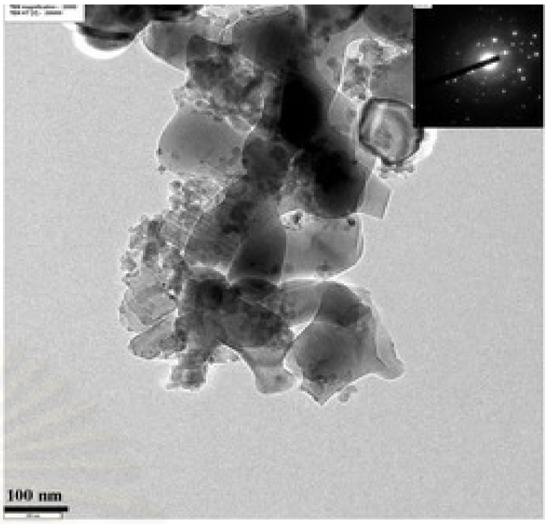
For the catalysts prepared by sol-gel and solvothermal methods, the amounts of CO chemisorption and percentage of Pd dispersion decreased when only $CoAl_2O_4$ was formed (Pd/Co0.5-Al_2O_3SG, Pd/Co0.3-Al_2O_3SV and Pd/Co0.5-Al_2O_3SV). The average Pd^0 particle sizes were ranged from 13-44 and 16-40 nm, respectively.

5.2.1.5 Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)

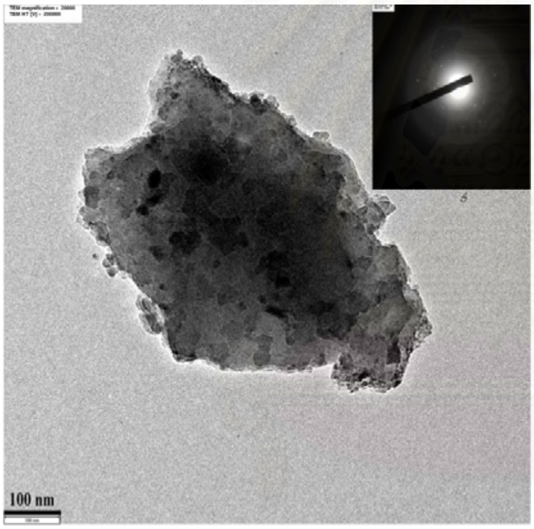
TEM micrographs of Pd catalyst supported on Co-modified Al_2O_3 with various molar ratios of Co to Al by sol-gel and solvothermal methods are shown in Figure 5.9



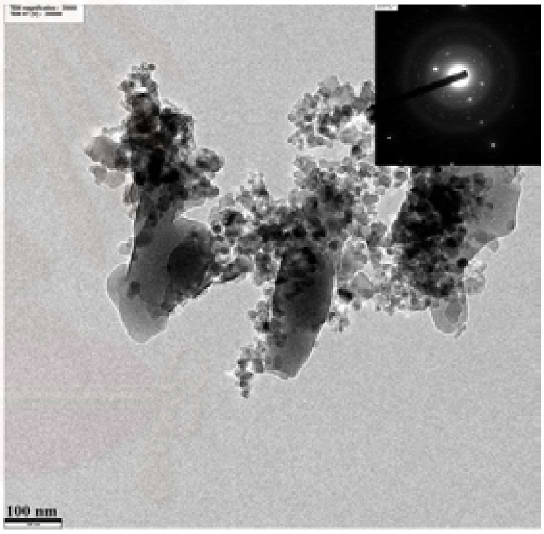
(A) Pd/Co0-Al_2O_3 SG



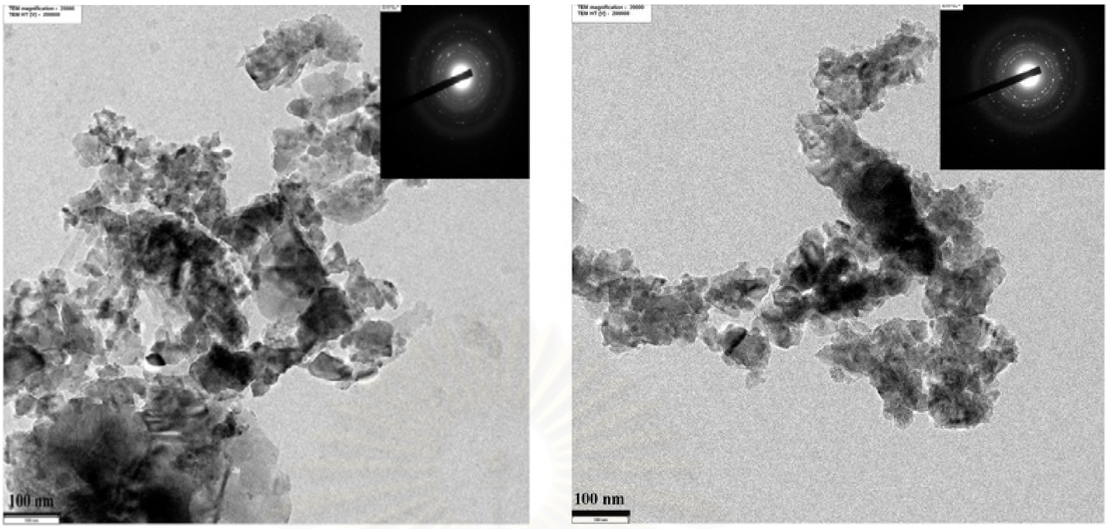
(B) Pd/Co0-Al_2O_3 SV



(C) Pd/Co0.1-Al_2O_3 SG



(D) Pd/Co.1-Al_2O_3 SV



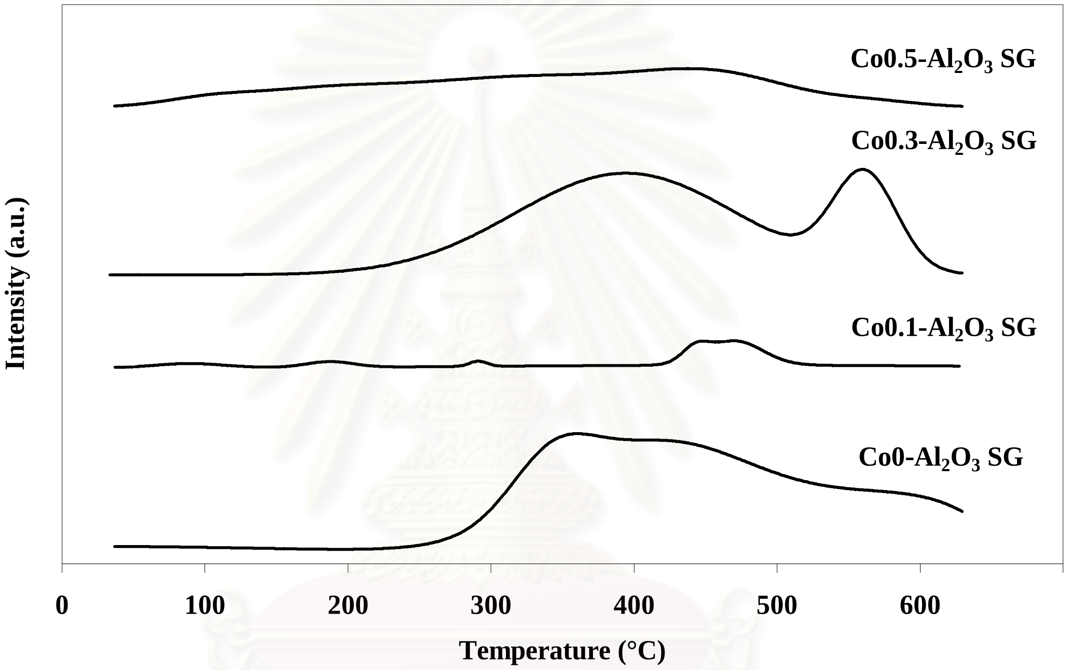
(E) Pd/Co0.5-Al_2O_3 SG (F) Pd/Co0.5-Al_2O_3 SV

Figure 5.9 TEM micrographs with SADE pattern of Pd supported on Co-modified Al_2O_3 with various molar ratios of Co to Al prepared by sol-gel and solvothermal methods.

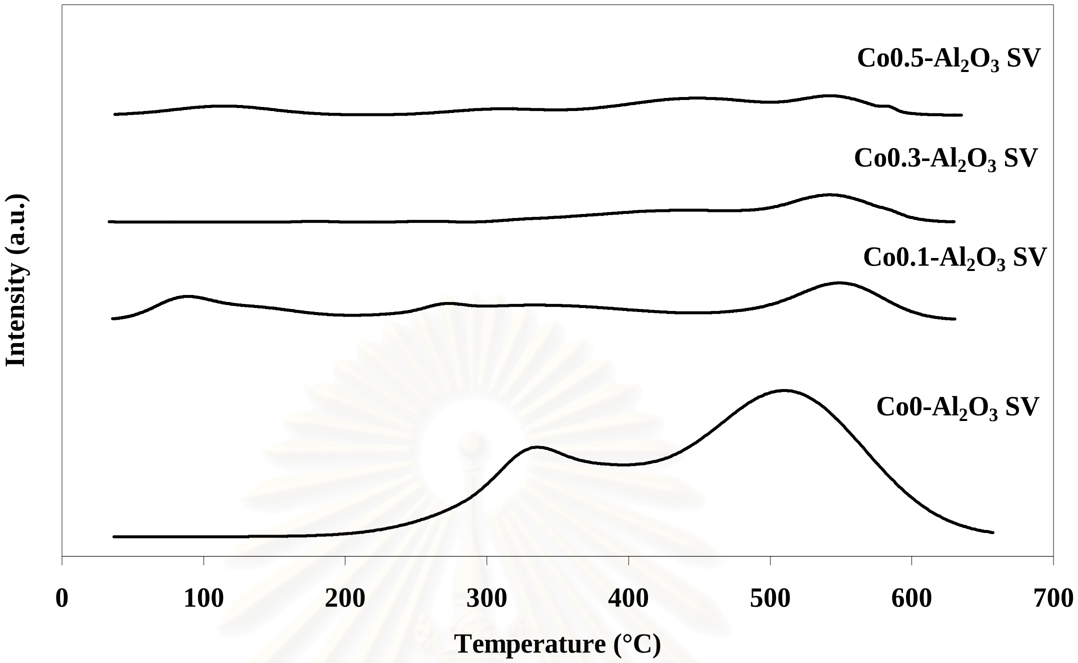
It can be seen that the sol-gel made catalysts (Pd/Co0-Al_2O_3SG, Pd/Co0.1-Al_2O_3SG and Pd/Co0.5-Al_2O_3SG) were consisted of agglomerated particles with primarily irregular shape structure. In case of the solvothermal made catalysts (Pd/Co0-Al_2O_3SV, Pd/Co0.1-Al_2O_3SV and Pd/Co0.5-Al_2O_3SV), agglomeration of finger-like particles were observed. The finger-like α-Al_2O_3 particles are normally obtained by calaination of the solvothermal-made α-Al_2O_3 powder at high temperature [Mekasuwandumrong and Pavarajarn, 2006]. For the SAED analyses indicate that the Co particles are mainly a close-packed hexagonal crystal structure [Santini O. *et al.*, 2005]. Based on TEM analysis, palladium particles/clusters with average paticle size ca. 5-10 nm were found to be deposited on the catalyst supports.

5.2.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

Temperature programmed desorption of NH_3 (NH_3-TPD) for catalyst supports prepared by sol-gel and solvothermal methods were performed in order to obtain information about ammonia adsorption behavior on the acid site of catalysts samples. The results are show in Figure 5.10.



(A)



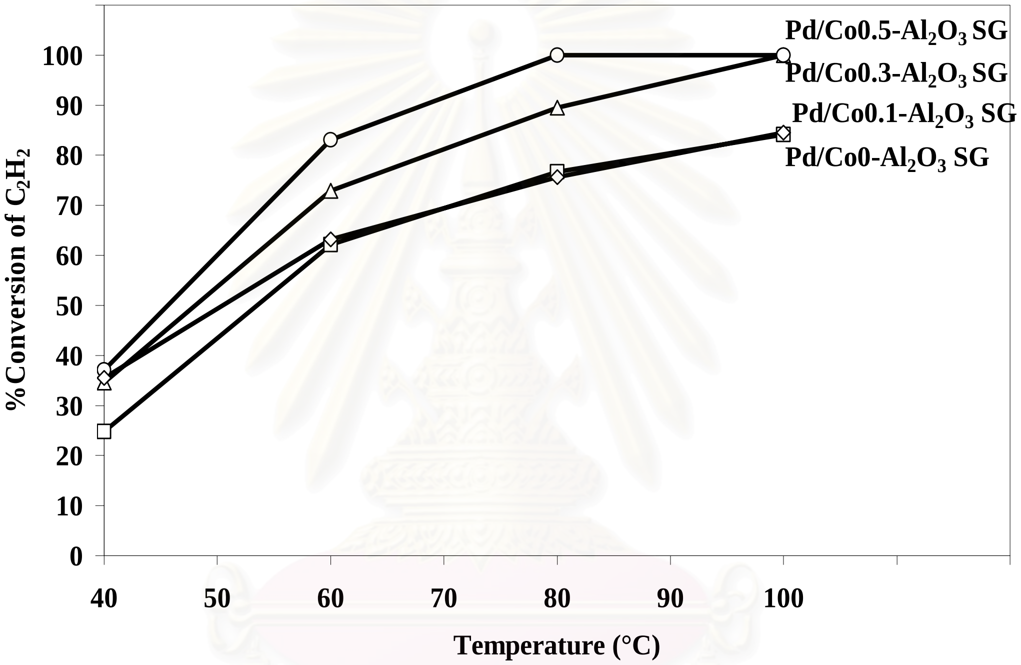
(B)

Figure 5.10 NH_3 temperature programmed desorption of Co-modified Al_2O_3 supports with various molar ratios of Co to Al by (A) sol-gel and (B) solvothermal methods.

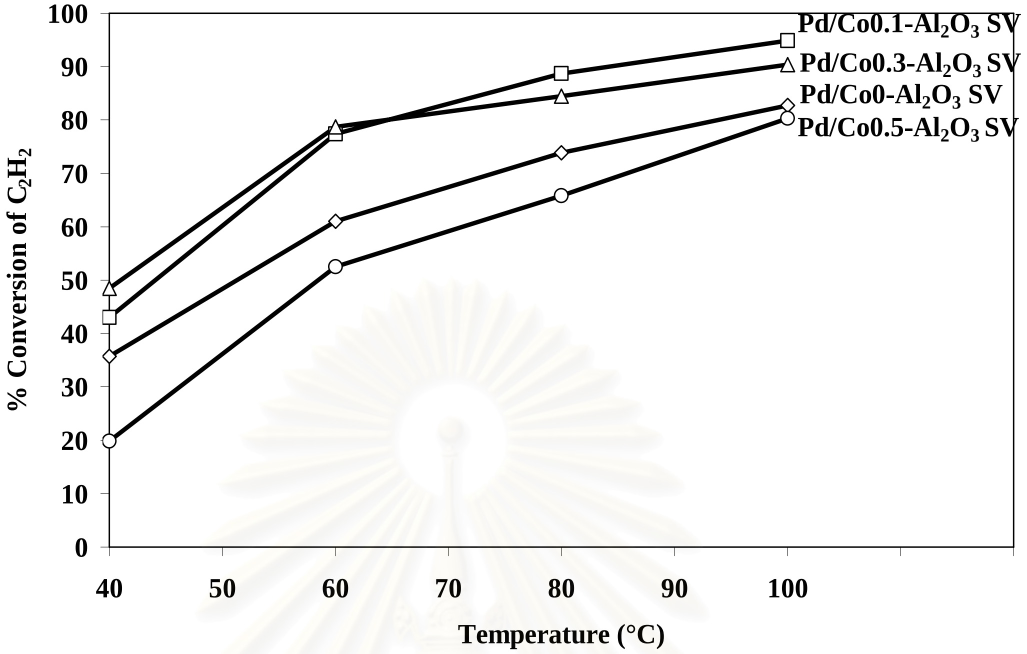
Figure 5.10(A) shows NH_3 temperature programmed desorption profiles for the sol-gel made α-Al_2O_3 and the Co-modified α-Al_2O_3 supports. The peak areas of the Co-modified α-Al_2O_3 supports (Co0.1-Al_2O_3SG and Co0.5-Al_2O_3SG) showed lower acidity than unmodified (Co0-Al_2O_3SG) excepted Co0.3-Al_2O_3SG. Co0.5-Al_2O_3SG had lower acidity than all the catalyst supports because it formed only $CoAl_2O_4$. In case of solvothermal made α-Al_2O_3 and the Co-modified α-Al_2O_3 supports. The peak areas of the all Co-modified α-Al_2O_3 supports (Co0.1-Al_2O_3SV, Co0.3-Al_2O_3SV and Co0.5-Al_2O_3SV) showed lower acidity than unmodified (Co0-Al_2O_3SV).

5.2.2 Catalytic Performance of 0.3%Pd/Co-modified Al_2O_3

In this study, the performance of 0.3%Pd catalysts supported on Fe-modified Al_2O_3 with various Fe/Al ratios in acetylene hydrogenation was evaluated at the temperature 40-100 °C. Feed gas composed of 1.5% C_2H_2, 1.7% H_2 and balanced C_2H_4 (TIG Co., Ltd.), a GSHV of 16901 h^{-1} were used. Figure 5.11 and 5.12 shows catalytic performance for the catalysts prepared by sol-gel and solvothermal methods.



(A)



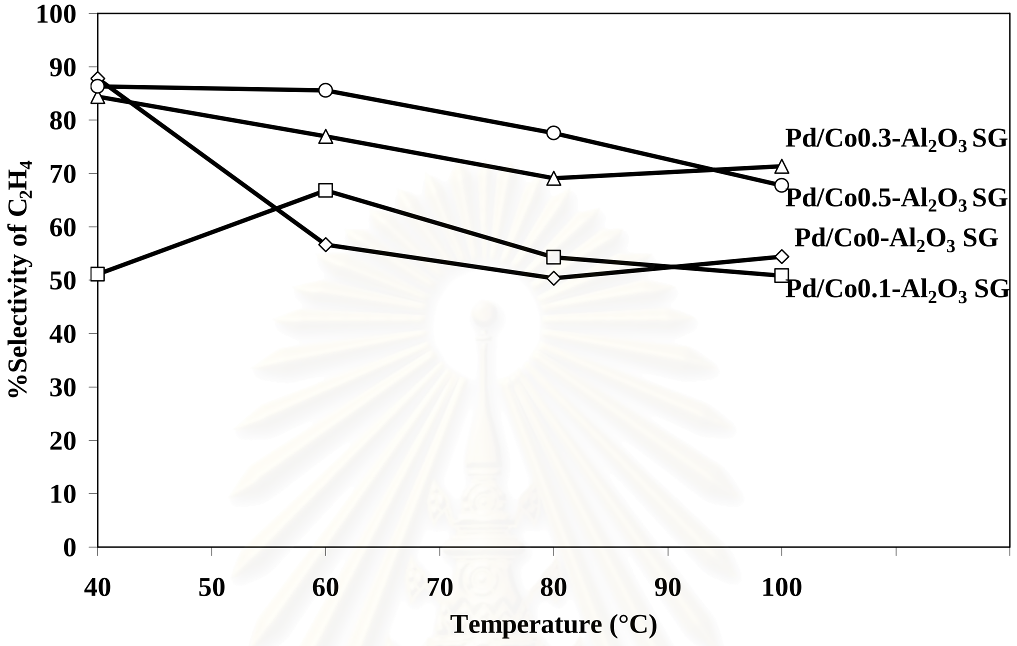
(B)

Figure 5.11 Temperature dependence of the catalytic performance (% conversion of C_2H_2) of Pd/Co-modified Al_2O_3 catalysts with various molar ratios of Co to Al prepared by (A) sol-gel and (B) solvothermal methods.

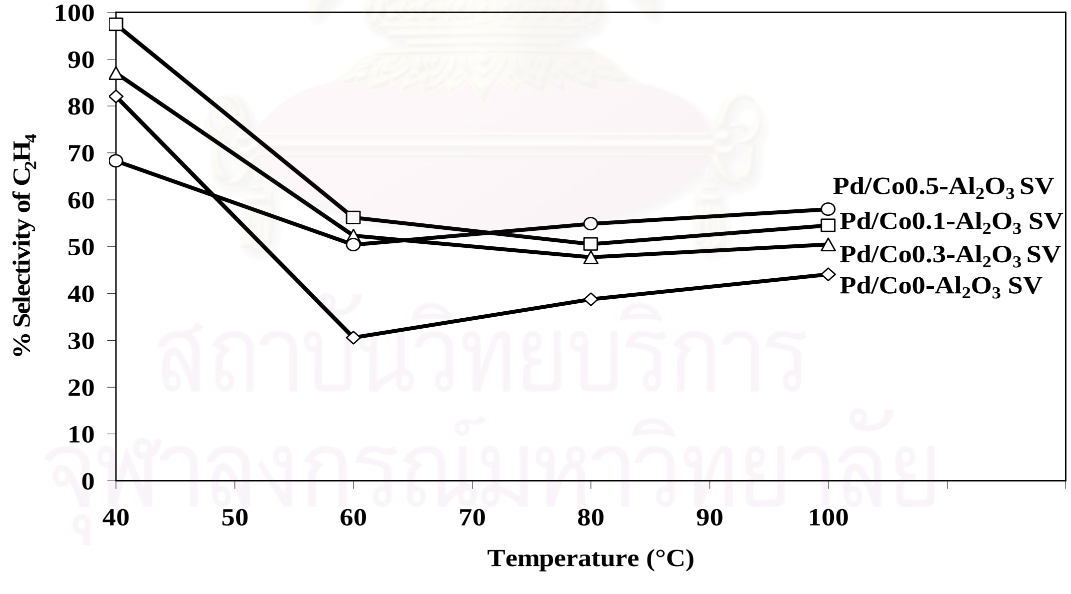
As shown in Figure 5.11, acetylene conversion of all the catalysts increased with increasing temperature. All the Pd catalysts supported on the Co-modified α-Al_2O_3 that were prepared by sol-gel method exhibited higher activity than that on the unmodified support (Pd/Co0-Al_2O_3SG). For the catalysts supported on Co-modified α-Al_2O_3 that were prepared by solvothermal method, Pd/Co-modified Al_2O_3 with molar ratio 0.1 and 0.3 exhibited higher activity than that on the unmodified support (Pd/Co0-Al_2O_3SG). However, Pd/Co0.5-Al_2O_3SV showed lower activity.

Ethylene selectivity, Figure 5.12, observed over all samples, declines when temperature is increased. Both of the catalyst modified supports prepared by sol-gel and solvothermal method showed higher ethylene selectivity at temperature 60-100°C. Ethylene selectivity was improved in the order: Pd/Co0.3-Al_2O_3SG ≈

Pd/Co0.5-Al_2O_3SG > Pd/Co0.5-Al_2O_3SV > Pd/Co0.1-Al_2O_3SV > Pd/Co0-Al_2O_3SG ≈ Pd/Co0.1-Al_2O_3SG > Pd/Co0.3-Al_2O_3SV > Pd/Co0-Al_2O_3SV.



(A)



(B)

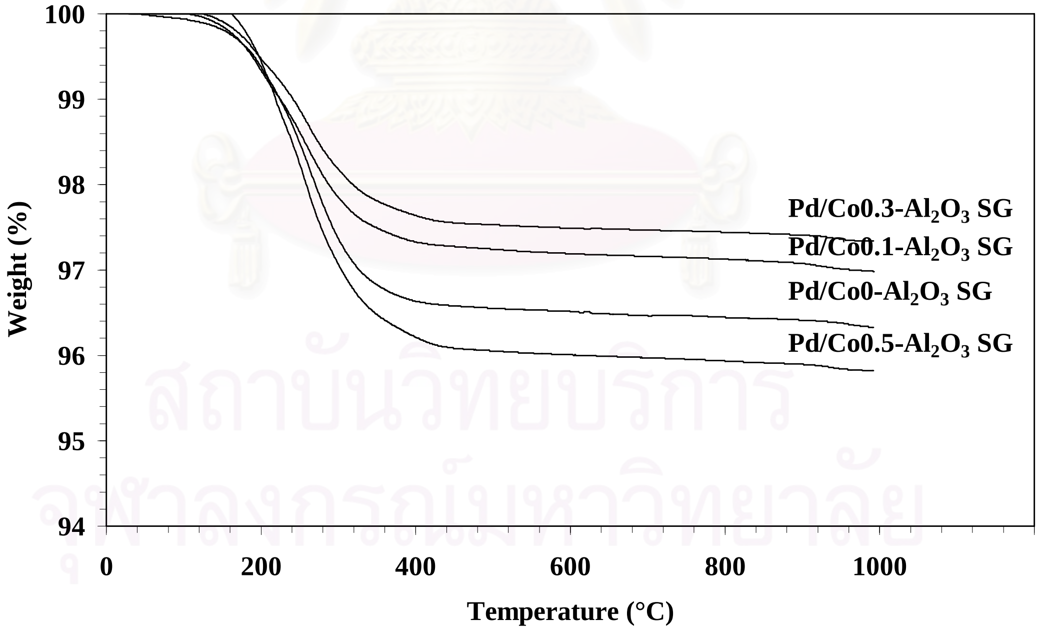
Figure 5.12 Temperature dependence of the catalytic performance (% selectivity of C_2H_2) of Pd/Co-modified Al_2O_3 catalysts with various molar ratios of Co to Al prepared by (A) sol-gel and (B) solvothermal methods.

5.2.3 Characterization of the Spent Catalysts

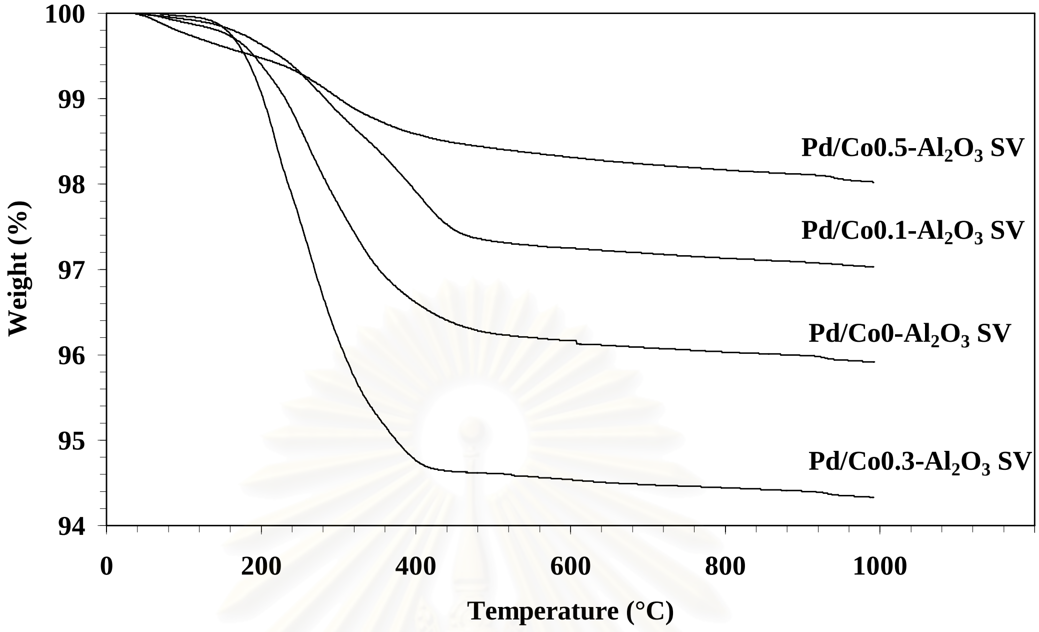
After reaction, the amount of carbonaceous deposits on the catalyst samples in selective hydrogenation of acetylene were measured by thermal gravimetric analysis and shown in Figure 5.13 and 5.14.

For the catalysts prepared by sol-gel method, the weight loss of all Pd/Co-modified Al_2O_3 were lower than unmodified (Pd/Co0-Al_2O_3SG) (3.0 wt. %) except Pd/Co0.5-Al_2O_3SG. While the weight loss of the catalysts prepared by solvothermal method, shown lower than unmodified (Pd/Co0-Al_2O_3SV) except Pd/Co0.3-Al_2O_3SV. They were not in agreement with acidity measured by NH_3-TPD.

The exothermic peaks observed in temperature difference profiles of all catalysts corresponding to the oxidation of one type of coke ‘‘soft-type’’ [Xiangjing *et al.*, 2006].

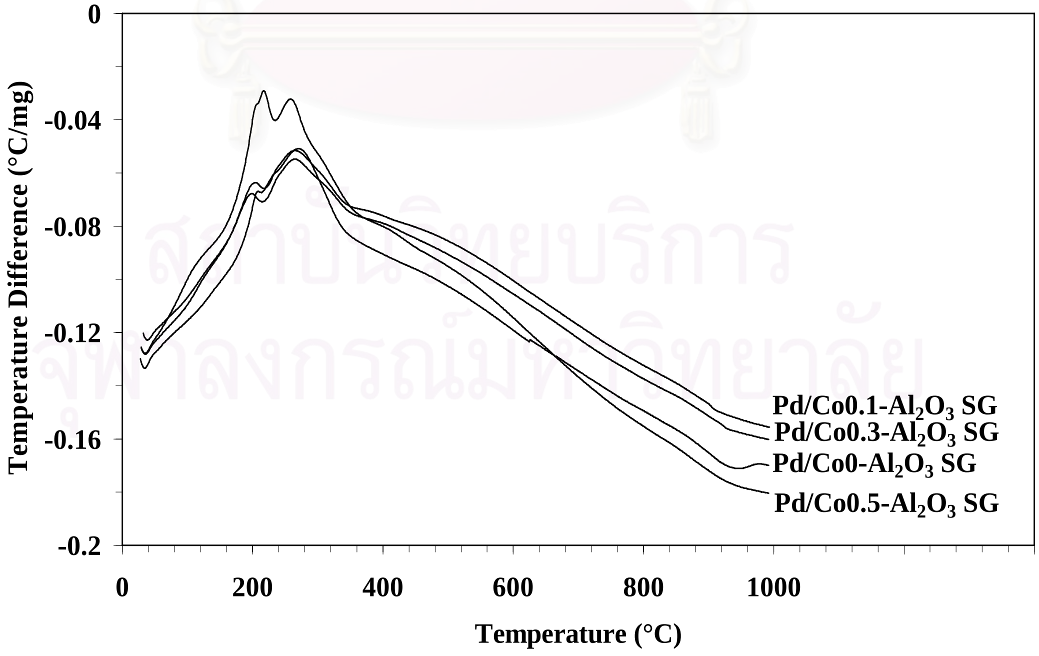


(A)

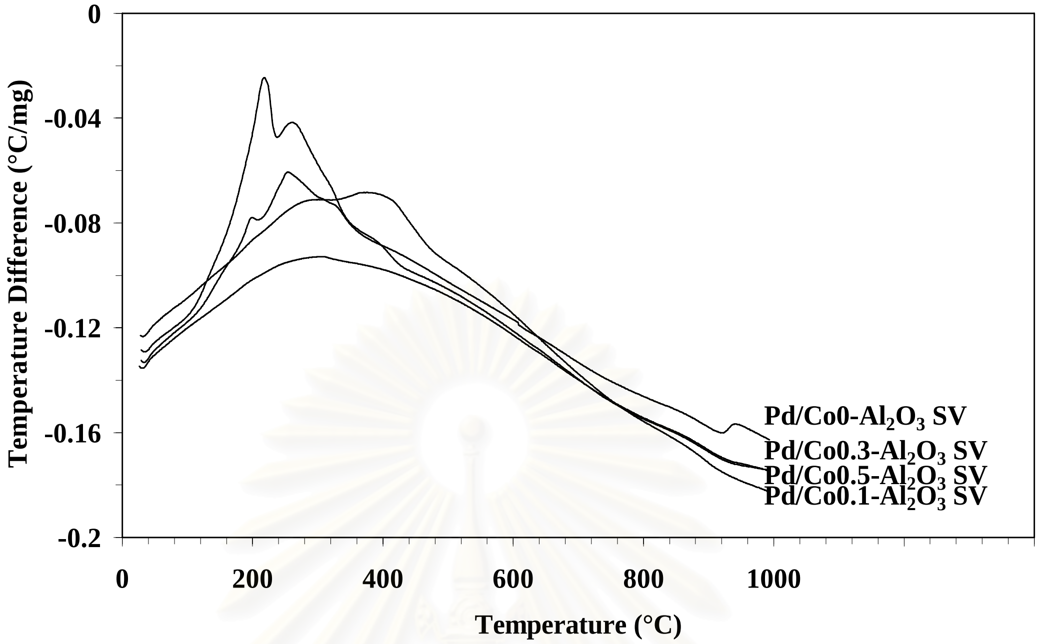


(B)

Figure 5.13 TGA profiles of Pd/Co-modified Al_2O_3 catalysts after reaction with various molar ratios of Co to Al prepared by (A) sol-gel and (B) solvothermal methods.



(A)



(B)

Figure 5.14 DTA profiles of Pd/Co-modified Al_2O_3 catalysts after reaction with various molar ratios of Co to Al prepared by (A) sol-gel and (B) solvothermal methods.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions obtain from the experimental results of Pd supported on Fe- and Co-modified Al_2O_3 supports with various molar ratios of Fe/Al and Co/Al (0, 0.1, 0.3 and 0.5) synthesized by different methods. Additionally, recommendations for further study are given in section 6.2.

6.1 Conclusions

1. For Fe-modified α-Al_2O_3 supported Pd catalysts, all of the modified catalysts (with Fe/Al=0.1-0.5) prepared by sol-gel method resulted in higher activity and ethylene selectivity while those prepared by solvothermal method, only the catalysts with Fe/Al=0.1 showed improvement in terms of C_2H_2 conversion and C_2H_4 selectivity.

2. All of the Fe-modified α-Al_2O_3 supported Pd catalysts produced less coke formation due to lower acidity as shown by NH_3-TPD results.

3. Activity and ethylene selectivity depended on Pd particle size which itself was a function of crystallite size of the supports (both α-Al_2O_3 and α-Fe_2O_3).

4. For Co-modified α-Al_2O_3 supported Pd catalysts, $CoAl_2O_4$ was formed at lower Co/Al ratio for those prepared by solvotermal method. However, dispersion of Pd decreased when $CoAl_2O_4$ was formed for both techniques.

5. In most cases, Pd catalysts on the Co-modified Al_2O_3 supports showed better performance than on the unmodified Al_2O_3 supports especially at nearly 100% C_2H_2 conversion. The effect of Co-modified Al_2O_3 on coke formation, however, was not clearly shown.

6.2 Recommendations

1. More characterization techniques such as X-ray photoelectron spectroscopy (XPS) should be applied in order to gain more information of the Pd catalysts.

2. The amounts of acidity of Co-modified Al_2O_3 should be confirmed by other techniques such as pyridine adsorption using in-situ IR spectroscopy so that the type of acidity can be identified.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of support composition (Fe-Modified Al_2O_3)

Preparation of Fe-modified Al_2O_3 with various molar ratios of Fe to Al (0.1, 0.3 and 0.5) by sol-gel and solvothermal methods.

Reagent: - Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$)
Molecular weight = 375.14 g/mol
- Aluminum isopropoxide ($((CH_3)_2CHO)_3Al$)
Molecular weight = 204.25 g/mol
Precursors: - Ferric nitrate nonahydrate ($FeN_3O_9 \cdot 9H_2O$)
Molecular weight = 404.00 g/mol
- Iron (III) acetylacetonate $(C_5H_8O_2)_3Fe$
Molecular weight = 353.18 g/mol
Calculation:

Sol-gel method

- For molar ratio of Fe/Al = 0.1 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

$$\text{Aluminium} = (26.9815\times24.0735)/375.14 = 1.7315 \text{ g}$$
$$= 1.7315/26.9815 = 0.0642 \text{ mol}$$

For Fe/Al = 0.1, 0.0642 mole of aluminium

$$\text{Iron required} = 0.0642\times0.1 = 0.00642 \text{ mol}$$
$$= 0.00642\times55.847 = 0.3584 \text{ g}$$

Iron 0.3584 g was prepared from $FeN_3O_9 \cdot 9H_2O$ and molecular weight of Fe is 55.847 mol

$FeN_3O_9\cdot 9H_2O$ required $= \dfrac{\text{MW of } (FeN_3O_9\cdot 9H_2O) \times \text{Iron required}}{\text{MW of Fe}}$

$= (404.00\times0.3584)/55.847 = 2.5926$ g

- For molar ratio of Fe/Al = 0.3 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium $= (26.9815\times24.0735)/375.14 = 1.73215$ g

$= 1.7315/26.9815 = 0.0642$ mol

For Fe/Al = 0.3, 0.0642 mole of aluminium

Iron required $= 0.0642\times0.3 = 0.0193$ mol

$= 0.0193\times55.847 = 1.0751$ g

Iron 1.0751 g was prepared from $FeN_3O_9\cdot 9H_2O$ and molecular weight of Fe is 55.847 mol

$FeN_3O_9\cdot 9H_2O$ required $= \dfrac{\text{MW of } (FeN_3O_9\cdot 9H_2O) \times \text{Iron required}}{\text{MW of Fe}}$

$= (404.00\times1.0751)/55.847 = 7.7777$ g

- For molar ratio Fe/Al = 0.5 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium $= (26.9815\times24.0735)/375.14 = 1.7315$ g

$= 1.7315/26.9815 = 0.0642$ mol

For Fe/Al = 0.5, 0.0642 mole of aluminium

Iron required $= 0.0642\times0.5 = 0.0321$ mol

$= 0.0321\times55.847 = 1.7920$ g

Iron 1.7920 g was prepared from $FeN_3O_9\cdot 9H_2O$ and molecular weight of Fe is 55.847 mol

$FeN_3O_9\cdot 9H_2O$ required $= \dfrac{\text{MW of } (FeN_3O_9\cdot 9H_2O) \times \text{Iron required}}{\text{MW of Fe}}$

$= (404.00\times1.7920)/55.847 = 12.9631$ g

Solvothermal method

- For molar ratio Fe/Al = 0.1 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/204.25 = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Fe/Al = 0.1, 0.0734 mole of aluminium

Iron required = 0.0734×0.1 = 0.0073 mol

= 0.0073×55.847 = 0.4101 g

Iron 0.4101 g was prepared from $(C_5H_8O_2)_3Fe$ and molecular weight of Fe is 55.847 mol

Thus, $(C_5H_8O_2)_3Fe$ required

$$= \frac{\text{MW of } ((C_5H_8O_2)_3Fe) \times \text{Iron required}}{\text{MW of Fe}}$$

= (353.18×0.4104) / 55.847 = 2.5937 g

- For molar ratio Fe/Al = 0.3 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/20254. = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Fe/Al = 0.3, 0.0734 mole of aluminium

Iron required = 0.0734×0.3 = 0.0220 mol

= 0.0220×55.847 = 1.2303 g

Iron 1.2303 g was prepared from $((C_5H_8O_2)_3Fe)$ and molecular weight of Fe is 55.847 mol

Thus, $((C_5H_8O_2)_3Fe)$ required

$$= \frac{\text{MW of } ((C_5H_8O_2)_3Fe) \times \text{Iron required}}{\text{MW of Fe}}$$

= (353.18×1.2303) /55.847 = 7.7806 g

- For molar ratio Fe/Al = 0.5 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/204.25 = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Fe/Al = 0.5, 0.0734 mole of aluminium

Iron required = 0.0734×0.5 = 0.0367 mol

= 0.0367×55.847 = 2.0507 g

Iron 2.0507 g was prepared from (($C_5H_8O_2)_3Fe$) and molecular weight of Fe is 55.847 mol

Thus, (($C_5H_8O_2)_3Fe$) required

$$= \frac{\text{MW of } ((C_5H_8O_2)_3Fe) \times \text{Iron required}}{\text{MW of Fe}}$$

= (353.18×2.0507)/55.847 = 12.9686 g

Calculation of support composition (Co-Modified Al_2O_3)

Preparation of Co-modified Al_2O_3 with various molar ratios of Co to Al (0.1, 0.3 and 0.5) by sol-gel and solvothermal methods.

Reagent: - Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$)

Molecular weight = 375.14 g/mol

- Aluminum isopropoxide ($((CH_3)_2CHO)_3Al$)

Molecular weight = 204.25 g/mol

Precursors: - Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$)

Molecular weight = 291.03 g/mol

- Cobalt (II) acetylacetonate $[CH_3COCH=C(O^-)CHO]_3Al$

Molecular weight = 257.15 g/mol

Calculation:

Sol-gel method

- For molar ratio of Co/Al = 0.1 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.9815×24.0735)/375.14 = 1.7315 g

= 1.7315/26.9815 = 0.0642 mol

For Co/Al = 0.1, 0.0642 mole of aluminium

Iron required = 0.0642×0.1 = 0.00642 mol

= 0.00642×58.933 = 0.3783 g

Cobalt 0.3783 g was prepared from ($Co(NO_3)_2\cdot 6H_2O$) and molecular weight of Co is 58.933 mol

$$(Co(NO_3)_2\cdot 6H_2O)\text{ required} = \frac{\text{MW of }(Co(NO_3)_2\cdot 6H_2O) \times \text{Cobalt required}}{\text{MW of Co}}$$

= (291.03×0.3783)/58.933 = 1.4868 g

- For molar ratio of Co/Al = 0.3 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.9815×24.0735)/375.14 = 1.7315 g

= 1.7315/26.9815 = 0.0642 mol

For Fe/Al = 0.3, 0.0642 mole of aluminium

Iron required = 0.0642×0.3 = 0.0193 mol

= 0.0193×58.933 = 1.1346 g

Cobalt 1.1346 g was prepared from ($Co(NO_3)_2\cdot 6H_2O$) and molecular weight of Co is 58.933 mol

$$(Co(NO_3)_2\cdot 6H_2O)\text{ required} = \frac{\text{MW of }(Co(NO_3)_2\cdot 6H_2O) \times \text{Cobalt required}}{\text{MW of Co}}$$

= (291.03×1.1346)/58.933 = 5.6028 g

- For molar ratio Co/Al = 0.5 is shown as follow:

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.9815×24.0735)/375.14 = 1.7315 g

= 1.7315/26.9815 = 0.0642 mol

For Co/Al = 0.5, 0.0642 mole of aluminium

Cobalt required = 0.0642×0.5 = 0.0321 mol

= 0.0321×58.933 = 1.8910 g

Cobalt 1.8910 g was prepared from ($Co(NO_3)_2 \cdot 6H_2O$) and molecular weight of Co is 58.933 mol

$$(Co(NO_3)_2 \cdot 6H_2O) \text{ required} = \frac{\text{MW of } (Co(NO_3)_2 \cdot 6H_2O) \times \text{Cobalt required}}{\text{MW of Co}}$$

= (291.03×1.8910)/58.933 = 9.3382 g

Solvothermal method

- For molar ratio Co/Al = 0.1 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/204.25 = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Co/Al = 0.1, 0.0734 mole of aluminium

Cobalt required = 0.0734×0.1 = 0.0073 mol

= 0.0073×58.933 = 0.4328 g

Cobalt 0.4328 g was prepared from $[CH_3COCH=C(O^-)CH_3]_2Co$ and molecular weight of Co is 58.933 mol

Thus, $[CH_3COCH=C(O^-)CH_3]_2Co$ required

$$= \frac{\text{MW of } [CH_3COCH=C(O^-)CH_3]_2Co \times \text{Cobalt required}}{\text{MW of Co}}$$

= (257.15×0.4328)/58.933 = 1.8885 g

- For molar ratio Co/Al = 0.3 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/204.25 = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Co/Al = 0.3, 0.0734 mole of aluminium

Cobalt required = 0.0734×0.3 = 0.0220 mol

= 0.0220×58.933 = 1.2984 g

Cobalt 1.2984 g was prepared from $[CH_3COCH{=}C(O^-)CH_3]_2Co$ and molecular weight of Co is 58.933 mol

Thus, $[CH_3COCH{=}C(O^-)CH_3]_2Co$ required

$$= \frac{\text{MW of } [CH_3COCH{=}C(O^-)CH_3]_2Co \times \text{Cobalt required}}{\text{MW of Co}}$$

= (257.15×1.2984)/58.933 = 5.6654 g

- For molar ratio Co/Al = 0.5 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.9815×15)/204.25 = 1.9815 g

= 1.9815/26.9815 = 0.0734 mol

For Co/Al = 0.5, 0.0734 mole of aluminium

Cobalt required = 0.0734×0.5 = 0.0367 mol

= 0.0367×58.933 = 2.1640 g

Cobalt 2.1640 g was prepared from $[CH_3COCH{=}C(O^-)CH_3]_2Co$ and molecular weight of Co is 58.933 mol

Thus, $[CH_3COCH{=}C(O^-)CH_3]_2Co$ required

$$= \frac{\text{MW of } [CH_3COCH{=}C(O^-)CH_3]_2Co \times \text{Cobalt required}}{\text{MW of Co}}$$

= (257.15×2.1640)/58.933 = 9.4424 g

Calculation of palladium loading

Preparations of 0.3%Pd/Fe- and Co-modified Al_2O_3 by the incipient wetness impregnation method are shown as follows:

Reagent: - Palladium (II) nitrate hexahydrate ($Pd(NO_3)_2 \cdot 6H_2O$)

Molecular weight = 338.42

- Support Fe- and Co-modified Al_2O_3 and α-Al_2O_3 (commercial)

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Palladium = 0.3 g
Iron or Cobalt = 100-0.3 = 99.7 g

For 1 g of Fe- or Co-modified Al_2O_3

Palladium required = 1×(0.3/99.7) = 0.003 g

Palladium 0.003 g was prepared from Pd $(NO_3)_2 \cdot 6H_2O$ and molecular weight of Pd is 106.42

$$\text{Pd } (NO_3)_2 \cdot 6H_2O \text{ required} = \frac{\text{MW of Pd}(NO_3)_2 \cdot 6H_2O \times \text{palladium required}}{\text{MW of Pd}}$$

$$= (338.42/106.42) \times 0.003 = 0.0095 \text{ g}$$

Since the pore volume of Al_2O_3 support is 0.4 ml/g. Thus, the total volume of impregnation solution which must be used is 0.4 ml for alumina by the requirement of incipient wetness impregnation method, the de-ionized water is added until equal pore volume for dissolve Palladium (II) nitrate hexahydrate.

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Scherrer equation

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

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \qquad \text{(B.1)}$$

where D = Crystallite size, Å
K = Crystallite-shape factor = 0.9
λ = X-ray wavelength, 1.5418 Å for CuKα
θ = Observed peak angle, degree
β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of a powder diffraction free of all broadening due to the experimental equipment. Standard α-alumina is used to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta^2 = B_M^2 - B_S^2 \qquad \text{(B.2)}$$

$$\beta = \sqrt{B_M^2 - B_S^2}$$

Where B_M = The measured peak width in radians at half peak height.
B_S = The corresponding width of a standard material.

Example: Calculation of the crystallite size of Co-modified Al_2O_3 (Co/Al=0.5) prepared by sol-gel method

The half-height width of peak = 0.40^o (from Figure B.1)

= $(2\pi \times 0.40)/360$

= 0.00692 radian

The corresponding half-height width of peak of α-alumina = 0.0041 radian

The pure width = $\sqrt{B_M^2 - B_S^2}$

= $\sqrt{0.00692^2 - 0.0041^2}$

= 0.00553 radian

β = 0.00553 radian

2θ = 36.76^o

θ = 18.38^o

λ = 1.5418 Å

The crystallite size = $\dfrac{0.9 \times 1.5418}{0.00553 \cos 18.38}$ = 264.41 Å

= 26.4 nm

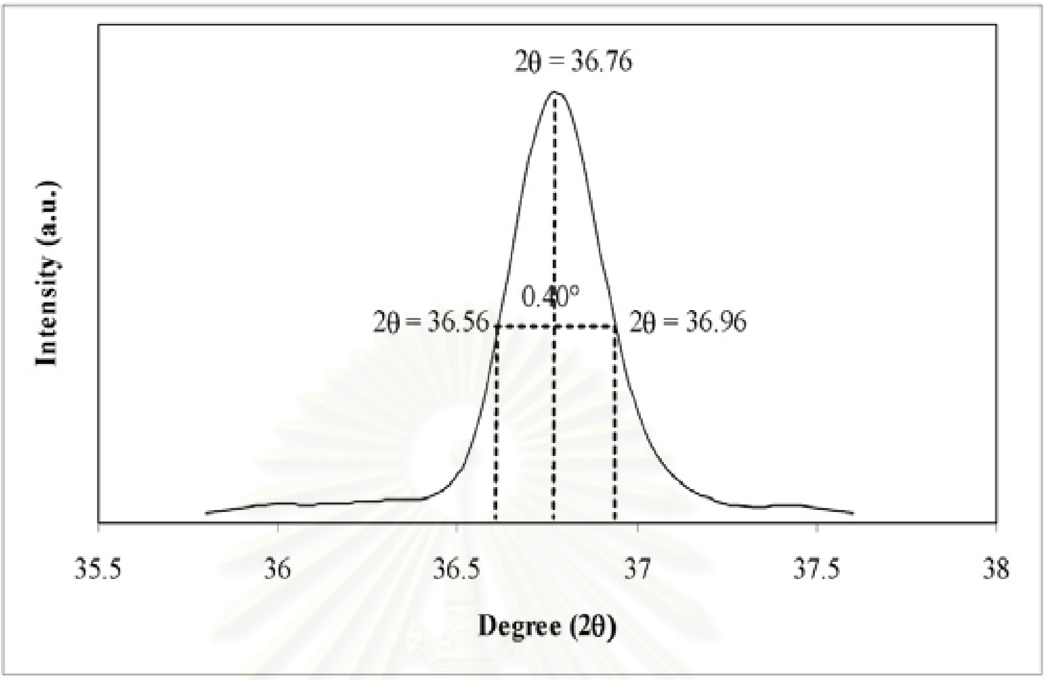

Figure B.1 The measured peak of Co-modified Al_2O_3 (Co/Al=0.5) prepared by sol-gel method to calculate the crystallite size.

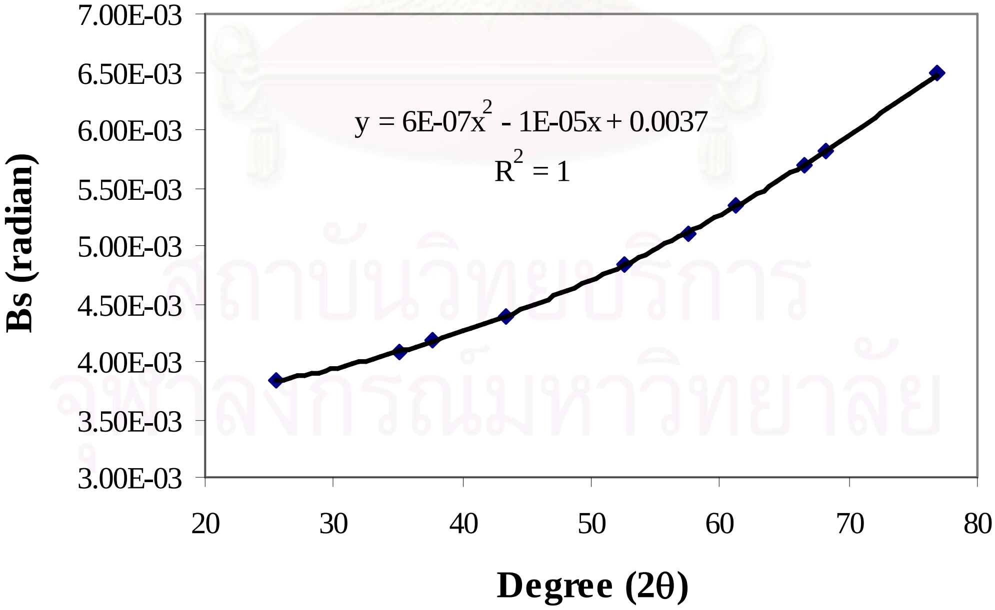

Figure B.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α-alumina as standard

APPENDIX C

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

Calculation of the metal active sites and metal dispersion of the catalyst measured by CO adsorption is as follows:

Let the weight of catalyst used = W g

Integral area of CO peak after adsorption = A unit

Integral area of 100 μl of standard CO peak = B unit

Amounts of CO adsorbed on catalyst = B-A unit

Volume of CO adsorbed on catalyst = 100×[(B-A)/B] μl

Volume of 1 mole of CO at 30°C = 24.86×10^{6} μl

Mole of CO adsorbed on catalyst = $[(B-A)/B]\times[100/24.86\times10^{6}]$ mole

Molecule of CO adsorbed on catalyst

= $[4.02\times10^{-6}]\times[6.02\times10^{23}]\times[(B-A)/B]$ molecules

Metal active sites

= $2.42\times10^{18}\times[(B-A)/B]\times[1/W]$ molecules of CO/g of catalyst

Molecules of Pd loaded

= [%wt of Pd] $\times[6.02\times10^{23}]$/ [MW of Pd] molecules/g of catalyst

Metal dispersion (%)

= 100×[molecules of Pd from CO adsorption/molecules of Pd loaded]

APPENDIX D

CALIBRATION CURVES

This appendix showed the calibration curves for calculation of composition of reactant and products in selective acetylene hydrogenation reaction. The reactant is 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd) and the desired product is ethylene. The other product is ethane.

The thermal conductivity detector, gas chromatography Shimadzu model 8A was used to analyze the concentration of H_2 by using Molecular sieve 5A column.

The carbosieve S-II column is used with a gas chromatography equipped with a flame ionization detector, Shimadzu model 9A, to analyze the concentration of products including of methane, ethane, acetylene and ethylene.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of acetylene and hydrogen are illustrated in the following figures.

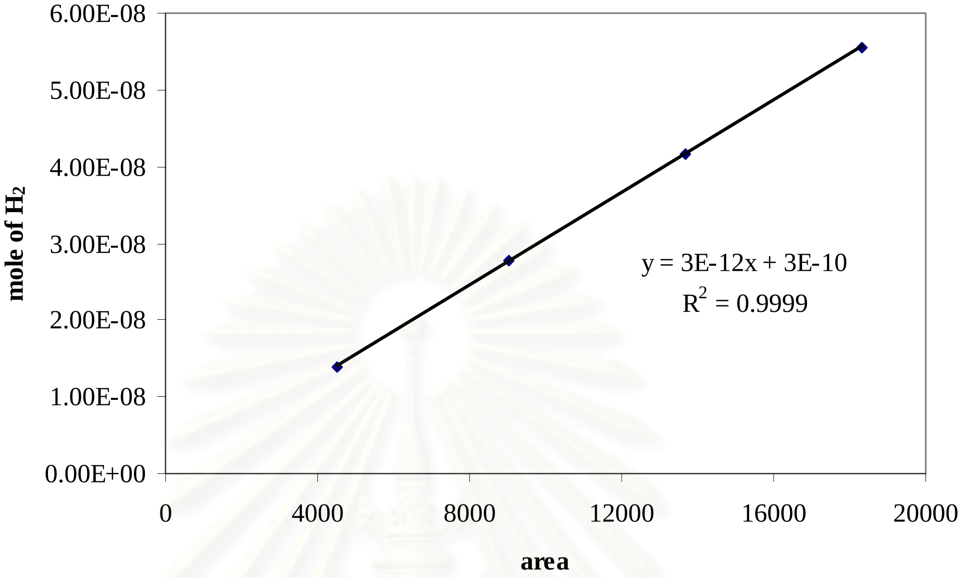

Figure D.1 The calibration curve of hydrogen from TCD of GC-8A.

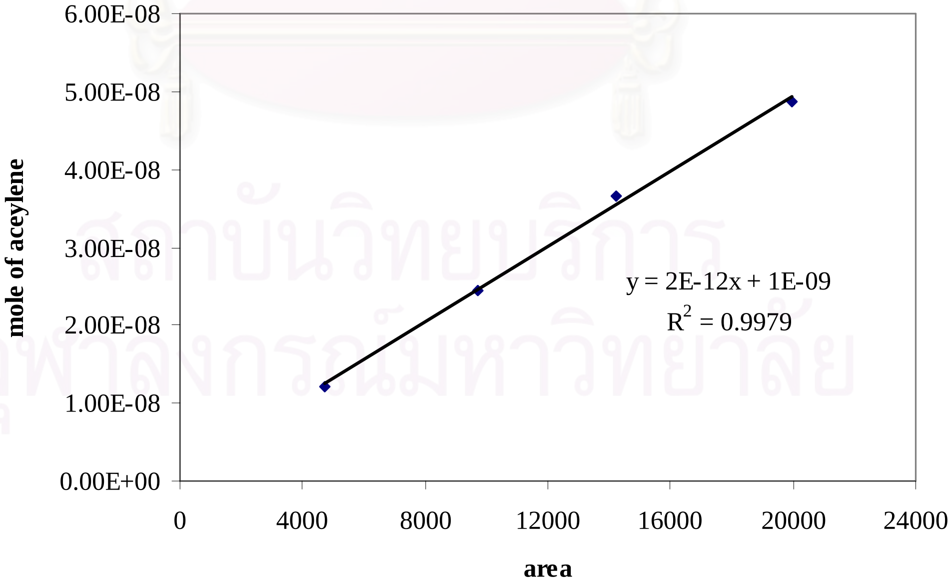

Figure D.2 The calibration curve of acetylene from FID of GC-9A.

APPENDIX E

CALCULATION OF CONVERSION AND SELECTIVITY

The catalyst performance for the selective hydrogenation of acetylene was evaluated in terms of activity for acetylene conversion and selectivity base on the following equation.

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \qquad (E.1)$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \qquad (E.2)$$

Activity of the catalyst performed in term of acetylene conversion is defined as moles of acetylene converted with respect to acetylene in feed:

$$C_2H_2 \text{ conversion (\%)} = \frac{100 \times [\text{mole of } C_2H_2 \text{ in feed} - \text{mole of } C_2H_2 \text{ in product}]}{\text{mole of } C_2H_2 \text{ in feed}} \qquad \text{(i)}$$

where mole of C_2H_2 can be measured employing the calibration curve of C_2H_2 in Figure D.2, Appendix D., i.e.,

mole of C_2H_2 = (area of C_2H_2 peak from integrator plot on GC-9A)$\times 2.0\times10^{-12}$ (ii)

Ethylene gain was calculated from moles of hydrogen and acetylene as explained in section 3.6:

$$C_2H_4 \text{ gain (\%)} = \frac{100 \text{ x } [dC_2H_2 - (dH_2 - dC_2H_2)]}{\text{mole of } C_2H_2 \text{ converted}} \qquad \text{(iii)}$$

where dC_2H_2 = mole of acetylene in feed – mole of acetylene in product (iv)

dH_2 = mole of hydrogenation in feed – mole of hydrogen in product (v)

mole of C_2H_2 is calculated by using (ii) whereas mole of H_2 can be measured employing the calibration curve of H_2 in Figure D.1, Appendix D., i.e.,

mole of H_2 = (area of H_2 peak from integrator plot on GC-8A)$\times 3.0\times10^{-12}$ (vi)

APPENDIX F

LIST OF PUBLICATION

1. Sangkhum, T., Panpranot, J., and Praserthdam, P., Effect of Fe-modified Al_2O_3 on the Properties of Pd/α-Al_2O_3 Catalysts in Selective Hydrogenation of Acetylene Reaction. Proceeding of the 17th Thailand Chemical Engineering and Applied Chemistry Conference, Chiang Mai Thailand, October, 2007.

VITA

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