ผลของอะลูมินาที่ปรับสภาพด้วยแกลเลียมและซิงค์ต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

นางสาวสุธนา จินายน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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EFFECT OF Ga- and Zn-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
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สุธนา จินายน: ผลของอะลูมินาที่ปรับสภาพด้วยแกลเลียมและซิงค์ต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน (EFFECT OF Ga- AND Zn-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION) อ.ที่ปรึกษา: ผศ.ดร. จูงใจ ปั้นประณต, 105 หน้า.

งานวิจัยนี้ ศึกษาผลของอะลูมินาที่ปรับสภาพด้วยแกลเลียมและซิงค์ที่อัตราส่วนโดยโมลของแกลเลียมต่ออะลูมิเนียมและซิงค์ต่ออะลูมิเนียมต่างๆ (0, 0.1, 0.3 และ 0.5) ซึ่งเตรียมโดยวิธีโซล-เจลและวิธีโซลโวเทอร์มอลต่อสมรรถนะของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีนเป็นเอทิลีน พบว่าสมรรถนะตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับตัวเร่งปฏิกิริยาที่ปรับสภาพด้วยแกลเลียมและซิงค์ซึ่งเตรียมโดยวิธีโซล-เจลให้ผลที่ดีกว่าตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับอะลูมินาที่ไม่ได้ปรับสภาพ ในทางกลับกัน ตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับตัวเร่งปฏิกิริยาที่ปรับสภาพด้วยแกลเลียมและซิงค์ซึ่งเตรียมโดยวิธีโซลโวเทอร์มอลให้ค่าเลือกเกิดของเอทิลีนลดลงเมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับอะลูมินาที่ไม่ได้ปรับสภาพยกเว้นตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับตัวเร่งปฏิกิริยาที่ปรับสภาพด้วยซิงค์ที่อัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมเท่ากับ 0.1 ผลวิเคราะห์จากการกระเจิงรังสีเอ็กซ์แสดงให้เห็นว่าอัตราส่วนโดยโมลของแกลเลียมต่ออะลูมิเนียมและซิงค์ต่ออะลูมิเนียมมีผลต่อโครงสร้างผลึกของตัวรองรับตัวเร่งปฏิกิริยาอะลูมินา จากการวิเคราะห์โดยการดูดซับแอมโมเนียแบบโปรแกรมอุณหภูมิแสดงให้เห็นว่าการปรับสภาพอะลูมินาด้วยแกลเลียมและซิงค์ส่งผลต่อการลดความเป็นกรดของอะลูมินาดังนั้นสมรรถนะของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาที่แตกต่างกันอาจเนื่องมาจากผลของ (1) อันตรกิริยาระหว่างตัวรองรับอะลูมินาและโลหะแพลเลเดียม (2) ขนาดอนุภาคของแพลเลเดียมและ (3) ความเป็นกรดของตัวรองรับตัวเร่งปฏิกิริยา

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต.....

สาขาวิชา.....วิศวกรรมเคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

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KEYWORDS: GALLIUM-MODIFIED ALUMINA/ ZINC-MODIFIED ALUMINA/ SOL-GEL METHOD/ SOLVOTHERMAL METHOD/ SUPPORTED PALLADIUM CATALYSTS/ SELECTIVE ACETYLENE HYDROGENATION

SUTHANA CHINAYON: EFFECT OF Ga- AND Zn-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION. THESIS ADVISOR: ASST. PROF. JOONGJAI PANPRANOT, Ph.D., 105 pp.

In this study, the effects of Ga- and Zn-modified Al_2O_3 prepared by sol-gel and solvothermal methods with various Ga/Al and Zn/Al molar ratios (0, 0.1, 0.3, and 0.5) on catalytic performance of alumina supported Pd catalysts for selective hydrogenation of acetylene were investigated. It was found that catalytic performances of the Pd catalyst supported on Ga- and Zn-modified Al_2O_3 prepared by sol-gel method were superior compared to those of Pd-supported on the unmodified Al_2O_3. Opposite to the catalysts prepared by sol-gel method, all the catalysts prepared by solvothermal method presented lower selectivity of ethylene than that of the unmodified catalyst except Pd/Zn0.1 Al_2O_3 SV that showed higher selectivity. From X-ray diffraction, it was suggested that varying Ga/Al and Zn/Al ratio directly affected the crystalline phases of alumina supports. As revealed by NH_3-TPD, modification of Al_2O_3 supports by Ga and Zn could decrease surface acidity of Al_2O_3 so that the catalysts exhibited lower amount of carbonaceous deposits during reaction and less over-hydrogenation of ethylene to ethane. Moreover, differences in the catalyst activity as well as ethylene selectivity of the various Pd/Al_2O_3 catalysts may be due to the differences in (1) the interaction between Pd and the alumina support, (2) the average Pd metal particle size, and (3) acidity of the supports.

Department ....Chemical Engineering.... Student's signature ....Suthana Chinayon.

Field of Study Chemical Engineering...... Advisor's signature ....

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CHAPTER I

INTRODUCTION

1.1 Rationale

Ethylene is the lightest olefin which does not occur in nature and is the basic chemical raw material for a large variety of industrial process, particularly for polyethylene production. Polyethylene is formed by polymerization of n molecules of the monomer ethylene. The total production of polyethylene exceeds 70 million metric tons per year (The Global Chemical Market: CMAI, 2007). In addition, polyethylene is used in large quantities of non-expensive synthetic material with modest physical properties like stiffness and excellent chemical resistance for nondurable applications which do not require properties like hardness or thermal resistance (Peacock *et al*.,2000).

Typically, ethylene stream from a naphtha cracker unit contains about 0.1-1 wt% of acetylene as an impurity that must be removed to the low ppm-range because it acts as a poison to the catalyst used in subsequent ethylene polymerization process due to acetylene adsorbs at the active sites for ethylene and blocks the polymerization. Moreover, presence of acetylene in ethylene stream leads to degrading of the selectivity at high acetylene conversion and reduces the quality of the produced polyethylene (Kim *et al*.,2004). Additionally, acetylene can form metal acetylides, which are explosive contaminants (Huang *et al*.,1994).

There have been two general methods to remove the amount of acetylene in ethylene stream. One is separation of acetylene from ethylene through adsorption using zeolite. However, this method is difficult and very costly. The other method is selective catalytic hydrogenation reaction of acetylene to ethylene which is more popular for the industrial process (Kang *et al*.,2000).

Supported palladium catalysts have proved to be the best catalysts so far for the reaction with good activity for the hydrogenation of acetylene in excess ethylene.

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). The most frequent support for palladium catalyst in selective acetylene hydrogenation is alumina.

Numerous factors have been focused on the factors which improve activity and selectivity of acetylene hydrogenation catalysts. Promotion with a second metal such as Ag (Ngamson *et al*.,2004 and Praserthdam *et al*.,2002), Au (Sárkany *et al*.,2002), Cu (Guczi *et al*.,1999), Si (Shin *et al*.,1998), K (Park *et al*.,1992) and Co (Sárkany *et al*.,1995) has been reported as an alternative way for selectivity enhancement for palladium catalysts.

However, modification of alumina support for palladium catalyst in selective acetylene hydrogenation has not been studied very often. Recently, modification of alumina by nickel has been reported (Wongwaranon *et al*.,2007). It was found that catalytic performances of the palladium catalyst supported on nickel modified alumina were superior compared to those of palladium supported on commercial alumina.

It is interesting to study the effect of gallium modified alumina on the properties of palladium catalyst because it can easily from mixed oxide Ga_2O_3-Al_2O_3 which are particularly promising as catalyst supports because of their tunable surface compositions, metal oxidation states and wall structures (amorphous or nanocrystalline) (Luo *et al*.,2006). In addition, the crystal structure of gallium oxide is similar to that of alumina (Roy *et al*.,1952). In the oxides systems, the catalytic activity strongly depend on crystalline structure. It is suppose that strong oxide-oxide interaction influences dramatically on the surface structure in the Ga_2O_3-Al_2O_3 mixed oxide. Ga^{3+} ions are known to substitute isomorphically Al^{3+} ions and under high temperature in the mixture of Ga_2O_3-Al_2O_3 oxides, the formation of solid solutions becomes favourable (Pushkar *et al*.,2000). As shown in the literature, Ga_2O_3-Al_2O_3 system exhibits high catalytic activity in the reaction of selective reduction of NO_x by hydrocarbons, including methane (Takahashi *et al*.,2006).

Moreover, the effect of zinc modified alumina is focused because it can from zinc aluminate ($ZnAl_2O_4$) spinel which is a stable material that can have beneficial effect on the catalyst properties. In Addition, the properties of metal aluminate make it an attractive material as a catalyst or support for active metal such as greater thermal stability, high resistance to acids, hydrophobicity, low surface acidity, high melting points and surface area, lower temperature sinterability, increase hardness, ductility, better diffusion, etc (Edelstein *et al*.,1996). Furthermore, zinc aluminate tend to prevent sintering of noble metals due to a strong metal-support interaction. The sintering resistance and chemical stability of catalytically active phases are a very important problem for high-temperature processes (Zawadzki *et al*.,2001).

As mentioned above, this thesis focuses on the investigation of characteristics and catalytic properties of gallium and zinc modified alumina supported palladium catalysts in selective hydrogenation of acetylene. In this research, the variables such as the molar ratio of Ga/Al and Zn/Al, as well as the preparation method between sol-gel and solvothermal method on the properties of the final Pd/Al_2O_3 catalysts were extensively studied.

1.2 Research Objective

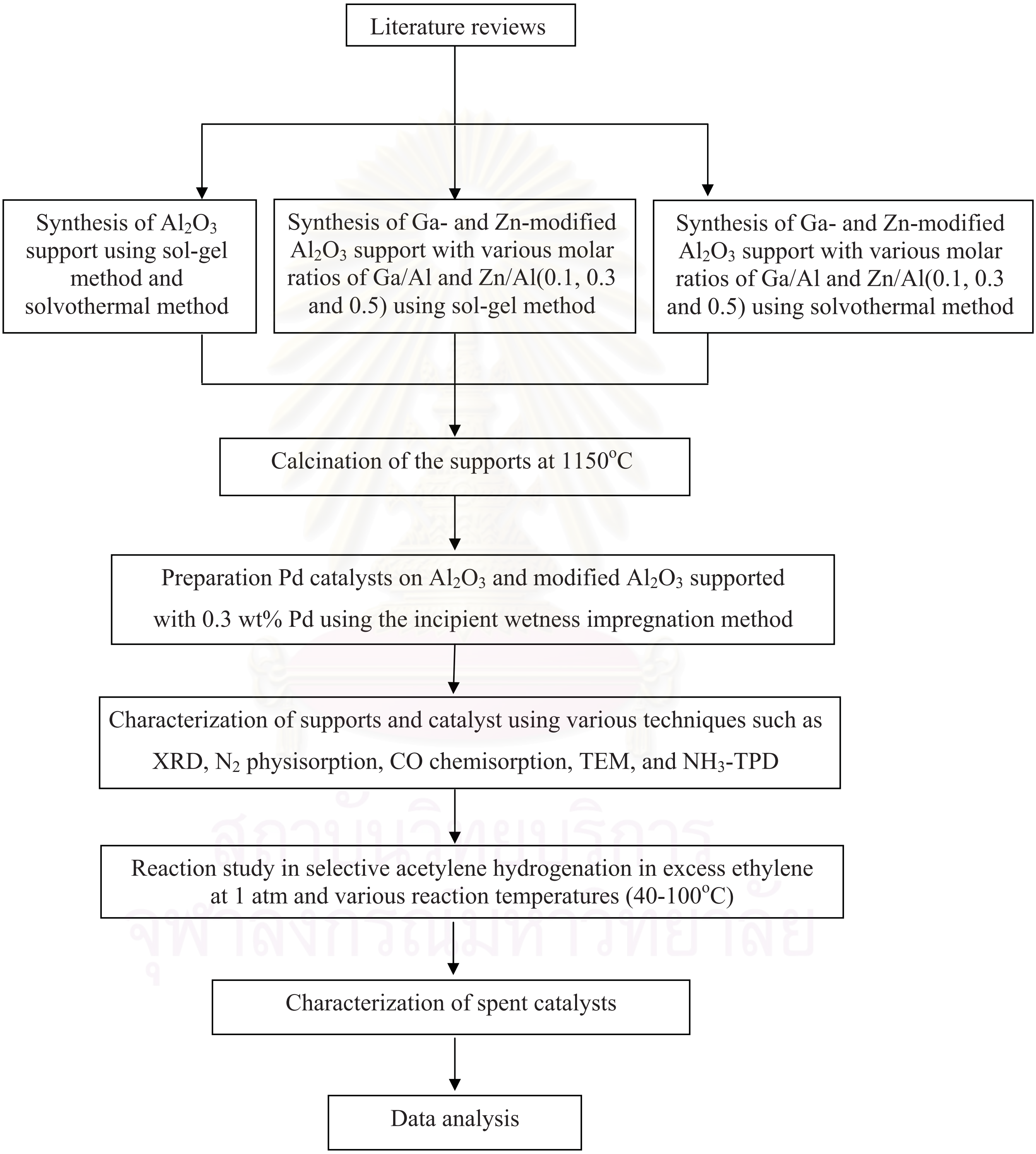
The objective of this research is to investigate the characteristics and catalytic properties of the Pd catalysts supported on Ga- and Zn-modified Al_2O_3 prepared by sol-gel and solvothermal method in selective acetylene hydrogenation in excess ethylene.

1.3 Research Scopes

1. Synthesis of Al_2O_3 supports using sol- gel method and solvothermal method.
2. Synthesis of Ga- and Zn-modified Al_2O_3 support with various molar ratios of Ga/Al and Zn/Al (0.1, 0.3, and 0.5) using sol-gel method and solvothermal method.
3. Calcination of the supports at 1150^{o}C.

4. Preparation of Pd catalysts on Al_2O_3 and modified Al_2O_3 supports with 0.3 wt% Pd using the incipient wetness impregnation method.
5. Characterization of the supports and the catalyst samples using X- ray diffraction (XRD), N_2 physisorption, CO pulse chemisorption, transmission electron microscopy (TEM), and NH_3-temperature program desorption (NH_3-TPD).
6. Study of catalyst performance in selective acetylene hydrogenation in excess ethylene at 1 atm and various reaction temperatures (40-100^{o}C).
7. Study of catalyst deactivation after performing acetylene hydrogenation using thermal gravimetric analysis (TGA).

1.4 Research Methodology



CHAPTER II

LITERATURE REVIEWS

2.1 Study on Ga_2O_3-Al_2O_3 Mixed Oxides

M. Haneda *et al.* (2001) investigated the structural effect of Ga_2O_3–Al_2O_3 prepared by sol-gel method on the catalytic performance for NO reduction by propene in the presence of oxygen. They suggested that the conversion of NO into N_2 over Ga_2O_3–Al_2O_3 increased with an increase in Ga_2O_3 loading up to around 50 wt% and decreased after that. On the other hand, The N_2 formation rate ($\mu molmin^{-1}g^{-1}$) as well as specific activity ($nmolmin^{-1}m^{-2}$) normalized by BET surface area at 673 K increased with increasing Ga_2O_3 loading and reached a maximum at around 50-60 wt%. In_2O_3 samples displayed a well-preserved amphoteric character. From XRD and EXAFS measurements, the formation of a new type solid solution expressed in terms of $[Ga_xAl_{(1-x)}]_2O_3$ ($x<1$) as the predominant compound for Ga_2O_3–Al_2O_3, where the value of "x" was changed depending upon Ga_2O_3 loading was confirmed.

A. L. Petre *et al.* (2002) investigated the effect of boria, gallia and india loadings on the surface acidities of Al_2O_3–M_2O_3 (M=B, Ga, In) systems as determined by the chemisorption of acidic and basic probe molecules (sulfur dioxide and ammonia). Each sample was prepared by a conventional impregnation method and calcined at 873 K in dry air for 3 hours. They were found that the addition of B_2O_3 on alumina increased the number of acid sites, while no real basicity could be evidenced. In the case of Al_2O_3–Ga_2O_3, they were also found that the addition of Ga_2O_3 on alumina caused a decrease in the acidity of alumina and did not affect markedly the basicity, while depositing indium oxide on alumina decreased both the acidity and basicity. Moreover, alumina-supported Ga_2O_3 and In_2O_3 samples displayed a well-preserved amphoteric character.

V. S. Escribano *et al.* (2005) prepared powders with composition $(Al_xGa_{1-x})_2O_3$ ($x = 0, 0.25, 0.50, 0.75, 1$) by coprecipitation from aluminum nitrate and gallium nitrate.

The obtained powders have been characterized after drying at 373 K and calcined at 673, 1073 and 1473 K. From the characteristic, they were found that alumina compound precipitated and dried at 373 K were essentially amorphous in all samples, whereas in the pure gallium and $Ga_{0.75}Al_{0.25}$ materials, the diaspore-type phase GaOOH was observed. In addition, the samples calcined at 673 K correspond to a poorly crystalline defective spinel-type phase γ-Al_2O_3 for the Al-rich compounds and a metastable corundum-type phase α-Ga_2O_3 for the Ga-rich ones. Moreover, calcination at 1073 K, γ-Al_2O_3 was also observed as only phase with a slightly higher degree of crystallinity than in those calcined at 673 K, while the pure Ga sample was composed of the thermodynamically stable β-Ga_2O_3 phase. The addition of aluminum (25%) resulted in the stabilization of $\alpha \rightarrow \beta$ phase transition of gallium oxide but a minority formation of the α-Ga_2O_3 was detected. Furthermore, calcination at 1474 K, pure and mixed oxides gave rise the thermodynamically stable α-Al_2O_3 and β-Ga_2O_3 phases. Finally, the specific surface areas of the pure Al and mixed oxides calcined up to 1073K were characteristic of mesoporous materials, thus present relatively high specific surface area due to the poorly crystalline defective spinel-type phase γ-Al_2O_3 presence. The addition of gallium to alumina generally resulted in a decrease of the surface area values, becoming for the pure Ga notably lower than those, according to its high crystallinity.

F. Domínguez *et al.* (2005) studied the effect of gallia (gallium oxide, Ga_2O_3) on the catalytic behavior for benzene hydrogenation reactions of platinum supported on alumina. Gallia/alumina supported 0.5% Pt catalysts with different gallia content (0, 1, 10 and 100 wt% of gallia), varying from pure alumina to pure gallia, were prepared. They were suggested that the increase of gallia content in the alumina reduced the surface area, the dispersion and the activity. Moreover, the addition of gallia to the alumina did not provide enough acidity to generate isomerization products. It was not possible to determine neither the effect on the activity of the gallium species reduced at high temperatures nor eliminate diffusional control at reaction temperature of 250°C.

T. Mathew *et al.* (2005) synthesized Ga_2O_3-Al_2O_3 mixed oxides by sol–gel method on catalytic performances for steam reforming of dimethyl ether (DME). They suggested that Ga_2O_3 significantly affected the catalytic performance with respect to the

DME conversion and H_2 yield. In addition, the catalytic activity increased with the gallium concentration in Ga_2O_3-Al_2O_3 mixed oxides. It was very interesting that without the aid of an additional transition metal component, Ga_2O_3 and Ga_2O_3-Al_2O_3 mixed oxide system exhibited good activity in the reforming reaction.

M. Takahashi *et al.* (2006) synthesized Ga_2O_3–Al_2O_3 solid solutions with aluminum isopropoxide and gallium acetylacetonate as precursor using glycothermal method. They were found that the reaction with a higher Al/(Ga+Al) charged ratio yielded the glycol derivative of boehmite as a by-product and increasing in the Al content in the solid solution increased the surface area and the thermal stability of the solid solution. The oxides system exhibited extremely high catalytic activity for selective catalytic reduction of NO_x with methane as a reducing agent. Moreover, the solid solution showed high durability under steaming conditions. In the solid solution, Ga^{3+} and Al^{3+} ions selectively occupied tetrahedral and octahedral sites of the spinel structure, respectively. From the characteristic, they concluded that tetrahedral Ga^{3+} ions were the active sites for this reaction. In the other words, tetrahedral Ga^{3+} ions with Al^{3+} ions in the next-nearest-neighbor (NNN) sites were the active sites for this reaction.

M. Takahashi *et al*. (2007) also investigated the effect of organic media used in synthesized Ga_2O_3–Al_2O_3 solid by solvothermal method on catalytic performances for selective catalytic reduction of NO_x with methane. In the solvothermal synthesized, the crystal structure of mixed oxides was controlled by the initial formation of Ga_2O_3 nuclei. When diethylenetriamine was used for prepared, the resulting catalyst extremely high activities for this reaction and had lower densities of acid sites than those prepared in other solvents.

2.2 Study on $ZnAl_2O_4$

M.A. Valenzuela *et al*. (1997) studied the effect of preparation method (sol-gel, wet mixing or coprecipitation) on the surface structure of zinc aluminate and the addition of calcium or tin in order to modify the spinel surface. It was indicated that coprecipitated and sol-gel prepared $ZnAl_2O_4$ were found to be present spinel structure. If calcium was added during synthesis, it was found to be deposited on top of the spinel surface. However, tin was added, the surface of $ZnAl_2O_4$ was reconstructed. These aluminates were impregnated with platinum and tested in the isobutane dehydrogenation.

M.A. Valenzuela *et al*. (1997) also synthesized $ZnAl_2O_4$ by hydrolyzing a mixture of aluminum alkoxide with zinc nitrate dissolved in hexylene glycol and calcining at 800°C. The results were compared with those obtained by wet mixing and coprecipitation. From the characteristic, it was suggested that the sol-gel synthesis provided a solid adequate to be used as a catalyst support because of its high surface area and monomodal pore size distribution. Furthermore, surface area and pore size distribution could be altering on purpose modifying the synthesis parameters.

M. Zawadzki *et al.* (2000) studied the hydrothermal synthesis of nanoporous zinc aluminate with high surface. Hydrothermal treatment at low temperatures was proposed for obtaining a nanocrystalline zinc aluminate spinel of interesting properties from catalytic point of view, including high specific surface area (up to 340 m^2/g), nanoporosity, and narrow pore size distribution. The precursors for hydrothermal synthesis were basic aluminium nitrate having the empirical formula $Al_2(OH)_{6-x}(NO_3)_x$ wherein x was equal or closed to 1, and hydrated zinc acetate. The proposed synthesis, in contrast to other methods, did not require a high temperature calcination to obtain the spinel phase. The properties of hydrothermally obtained zinc aluminate spinel made them an advanced material suitable for use in catalytic or high-tech ceramic applications.

J. Wrzyszcz *et al.* (2001) synthesized zinc aluminate from zinc acetate and different aluminium sources (basic aluminium nitrate or aluminium hydroxide) using hydrothermal method. They were indicated that the textural properties of the prepared $ZnAl_2O_4$ samples were different from these one of the zinc aluminate prepared by conventional way. Surface area as well as mean pore radius of hydrothermal zinc aluminate can be controlled by the use of various aluminium compounds and zinc salt for the synthesis at relatively low temperature. From XRD and TEM analysis revealed that samples were single-phase material or mixture of $ZnAl_2O_4$ with small amount of γ-Al_2O_3, with morphology of quasi-spherical shape. Applied method of synthesis, in contrast to other methods, did not require the high temperature calcination to obtain the spinel phase and provided an attractive alternative to method of zinc aluminate preparation.

M. Zawadzki *et al*. (2001) synthesized nanocrystalline and nanoporous zinc aluminate spinel $ZnAl_2O_4$ with a large specific surface area and a narrow pore size distribution from hydrothermal conditions at low temperature. $ZnAl_2O_4$ support was impregnated by incipient wetness technique to obtain 1%wtPt/$ZnAl_2O_4$ and tested in total oxidation of *iso*-butene. They suggested that platinum on zinc aluminate might strongly interact with the support in the reducing atmosphere. The origin of this interaction may be ascribed to the changes in the surface composition of the metal particle from Pt to Pt-Zn alloys. They concluded that the presence of Pt-Zn alloys on the surface of a catalyst leaded to a reversible deactivation of Pt/$ZnAl_2O_4$ catalyst and the significant thermal stability of the Pt/$ZnAl_2O_4$ system made it a promising catalyst for high temperature combustion of light hydrocarbons.

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

X. Wei *et al.* (2006) studied the synthesis and characterization of nanosized $ZnAl_2O_4$ spinel by sol-gel technique. Nanosized zinc aluminate spinel has been obtained by the thermal decomposition of Zn–Al gel prepared by sol–gel technique using oxalic acid as a chelating agent. Stirring an ethanol solution of zinc nitrate, aluminium nitrate and oxalic acid yielded a gel precursor, followed by calcination of the resulting gel at different temperatures. From characterization, XRD showed the sample obtained by heating the precursor at 700°C for 5 hours was single-phase cubic material having the spinel-type structure, which can be confirmed IR. The particle size of 15–20 nm has been measured by TEM. The specific surface area was found to be 58 $m^2 g^{-1}$.

2.3 Al_2O_3 Supported Pd Catalyst in Selective Acetylene Hydrogenation in the Past 5 Years.

P. Praserthdam *et al.* (2002) studied catalytic performance of Pd-Ag/α-Al_2O_3 for the selective hydrogenation of acetylene in the presence of excess ethylene. The catalyst activation was undertaken prior to the reaction test by the pretreatment with oxygen and/or oxygen-containing compounds, i.e. O_2, NO, N_2O, CO and CO_2. They were suggested that the pretreatment with oxygen and/or oxygen containing compounds resulted in the formation of Ag_2O, which will expose the accessible Pd sites to react with C_2H_2 and H_2 in the feed stream, thereby enhancing the catalytic activity of Pd-Ag/Al_2O_3 catalysts. In addition, the different behaviors of the pretreatment with O_2, NO_x and CO_x were examined. It was found that NO_x-treated catalysts gave higher ethylene gains because the number of sites for direct ethane formation was lessened, whereas the opposite behaviors were revealed for O_2-treated or CO_x-treated catalysts.

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.

W. J. Kim *et al.* (2003) studied the deactivation behavior of Si-modified Pd catalysts in acetylene hydrogenation. They reported that TGA and IR analyses of green oil produced on the catalyst indicated that it was produced in smaller amounts and its average chain length was shorter on a Si-modified catalyst than on an unmodified one. The above findings were due to deposition of Si species on the Pd surface; such deposits effectively block multiply-coordinated adsorption sites on the catalyst and suppress the formation of green oil on the catalyst surface, specifically on or in the vicinity of Pd. The Si species also retard the sintering of Pd crystallites during the regeneration step and allow for the slow deactivation of the catalyst during acetylene hydrogenation, after regeneration. They also suggested that the improvement in the deactivation behavior of the Si-modified catalyst was believed to arise from the geometric modification of the Pd surface with small clusters of the Si species.

M. H. Chen *et al.* (2004) prepared the novel $Pd/\alpha\text{-}Al_2O_3$ catalysts prepared by plasma method and investigated the influence of the preparation method, content of Pd active component, catalyst promoter and reaction temperature. They were found that the plasma processing exhibited the obvious advantages in catalytic performance at low temperature ($<110^{o}C$). Compared to the samples prepared by conventional impregnation, the acetylene conversion of 100% with a selectivity of 71.3% for ethylene were obtained at $50^{o}C$ over the plasma-prepared sample (0.15% Pd) on the palladium catalyst. This catalyst was stable during a test for more than 20 hours.

S. Aungkapipatanachai *et al.* (2005) studied the effect of regeneration of spent catalyst on the properties of $Pd/Ag/Al_2O_3$ catalysts in selective hydrogenation of acetylene. It was found that enhancement of the catalyst activity and ethylene selectivity during C_2H_2 hydrogenation by N_2O pretreatment found only for fresh catalysts. From bulk and surface characterization, the amounts of coke deposited on catalyst surface as well as oxygen concentration used in regeneration did not affect the number of metal active sites of catalysts recovered after regeneration. However, change in geometry/morphology of metal on surface has been found. From the XRD results, palladium particle size (ca. 6nm) was not changed after regeneration but a decrease in particle size of silver has been found since the Tamman temperature of silver was below regeneration temperature. In addition, CO-adsorption indicated that the increasing of metal active sites of Pd-Ag catalyst after N_2O pretreatment was found only in Pd-Ag catalyst prepared by sequential-impregnation. It was confirmed by XPS analysis that the existence of surface Pd-Ag alloy with Ag enrichment after reduction. Significant shift of the Ag 3d binding energy was revealed after N_2O pretreatment. Moreover, pretreatment with N_2O create a new site for ethylene adsorption and it was postulated to be the origin of enhancement in ethylene selectivity. Furthermore, significant decrease in amount of ethylene adsorbed on regenerated catalyst surface has also observed. They were also suggested that changes in the surface properties of Pd-Ag catalysts during regeneration made the catalysts not able to be activated by N_2O pretreatment.

N. Wongwaranon *et al*. (2006) studied the effect of nickel modified alumina using sol-gel and solvothermal methods with varying Ni/Al molar ratios on catalytic performances of supported Pd catalysts for selective hydrogenation of acetylene. They were suggested that catalytic performances of Pd catalyst supported on nickel modified alumina were superior compared to those of Pd- supported on commercial α-Al_2O_3. For the sol-gel-made samples, when Ni/Al ratio was 1, the highest ethylene selectivity was achieved whereas for the solvothermal-made samples, the ethylene selectivity was obtained when Ni/Al was 0.3. For the same Ni/Al (0.5), ethylene selectivity of the sol-gel-made samples was higher than that of solvothermal-made. They reported that XRD and NH_3 TPD analyses indicated that varying Ni/Al ratio directly affected the crystalline phase of alumina supports and formation of nickel-alumina compounds. Moreover, incorporation of Ni atoms into α-Al_2O_3 resulted in a significant decrease of acid sites on the alumina supports hence reducing coke deposition on the catalyst surface. They also suggested that the formation of $NiAl_2O_4$ could modify the properties of Pd surface so that high ethylene selectivities were obtained.

2.4 Comments on the Previous Studies

From the previous studies, it was found that selectivity of ethylene over palladium catalysts during selective hydrogenation of acetylene can be increased by addition of a second metal such as Ag and Si on the catalysts. The most frequent support for palladium catalyst in selective acetylene hydrogenation is alumina. However, the effect of addition of a second metal on the alumina supports has not often been studied. The investigation of Ga_2O_3–Al_2O_3 surface has been reported that addition of Ga_2O_3 on Al_2O_3 caused a decrease in the acidity of Al_2O_3 (Petre *et al.*,2002). In addition, the crystal structure of gallium oxide is similar to that of alumina (Roy *et al.*,1952). Mixed oxide Ga_2O_3–Al_2O_3 has been applied as a support of platinum catalyst for the benzene hydrogenation reactions (Domínguez *et al.*,2005), used as a catalyst in the reaction of selective reduction of NO_x by hydrocarbons (Takahashi *et al.*,2006), and steam reforming of dimethyl ether (DME). Significant improvement for catalytic performance has been obtained (Mathew *et al*.,2005). Furthermore, formation of zinc aluminate spinel showed its good properties such as high thermal stability and low surface acidity which can have beneficial effect on the support properties (Zawadzki *et al*.,2001). Therefore, it is interesting to study the properties of gallium and zinc modified alumina supported palladium catalysts in selective hydrogenation of acetylene.

CHAPTER III

THEORY

3.1 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	106.42 atomic
diameter	275.2 pm
melting point	1827 K
crystal structure	cubic closed packed
electron configuration	[Kr] $4d^{10}$
electron negativity	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 (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 (Pallassana *et al*.,2000 and 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. (Derouane *et al.*, 1984: Coq *et al.*,2001 and 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 3.1 Di-σ bonded acetylene molecule to two neighboring 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.

3.2 Aluminium Oxides or Alumina (Al_2O_3)

Aluminum oxides, which are a term of alumina compounds, had transition phase and alpha phase alumina.

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°C due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000°C when the crystallization to the thermodynamically stable α- alumina occurs (Dynys *et al.*,1982).

Several studies have been carried out on the direct phase transformation of alumina. The mechanism of direct phase transformation and the direct phase transformation from γ-alumina to α-alumina involving the conversion of the cubic close packing of oxygen ions into a stable hexagonal close packing (Simpson *et al.*,1998; Levin *et al.*,1998).

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 3.2 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

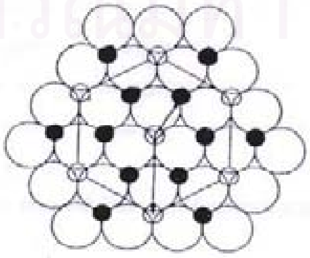


Figure 3.2 Illustration of Al and O atom packing in the basal plan.

3.3 Ga_2O_3-Al_2O_3 Mixed Oxide

Ga_2O_3-Al_2O_3 is a mixed oxide consisting of gallium oxides and aluminum oxides. Ga^{3+} ions preferentially occupy the tetrahedral sites of defect spinel structure of the Ga_2O_3-Al_2O_3 solid solution (Takahashi *et al.*,2007).

3.4 Zinc Aluminate ($ZnAl_2O_4$)

$ZnA1_2O_4$ is a binary oxide consisting of zinc oxides and aluminum oxides that crystallize in spinel structure. The unit cell of spinels is represented by formula of AB_2O_4. The Zn^{2+} ions occupy the tetrahedrally coordinated A site and $A1^{3+}$ ions occupy the octahedrally coordinated B site. The structure of zinc aluminate is shown in Figure 3.3

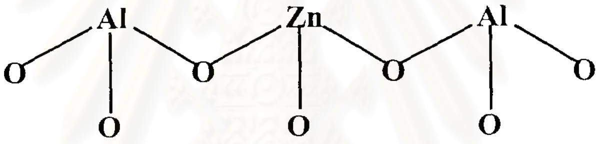


Figure 3.3 Structure of zinc aluminate

3.5 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°C yielded glycol derivative of boehmite (Inoue *et al.*,1988). In 1992, they have found that the reaction of aluminum isopropoxide (AIP) in toluene at 300°C resulted in χ-alumina (Inoue *et al.*,1992). Mekasuwandumrong *et al*. (2006) have reported that thermal decomposition of aluminum isopropoxide in mineral oil at 250-300°C over 2 hours resulted in χ-alumina powder having high thermal stability and clued be transformed directly to α-alumina at temperature higher than 1000°C.

3.6 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 controlling 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 their unavailability and/or difficulties in synthesis, alternative precursors may have to be employed. Metal salts provide a viable alterative, because of the advantage in their 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 (Aegerter *et al.*).

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 liquid, 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 (Ertl *et al.*,1997). Alternatively, gel can be produced by destabilizing the solution of preformed sols. Therefore, control of the gelation condition is important. Operations 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 (Yoldas *et al.*,1973; Yoldas *et al.*,1975), 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 hours. At 80^oC, the reaction produces boehmite [$AlO(OH)$]. If the process is starts at room temperature and continue heating to 80^oC, the product obtained is bayerite.

3.7 Acetylene Hydrogenation Reaction

Presence of acetylene in ethylene stream leads to poisoning of the polymerization catalyst because acetylene adsorbs at the active sites for ethylene and blocks the polymerization process. Therefore, the acetylene content in the ethylene feed has to be reduced to the low ppm-range. Hydrogenation of acetylene in the presence of ethylene requires high selectivity to ethylene to prevent hydrogenation of ethylene to ethane (Bos *et al.*,1993).

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^{o}C) 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: Molnár *et al.*,2001).

The mechanism of acetylene hydrogenation involves four major paths as shown in Fig. 3.4. 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).

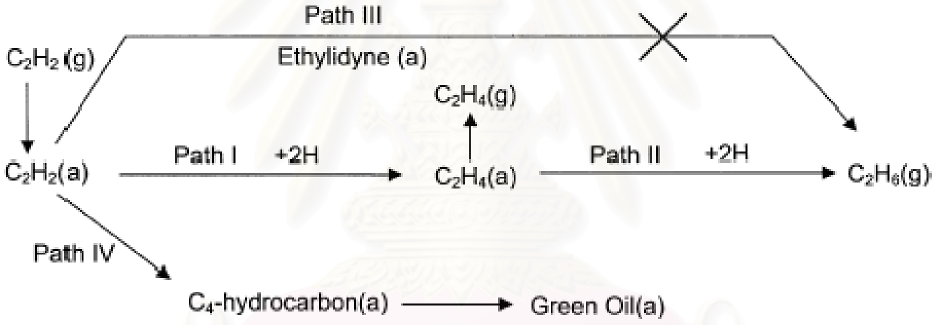


Figure 3.4 Major reaction path of acetylene hydrogenation. (Kang *et al*.,2002)

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 :

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

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

$$C_2H_4 \text{ gain (\%)} = 100 \text{ x } \frac{\text{acetylene hydrogenated to ethylene}}{\text{totally hydrogenated acetylene}} \qquad \text{(ii)}$$

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 works, 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.

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

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:

$$C_2H_4 \text{ gain (\%)} = 100 \text{ x } [2 - \frac{dH_2}{dC_2H_2}] \qquad \text{(iii)}$$

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.

CHAPTER IV

EXPERIMENTAL

4.1 Materials

The chemical used in this experiment are specified as follows in Table 4.1

Table 4.1 Chemicals used in catalyst preparation

Chemical	Supplier
Aluminium Isopropoxide 98%+	Aldrich
Gallium (III) acetylacetonate 99.99%	Aldrich
Zinc (II) acetylacetonate 95%+	Merck
Aluminum nitrate nonahydrate 98%+	Aldrich
Gallium (III) nitrate hydrate 99.9%	Aldrich
Zinc (II) nitrate hexahydrate 99.0%+	Fluka
Palladium (II) nitrate hydrate	Aldrich
Toluene 99.5%	Carlo Erba Reagenti
Methyl alcohol	Aldrich
Ethyl alcohol absolute anhydrous	Mallinckrodt Baker
Urea 99.5%	Univar

4.2 Catalyst Preparation

4.2.1 Synthesis of Al_2O_3

4.2.1.1 Sol-Gel Method

A mixture of aluminium nitrate nonahydrate and ethanol used as starting solution was prepared by dissolving 24 grams of aluminium nitrate in 50 ml of ethanol at room temperature. A homogeneous solution was obtained after mixing for approximately 15 minutes using magnetic stirrer. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80°C for 18 hours. Then, urea solution consisting 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 hours 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 and held at that temperature for 3 hours.

4.2.1.2 Solvothermal Method

Aluminum isopropoxide 15 grams was suspended in 100 ml of toluene in test tube and then set up in 300 ml autoclave. In the gap between the test tube and autoclave wall, 40 ml of toluene was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to 300°C at the rate of 2.5°C/min and held at that temperature for 2 hours. Autogenous pressure during the reaction gradually increased as temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting products were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature.

The obtained product was calcined in furnace, the product was heated at a rate of 10°C/min to 1150°C and held at that temperature for 1 hour.

4.2.2 Synthesis of Ga- and Zn-Modified Alumina

4.2.2.1 Sol-Gel Method

For gallium modified alumina, a mixture of aluminium nitrate nonahydrate 24 grams and appropriate amount of gallium (III) nitrate hydrate (Ga/Al molar ratio =0.1, 0.3 and 0.5) were dissolved in 50 ml of ethanol at room temperature. A homogeneous solution was obtained after mixing for approximately 15 minutes using magnetic stirrer. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80°C for 18 hours. 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 hours 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 and held at that temperature for 3 hours.

In the case of zinc modified alumina, the procedure was similar to the synthesis of gallium modified alumina but different precursor was used. In this case, zinc (II) nitrate hexahydrate was used instead of gallium (III) nitrate hydrate.

4.2.2.2 Solvothermal Method

For gallium modified alumina, a mixture of aluminium isopropoxide 15 grams and appropriate amount of gallium (III) acetylacetonate (Ga/Al molar ratio =0.1, 0.3 and 0.5) were suspended in 100 ml of toluene in test tube and then set up in 300 ml autoclave. In the gap between the test tube and autoclave wall, 40 ml of toluene was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to 300^{o}C at the rate of 2.5^{o}C/min and held at that temperature for 2 hours. Autogenous pressure during the reaction gradually increased as temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting products were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature.

The obtained product was calcined in furnace, the product was heated at a rate of 10^{o}C/min to 1150^{o}C and held at that temperature for 1 hours.

In the case of zinc modified alumina, the procedure was similar to the synthesis of gallium modified alumina but different precursor was used. In this case, zinc (II) acetylacetonate was used instead of gallium (III) acetylacetonate.

4.2.3 Palladium loading

0.3 wt% palladium on alumina and modified alumina supports were prepared by the incipient wetness impregnation technique detailed as follow:

1. Alumina and modified alumina supports were impregnated with a solution of palladium by the incipient wetness technique. Using the water capacity measurement obtained previously for alumina and modified alumina 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 for later use.

4.3 Catalyst Characterization

4.3.1 X-Ray Diffraction (XRD)

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer using CuK_{α} radiation with Ni filter in the 2θ range of 20-80 degrees resolution 0.04°. The crystallite size was calculated from Scherrer's equation.

4.3.2 N_2 Physisorption

Surface area measurements were carried out by low temperature nitrogen adsorption in a Micromeritic ChemiSorb 2750 system. Calculations were performed on the basis of the BET isotherm. 0.2 grams of sample was loaded into u-shape cell made from Pyrex and heated in helium to 200^oC for 1 hour in order to eliminate trace amount of water adsorbed on surface, then cooled down to room temperature. The analysis gas consist of 30% N_2 in helium was introduced to Pyrex cell. Sample adsorbed nitrogen at low temperature by dipped cell into liquid nitrogen dewar until it's surface was saturated with nitrogen and desorped nitrogen at room temperature at room temperature by moving away the dewar. The nitrogen that was desorbed from sample was measured by TCD detector.

4.3.3 Transmission Electron Microscopy (TEM)

The particle size and distribution of palladium on the catalyst supports were observed using JEOL Model JEM-2010 transmission electron microscope operated at 200 keV at the National Metal and Materials Technology Center (MTEC).

4.3.4 CO-Pulse Chemisorption

Metal active sites and metal dispersion were determined by pulsing carbon monoxide over the reduced catalyst. The amounts of CO chemisorbed on the catalysts were measured using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. The number of metal active sites was measured in the basis 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).

Approximately 0.2 grams of catalyst was filled in a Pyrex tube, incorporated in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). He was introduced into the reactor at the flow rate of 30 ml/min in order to remove remaining air. Prior to chemisorption, the samples were reduced in a H_2 flow rate at 50 ml/min with heated at an increasing rate of 10°C/min from room temperature to 500°C and held at this temperature for 2 hours after that cooled down to ambient temperature in a He flow, then CO was plused into the catalyst bed at room temperature. Carbon monoxide that was not adsorbed was measured using thermal conductivity detector. Pulsing was continued until no further carbon monoxide adsorption was observed.

4.3.5 NH_3-Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) of NH_3 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 grams 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 sample. The sample was heated from room temperature to 200^{o}C with a heating rate of 10^{o}C/min and held 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 flowed through our sample instead of ammonium and also holds for another hour. In the final step which was the desorption step; 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.

4.3.6 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using an SDT Analyzer Model Q600 from TA Instruments, USA. The TGA/DTA analysis of the spent catalysts were carried out from room temperature to 1000ºC at a heating rate of 5ºC/min in oxygen.

4.4 Reaction Study in Selective Acetylene Hydrogenation

Selective acetylene hydrogenation was performed in a pyrex tube reactor (i.d. 10.1 mm). Prior to the start of each experimental run, the catalyst was reduced in-situ in H_2 at 150^{o}C for 2 h. Then the reactor was purged with Ar and cooled down to the reaction temperature. Feed gas was composed of 1.5% C_2H_2, 1.7% H_2 and balanced C_2H_4 (TIG Co., Ltd.) with a GHSV of 16901 h^{-1}. The composition of products and feeds were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S-II columns, respectively). The temperature dependence of the catalytic performance was observed at the temperature range between 40–100^{o}C with

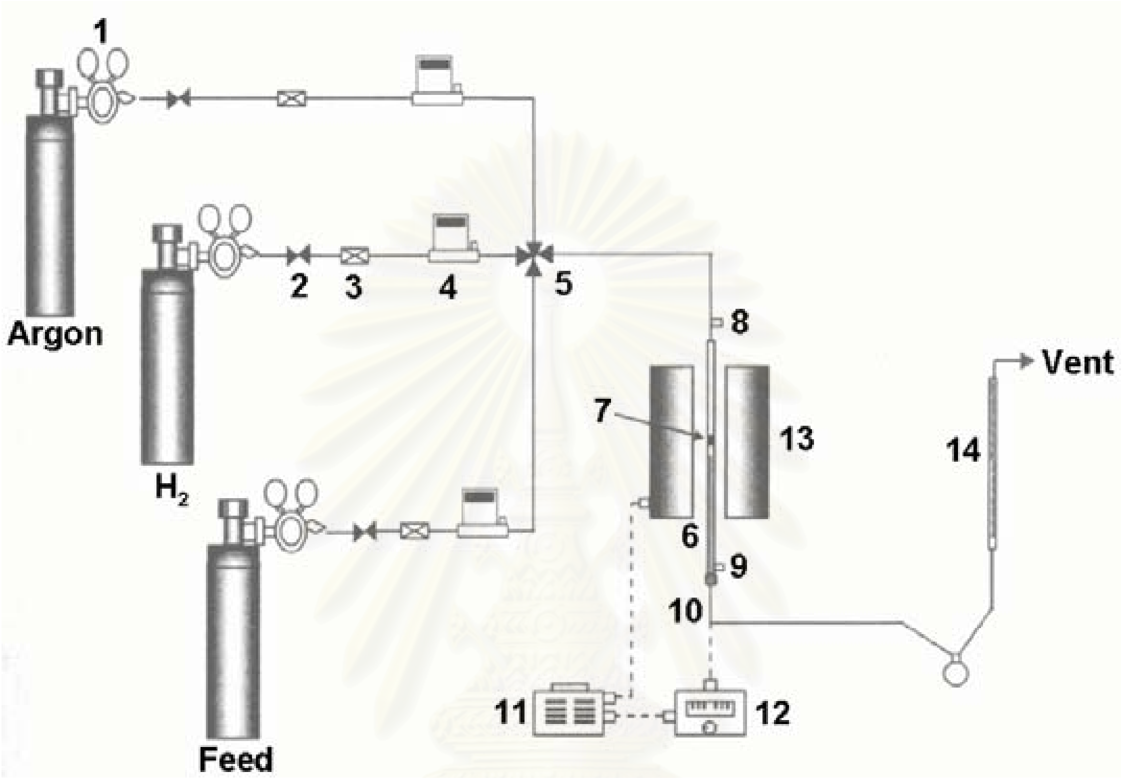
20°C increments. The operating conditions for each instrument are summarized in Table 4.2.

Table 4.2 Operating conditions of gas chromatograph

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 hight purity N2	Ultra high purity Ar
Carrier gas flow rate (ml/min)	30	30
Injector temperature (°C)	185	80
Detector temperature (°C)	185	80
Initial column temperature	100	50
Initial holding time (min)	50	-
Programmed rate (°C/min)	10	-
Final column temperature (°C)	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 grams of catalyst was packed in a pyrex 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 hours. Afterwards, argon was switched in to replace hydrogen for cooling down to the reaction temperature, 40°C and to remove the remaining hydrogen.

The reactant gases was introduced at elevated temperature from 40ºC to 100°C (40, 60, 80, and 100°C), 1 atm, and flow rate 40 of ml/min. The sampling was undertaken when the steady state of the system was reached, which was approximately within 1 hour. 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 4.1



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 4.1 A schematic of acetylene hydrogenation system

CHAPTER V

RESULTS AND DISCUSSION

The main topic of this study involves an attempt to investigate the characteristics and catalytic properties of the Pd catalysts supported on Al_2O_3 and Ga- and Zn-modified Al_2O_3 with various molar ratio of Ga/Al and Zn/Al (0.1, 0.3, and 0.5) prepared by sol-gel and solvothermal method in selective acetylene hydrogenation in excess ethylene. In this chapter, the experimental results and discussion are described. The results in this chapter are divided into three major parts. The first part describes the effect of Ga-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts. The second part describes the effect of Zn-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts. The other part describes the effect of Ga- and Zn-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalysts.

5.1 Ga-modified Al_2O_3 Supported Pd Catalyst

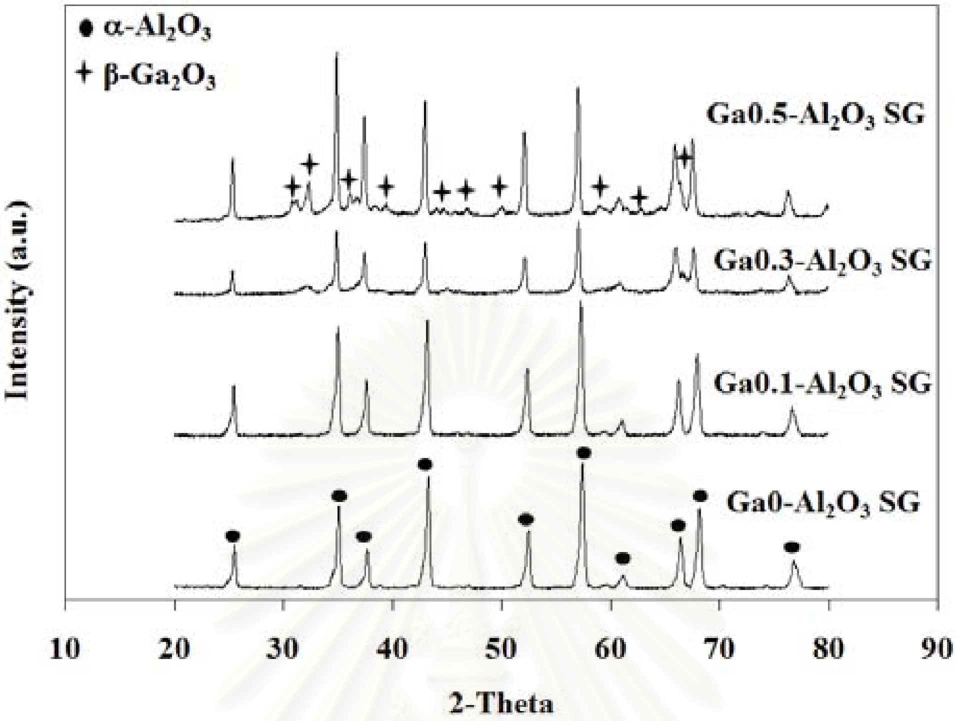
For nomenclature of the samples, the samples of Ga-modified Al_2O_3 with various molar ratios of Ga to Al 0, 0.1, 0.3, and 0.5 synthesized by sol-gel method were named as Ga0-Al_2O_3SG, Ga0.1-Al_2O_3SG, Ga0.3-Al_2O_3SG, and Ga0.5-Al_2O_3SG, respectively. The samples prepared by solvothermal method were named as Ga0-Al_2O_3SV, Ga0.1-Al_2O_3SV, Ga0.3-Al_2O_3SV, and Ga0.5-Al_2O_3SV, respectively. Pd catalysts supported on the corresponding Ga-modified Al_2O_3 were called as Pd/Ga0-Al_2O_3SG, Pd/Ga0.1-Al_2O_3SG, Pd/Ga0.3-Al_2O_3SG, Pd/Ga0.5-Al_2O_3SG, Pd/Ga0-Al_2O_3SV, Pd/Ga0.1-Al_2O_3SV, Pd/Ga0.3-Al_2O_3SV, Pd/Ga0.5-Al_2O_3SV, respectively.

5.1.1 Characterization of the Catalysts

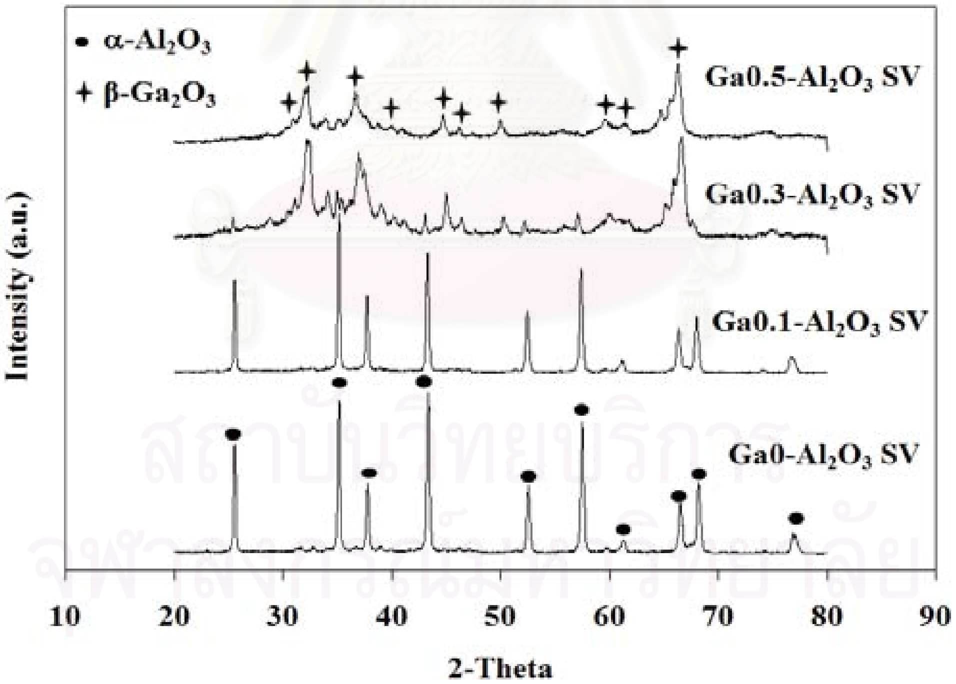
5.1.1.1 X-ray Diffraction (XRD)

X-ray diffraction is used to reveal material structures because of its qualitative and nondestructive analysis. The phase identification is carried out on the basis of data from X-ray diffraction. The XRD patterns of the Al_2O_3 and Ga-modified Al_2O_3 supports with various molar ratios of Ga to Al prepared by sol-gel and solvothermal methods are shown in Figure 5.1.

Without Ga modification (Ga0-Al_2O_3 SG and Ga0-Al_2O_3 SV), the alumina supports prepared by sol-gel or solvothermal methods exhibited the same results of XRD characteristic peaks. The characteristic peaks of α-Al_2O_3 structure were observed at 25.52°, 35.10°, 37.74°, 43.32°, 52.52°, 57.46°, 61.22°, 66.50°, 68.18°, and 77.86° 2θ (Mekasuwandumrong *et al.*,2006). In the case of Ga-modified Al_2O_3 supports, a solid solution of Ga_2O_3-Al_2O_3 systems has been reported (Petre *et al.*,2002). For Ga0.1-Al_2O_3, only the characteristic peaks of α-Al_2O_3 were detected and the characteristic peaks associated with Ga_2O_3 were not found. This was probably due to low amount of Ga present or the Ga_2O_3 was highly dispersed on the Al_2O_3 (Domínguez *et al.*,2005). For Ga0.3-Al_2O_3, both α-Al_2O_3 and β-Ga_2O_3 XRD characteristic peaks were apparent in the samples prepared by both sol-gel and solvothermal methods. As evident from XRD analysis, characteristic peaks of β-Ga_2O_3 of the sample prepared by solvothermal method were more distinct than those prepared by sol-gel method. For Ga0.5-Al_2O_3, both α-Al_2O_3 and β-Ga_2O_3 peaks were apparent in the samples prepared by sol-gel while only the characteristic peaks of β-Ga_2O_3 were found in the sample prepared by solvothermal method. Escribano and co-worker reported the reciprocal solubilities of Al_2O_3-Ga_2O_3 mixed oxide. The authors suggested that the characteristic peaks of α-Al_2O_3 were detected for Ga-content up to 25%. On the other hand, β-Ga_2O_3 was the only gallium oxide detected in samples up to a 75% Ga composition (Escribano *et al.*,2005).



(A)



(B)

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

5.1.1.2 Average Crystallite Size

The average crystallite sizes of each crystal phase were calculated from the Scherrer equation. The crystallite size of the Ga-modified Al_2O_3 supports with various molar ratios of Ga to Al prepared by sol-gel and solvothermal methods are shown in Table 5.1

Table 5.1 The average crystallite sizes of Ga-modified Al_2O_3 supports with various molar ratios of Ga to Al synthesized by sol-gel and solvothermal methods.

Sample	Crystallite size (nm)
Ga0-Al_2O_3 SG	31.0^{Al}
Ga0.1-Al_2O_3 SG	29.4^{Al}
Ga0.3-Al_2O_3 SG	33.5^{Al}
Ga0.5-Al_2O_3 SG	41.6^{Al}
Ga0-Al_2O_3 SV	69.5^{Al}
Ga0.1-Al_2O_3 SV	94.5^{Al}
Ga0.3-Al_2O_3 SV	19.3^{Ga}
Ga0.5-Al_2O_3 SV	18.6^{Ga}

Al : α-Al_2O_3
Ga : β-Ga_2O_3

The average crystallite sizes of the α-Al_2O_3 prepared by sol-gel and solvothermal method were 31 and 69.5 nm, respectively. For the supports prepared by sol-gel method, the average crystallite sizes of the supports were presented in term of α-Al_2O_3. The average crystallite sizes of the supports were ranged from 29.4-41.6 nm. In case of the supports prepared by solvothermal method, both Ga0-Al_2O_3 SV and Ga0.1-Al_2O_3 SV showed the average crystallite sizes of the supports in term of α-Al_2O_3 while the average crystallite sizes of supports in term of β-Ga_2O_3 presented in Ga0.3-Al_2O_3 SV and Ga0.5-Al_2O_3 SV. It was obvious that the average crystallite sizes of α-Al_2O_3 prepared by sol-gel method were smaller than those of α-Al_2O_3 prepared by solvothermal. Moreover, the average crystallite sizes of β-Ga_2O_3 were smaller than α-Al_2O_3.

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 Al_2O_3 and Ga-modified Al_2O_3 supports are shown in Table 5.2.

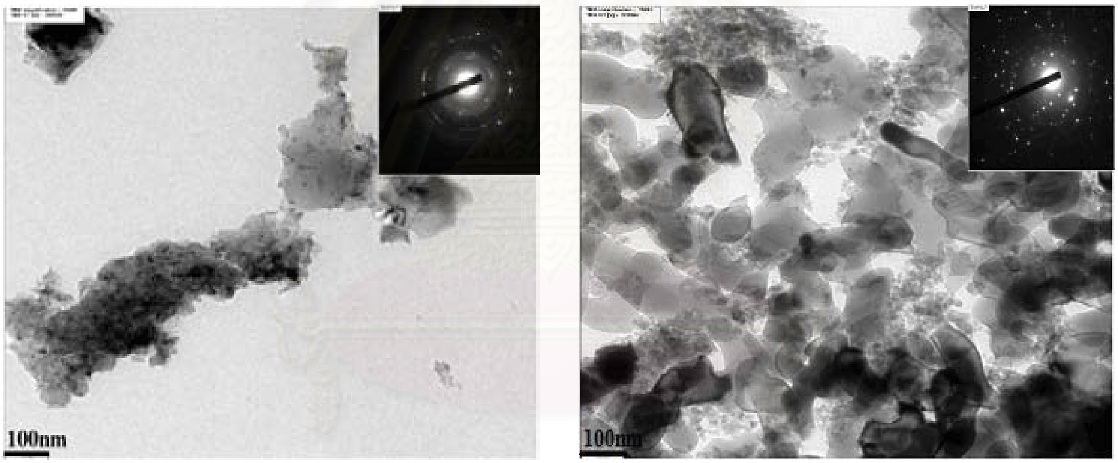
Table 5.2 BET surface areas of of Ga-modified Al_2O_3 supports with various molar ratios of Ga to Al synthesized by sol-gel and solvothermal methods.

Sample	BET Surface areas (m^2/g)
Ga0-Al_2O_3 SG	1.6
Ga0.1-Al_2O_3 SG	2.3
Ga0.3-Al_2O_3 SG	1.5
Ga0.5-Al_2O_3 SG	1.0
Ga0-Al_2O_3 SV	14.9
Ga0.1-Al_2O_3 SV	4.6
Ga0.3-Al_2O_3 SV	11.7
Ga0.5-Al_2O_3 SV	9.6

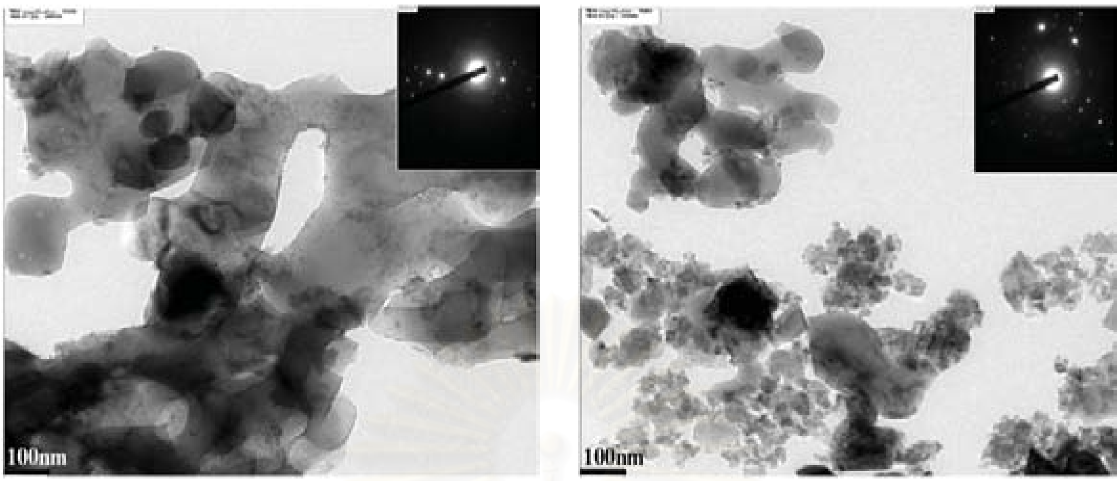
The surface areas of the supports prepared by sol-gel method were ranged from 1.0-2.3 m^2/g while those prepared by solvothermal were ranged from 4.6-14.9 m^2/g. Corresponding to the experiment, the modification of Ga on Al_2O_3 did not affect significantly the surface areas of the resulting samples. Moreover, the surface areas were quite low probably due to high agglomeration of these particles during calcinations at high temperature.

5.1.1.4 Transmission Electron Microscopy (TEM)

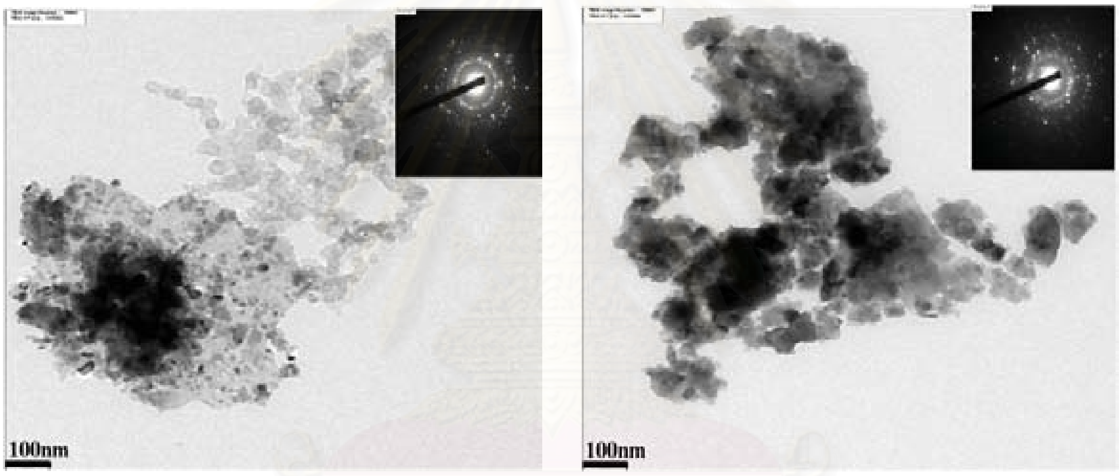
TEM is a useful tool for determining particle size and particle size distribution of supported metals. TEM micrographs with SAED patterns of Pd catalyst supported on Ga-modified Al_2O_3 with various molar ratios of Ga to Al prepared by sol-gel and solvothermal methods are shown in Figure 5.2.



(A) Pd/Ga0-Al_2O_3 SG (B) Pd/Ga0-Al_2O_3 SV



(C) Pd/Ga0.1-Al_2O_3 SG (D) Pd/Ga0.1-Al_2O_3 SV



(E) Pd/Ga0.5-Al_2O_3SG (F) Pd/Ga0.5-Al_2O_3SV

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

It can be seen that the sol-gel made catalysts (Pd/Ga0-Al_2O_3 SG and Pd/Ga0.1-Al_2O_3 SG) consisted of agglomerated particles with primarily irregular shape structure (average particle size around 0.5-1 μm) whereas spherical shape particles were observed for Pd/Ga0.5-Al_2O_3SG. In the case of solvothermal method, agglomeration of finger-like particles were observed for Pd/Ga0-Al_2O_3 SV and Pd/Ga0.1-Al_2O_3 SV whereas Pd/Ga0.5-Al_2O_3 SV presented spherical shape particles. The finger-like α-Al_2O_3 particles were normally obtained by calcination of the solvothermal made α-Al_2O_3 powders at high temperature (Mekasuwandumrong *et al*.,2003, 2006). For Pd/Ga-modified Al_2O_3, the corresponding selected area diffraction patterns showed structure that could be indexed for β-Ga_2O_3 (Ohira *et al*.,2005). Based on TEM analysis, palladium particles/clusters with average particle size ca. 5-10 nm were found to be deposited on both of the alumina supports.

5.1.1.5 Metal Active Sites

The metal active sites, the Pd dispersion, and the average Pd metal particle size from CO chemisorption experimental are summarized in Table 5.3. The technique is based on the assumption that only one CO molecule adsorbed on one metal active site (Anderson *et* al.,1985). It is also known that CO did not chemisorb on Al_2O_3 support (Soma-Noto *et al*.,1974, Cormack *et al*.,1975, and Heinrichs *et al*.,1997). The details for calculation of the metal active sites, the Pd dispersion, and the average Pd metal particle size are given in Appendix C.

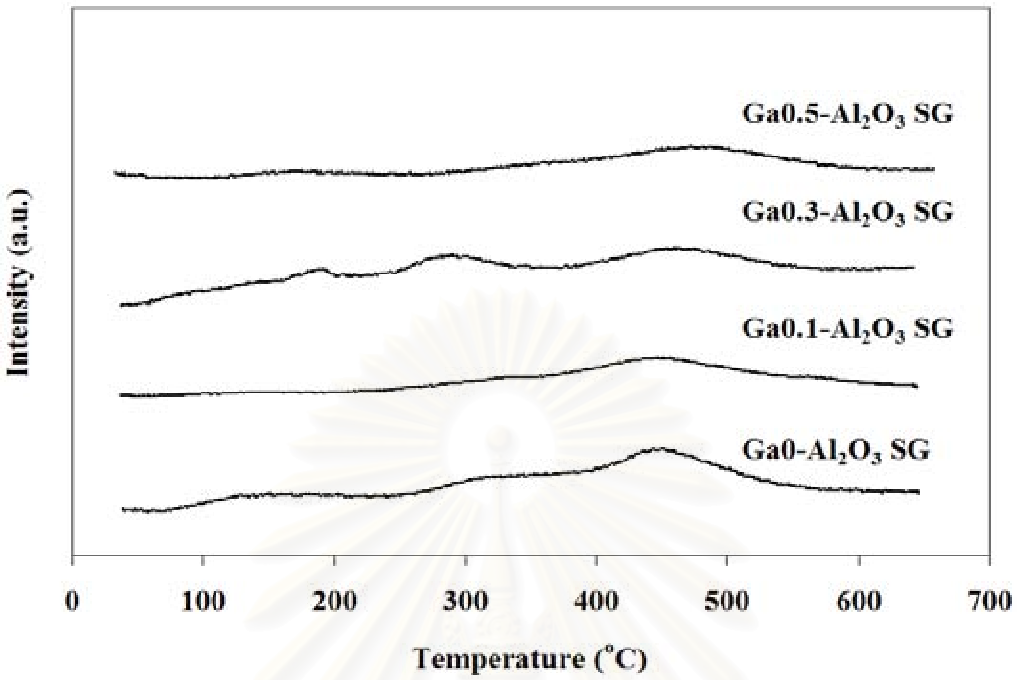
Without Ga addition on the Al_2O_3 supports, Pd/Ga0-Al_2O_3 SG and Pd/Ga0-Al_2O_3 SV possessed the amounts of Pd active sites 11.3 x 10^{17} and 32.8 x 10^{17} sites/g cat., respectively. The Pd active sites significantly decreased when the catalysts were supported on Ga-modified Al_2O_3 corresponding to the decreasing in Pd metal dispersion and increasing in the average Pd metal particle sizes. Comparing the samples prepared by different techniques, the catalysts prepared by sol-gel method showed lower amount of Pd active sites and Pd dispersion than the catalysts prepared by solvothermal method due probably to more agglomeration of the Al_2O_3 supports as noticed from TEM measurements. The average Pd metal particle sizes for the catalysts prepared by sol-gel were ranged from 13-36 nm while the catalysts prepared by solvothermal were ranged from 5-15 nm.

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

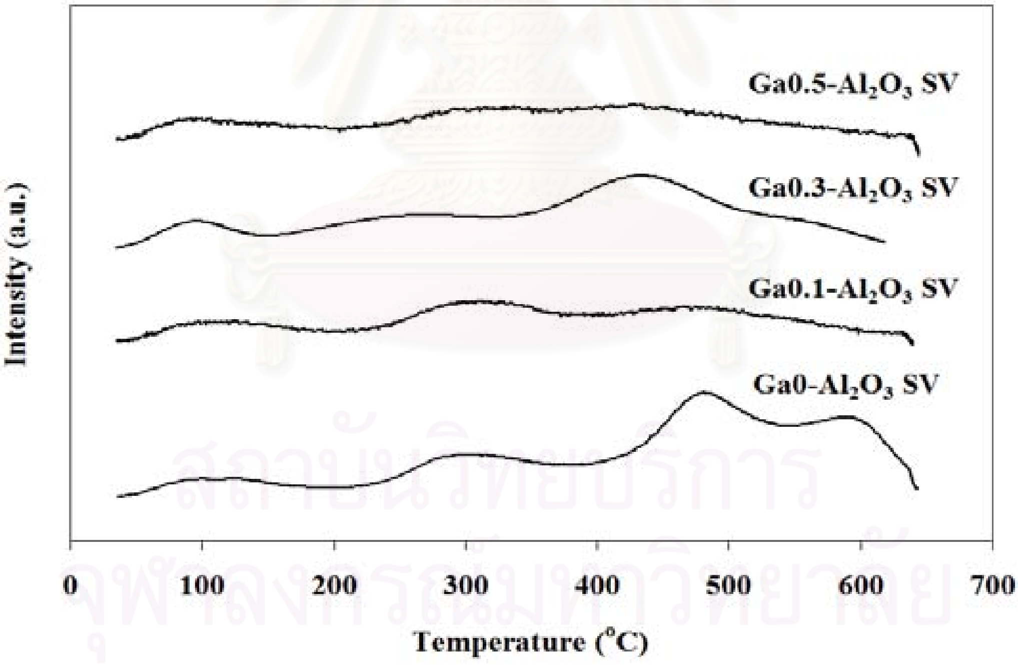
Sample	CO chemisorption $\times 10^{17}$ (molecule CO/g cat.)	Pd dispersion (%)	d_P Pd^0 (nm)
Pd/Ga0-Al_2O_3 SG	11.3	8.8	13
Pd/Ga0.1-Al_2O_3 SG	10.8	6.8	17
Pd/Ga0.3-Al_2O_3 SG	5.3	5.0	22
Pd/Ga0.5-Al_2O_3 SG	4.3	3.1	36
Pd/Ga0-Al_2O_3 SV	32.8	20.7	5
Pd/Ga0.1-Al_2O_3 SV	20.1	16.1	7
Pd/Ga0.3-Al_2O_3 SV	12.9	10.8	10
Pd/Ga0.5-Al_2O_3 SV	8.5	7.6	15

5.1.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

NH_3 temperature program desorption was a commonly used technique for the titration of surface acid sites. The strength of an acid site could be related to the corresponding desorption temperature, while the total amount of ammonia desorption after saturation coverage permits quantification of the number of acid sites at the surface (Kung *et al.*,1985). The temperature-programmed desorption profiles for the Al_2O_3 and Ga-modified Al_2O_3 supports are shown in Figure 5.3.



(A)



(B)

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

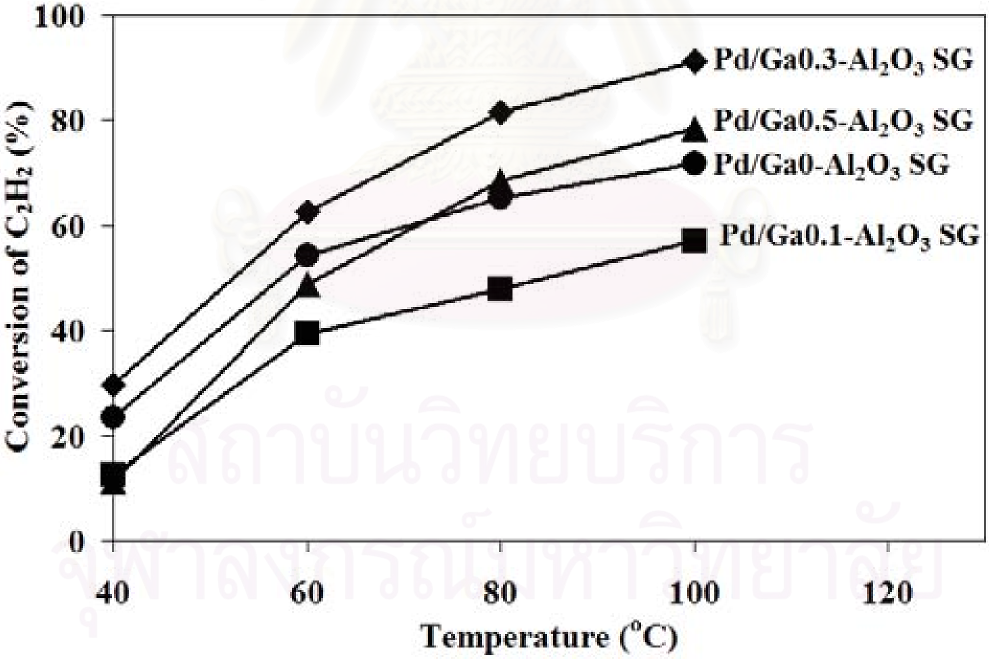
The desorption peak areas of all the supports showed relatively lower acidity than other 'transition' alumina due to the dramatically decrease of the surface area after calcination at high temperature. However, desorption peaks could still be observed for all samples. From experimental, It was found that the desoprtion peak areas of the Al_2O_3 samples prepared by sol-gel method were lower than that prepared by solvothermal method. Moreover, regardless of the preparation method used, the desorption peak areas of Ga-modified Al_2O_3 decreased. It was suggested that the modification of Ga on Al_2O_3 led to a decrease in the acidity of Al_2O_3. The results were in good agreement with those reported by Petre *et al.* They have shown that depositing Ga_2O_3 on acidic supports led to a decrease in the acidic character of the resulting catalysts. They also reported that the addition of Ga on Al_2O_3 led to a decrease in the acidity of Al_2O_3 (Petre *et al*.,2001, 2002).

5.1.2 Catalytic Performance of the Catalysts

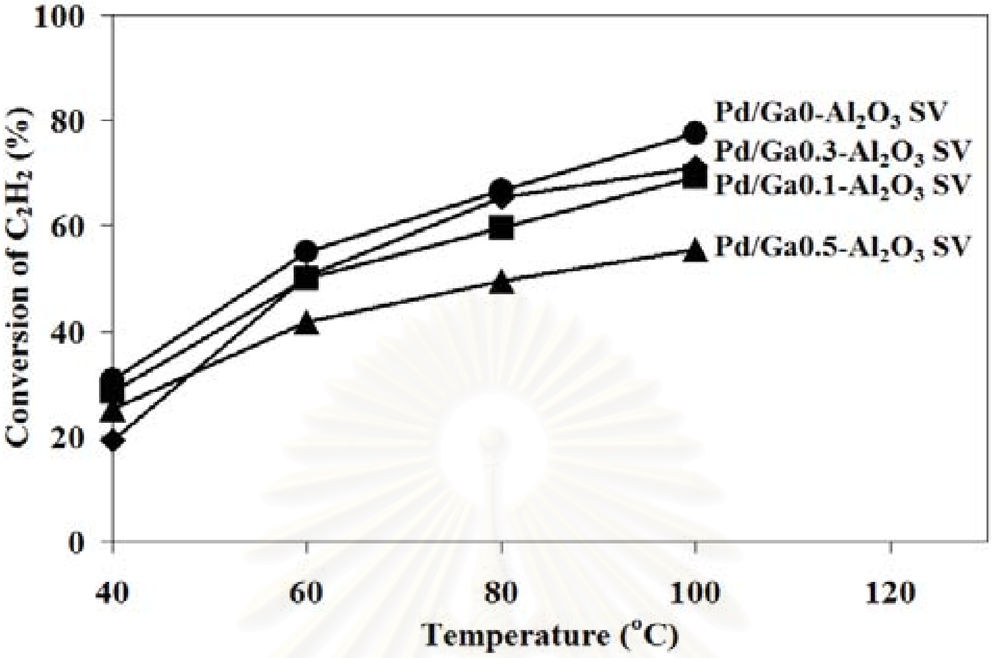
The performance of a catalyst for the selective hydrogenation of acetylene is evaluated in terms of acetylene conversion and selectivity towards ethylene. Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in the feed. Selectivity is the ratio of the amount of acetylene 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.

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. 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. As previously described, the reaction during 2-60 min on stream is in the constant rate period, consequently, the performance of the catalyst as a function of reaction temperature is evaluated from the data taken in this period.

The catalytic properties of Pd/Ga-modified Al_2O_3 catalysts were evaluated in the selective hydrogenation of acetylene using a fixed bed flow reactor with a GHSV of 16901 h^{-1}. For study of temperature dependence of the catalysts on acetylene conversion and selectivity toward ethylene, the temperature range between 40-100^oC and feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.) were used.



(A)

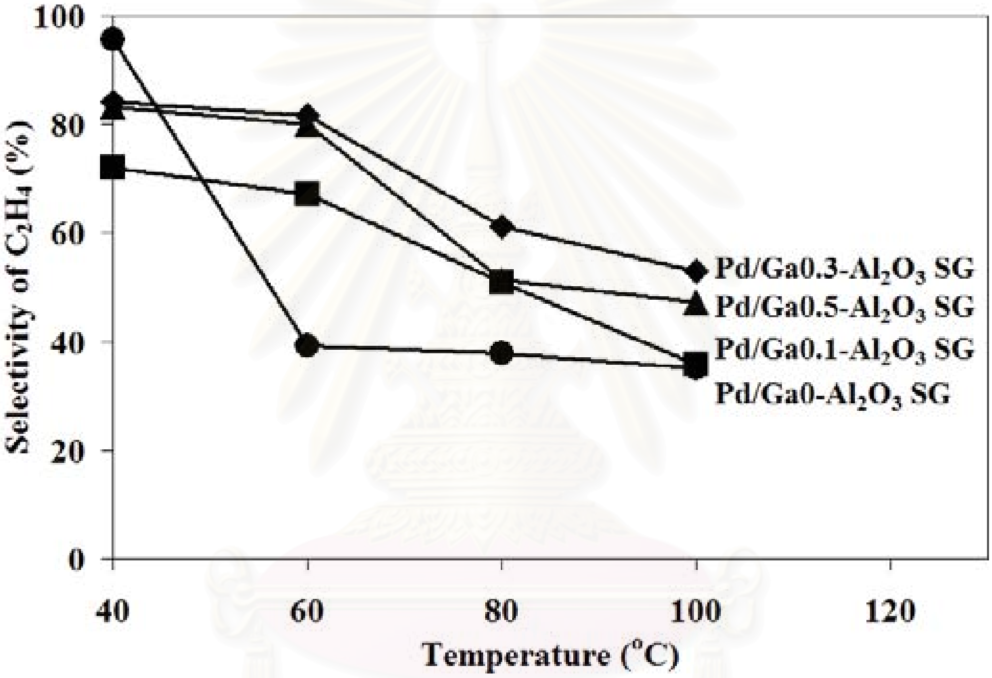


(B)

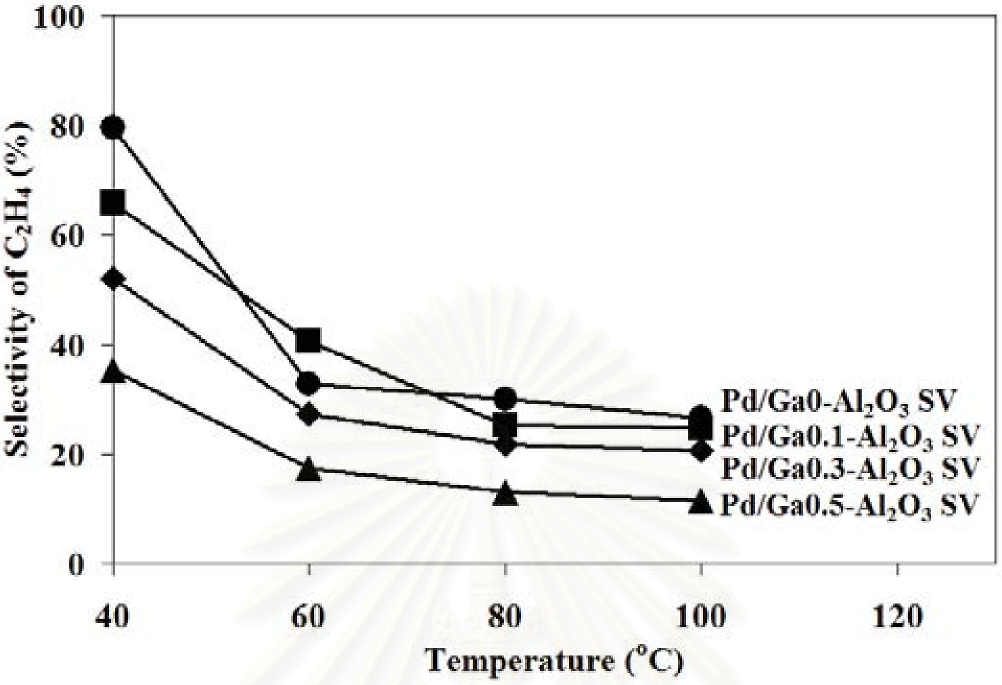
Figure 5.4 Temperature dependence of the catalytic performance (% conversion of C_2H_2) of Pd/Ga-modified Al_2O_3 catalysts with various molar ratios of Ga to Al synthesized by (A) sol-gel and (B) solvothermal methods.

As shown in Figure 5.4., activity of all the catalysts directly increased with rising temperature as the kinetic energy of the system increased with increasing temperature. In case of the catalysts prepared by sol-gel method, all the modified catalysts exhibited higher activity than that of the unmodified catalyst except the Pd/Ga0.1-Al_2O_3 SG that showed the lowest activity while Pd/Ga0.3-Al_2O_3 SG showed the highest activity. Opposite to the catalysts prepared by sol-gel method, all the Ga modified catalysts prepared by solvothermal method showed lower activity than that of the unmodified catalyst. The selectivity of ethylene (Figure 5.5) observed over all the samples was declined when the temperature was increased due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction (Ngamsom *et al.*,2004). For the catalysts prepared by sol-gel method, with respect to the unmodified catalyst, the catalysts modified by Ga showed higher selectivity of ethylene. It was found that Pd/Ga0.3-Al_2O_3 SG exhibited higher selectivity of ethylene than any other catalysts.

Opposite to the catalysts prepared by sol-gel method, all the Ga modified catalysts prepared by solvothermal method presented lower selectivity of ethylene than that of the unmodified catalyst. Overall, it was clearly seen that the catalysts prepared by sol-gel method showed better catalytic properties than the catalysts prepared by solvothermal method. Ethylene selectivity was found to improved in the order: Pd/Ga0.3-Al_2O_3 SG > Pd/Ga0.5-Al_2O_3 SG > Pd/Ga0.1-Al_2O_3 SG > Pd/Ga0-Al_2O_3 SG > Pd/Ga0-Al_2O_3 SV > Pd/Ga0.1-Al_2O_3 SV > Pd/Ga0.3-Al_2O_3 SV > Pd/Ga0.5-Al_2O_3 SV.



(A)

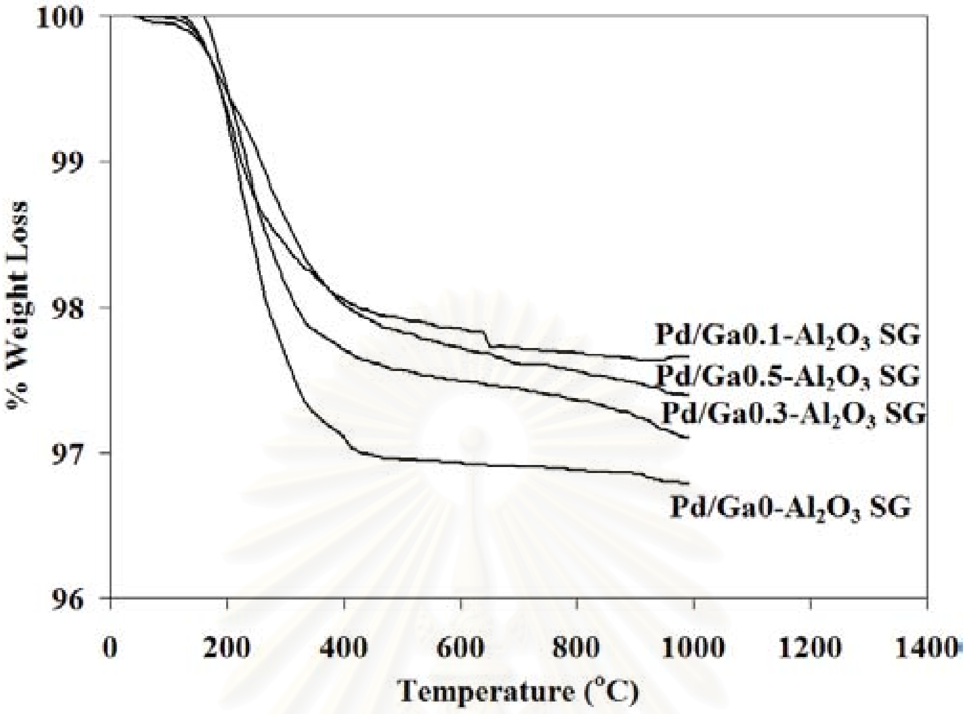


(B)

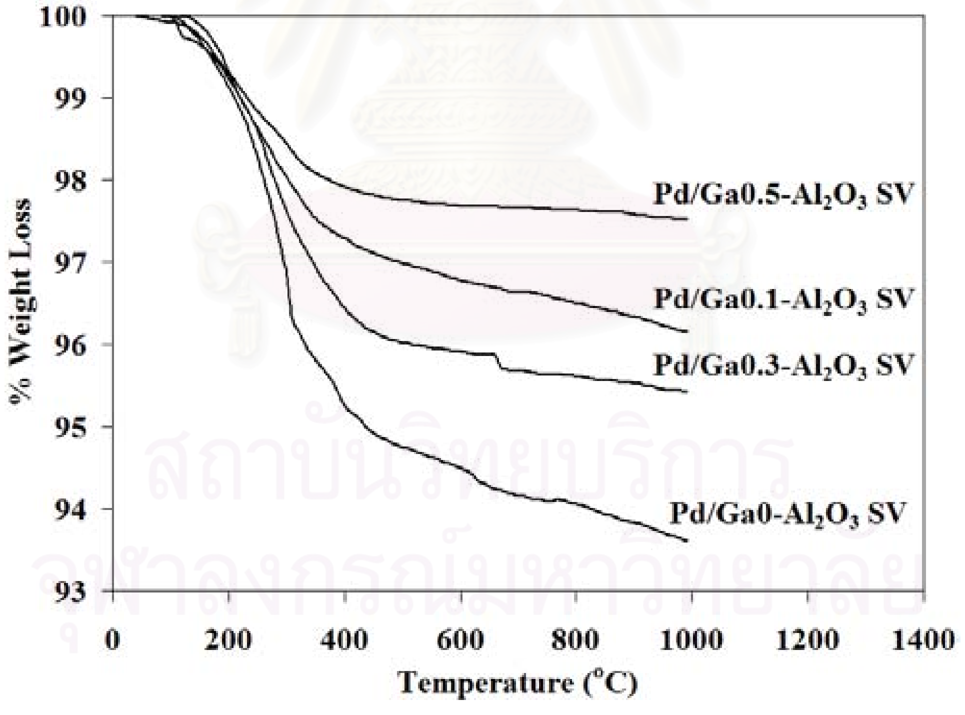
Figure 5.5 Temperature dependence of the catalytic performance (% selectivity of C_2H_4) of Pd/Ga-modified Al_2O_3 catalysts with various molar ratios of Ga to Al synthesized by (A) sol-gel and (B) solvothermal methods.

5.1.3 Characterization of the Spent Catalysts

After reaction, some amounts of carbonaceous may deposit on the catalyst surface and cover the active metal resulting in loss of activity and selectivity. The amounts of coke deposited on the samples in selective hydrogenation of acetylene were measured by thermal gravimetric analysis and the results are shown in Figure 5.6 and 5.7.



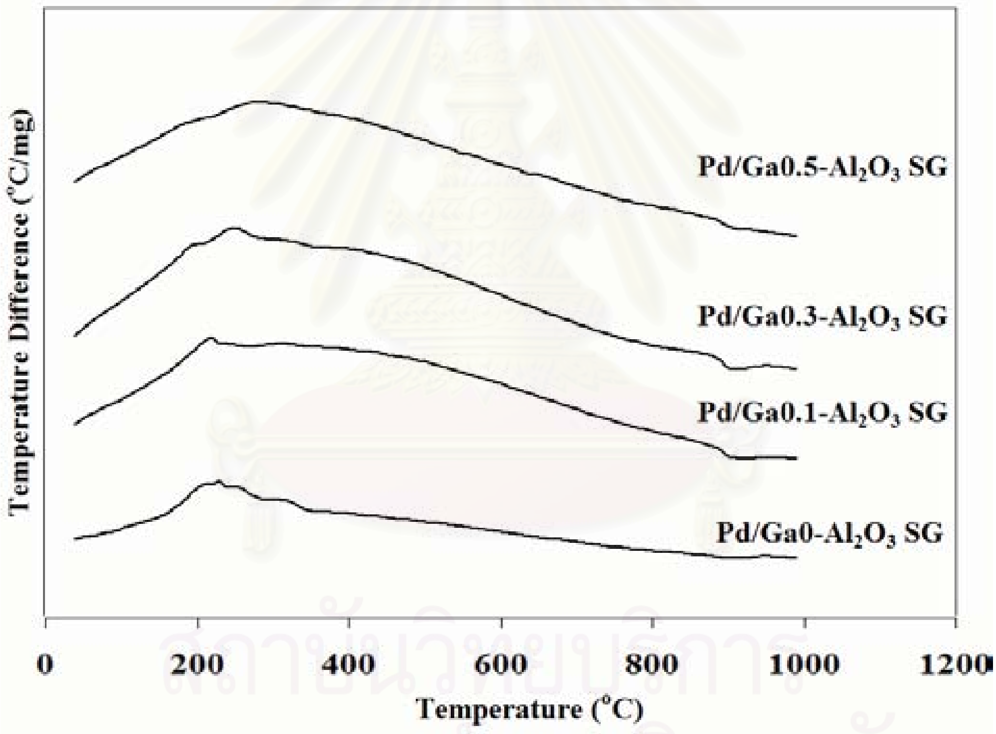
(A)



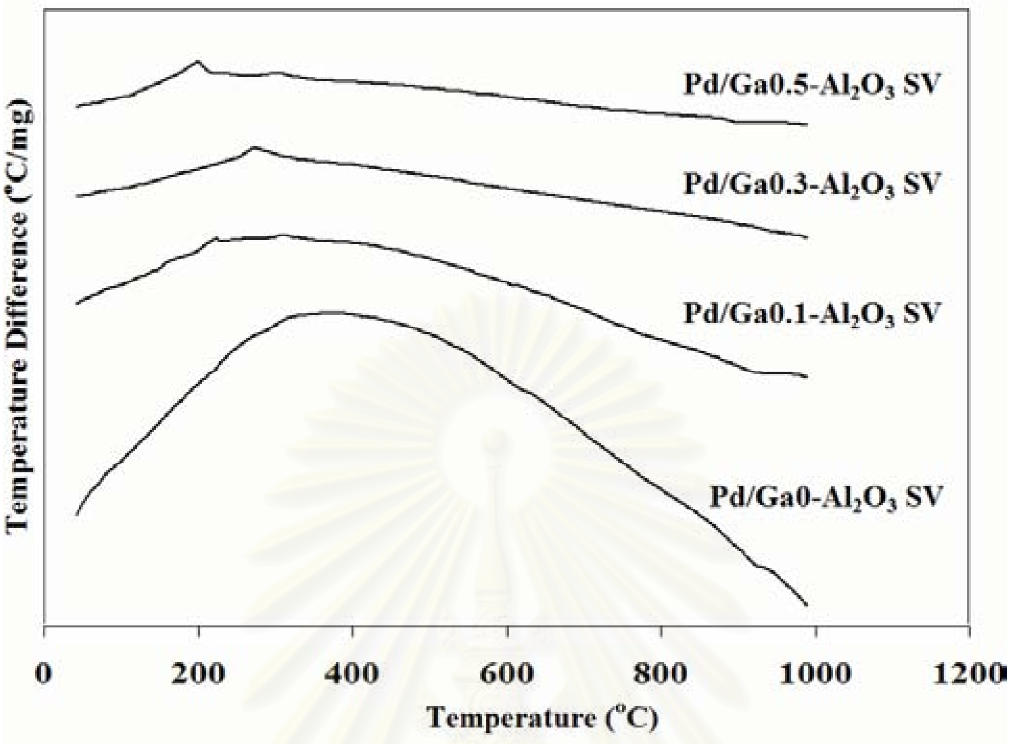
(B)

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

From Figure 5.6, the weight loss observed in the TGA profiles was due to oxidation of the carbonaceous deposited on the surface of used catalysts (Soares *et al.,* 1997). As shown by the exothermic peaks in Figure 5.7, the type of coke species occurred during reaction was probably "soft coke" since it could be removed from the used catalysts by oxidation at a relative lower temperature (~350°C) as suggested by Xiangjing *et al.* (Xiangjing *et al.,*2006). Based on the TGA results, the amount of coke deposits on the catalysts prepared by sol-gel method were lower than those prepared by solvothermal method while Pd/Ga0.1-Al_2O_3 SG, Pd/Ga0.3-Al_2O_3 SG, and Pd/Ga0.5-Al_2O_3 SG showed no significantly differences values (2.34-2.90%wt). The results were in good agreement with acidity of the Al_2O_3 supports measured from NH_3 TPD technique.



(A)



(B)

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

5.2 Zn-modified Al_2O_3 Supported Pd Catalyst

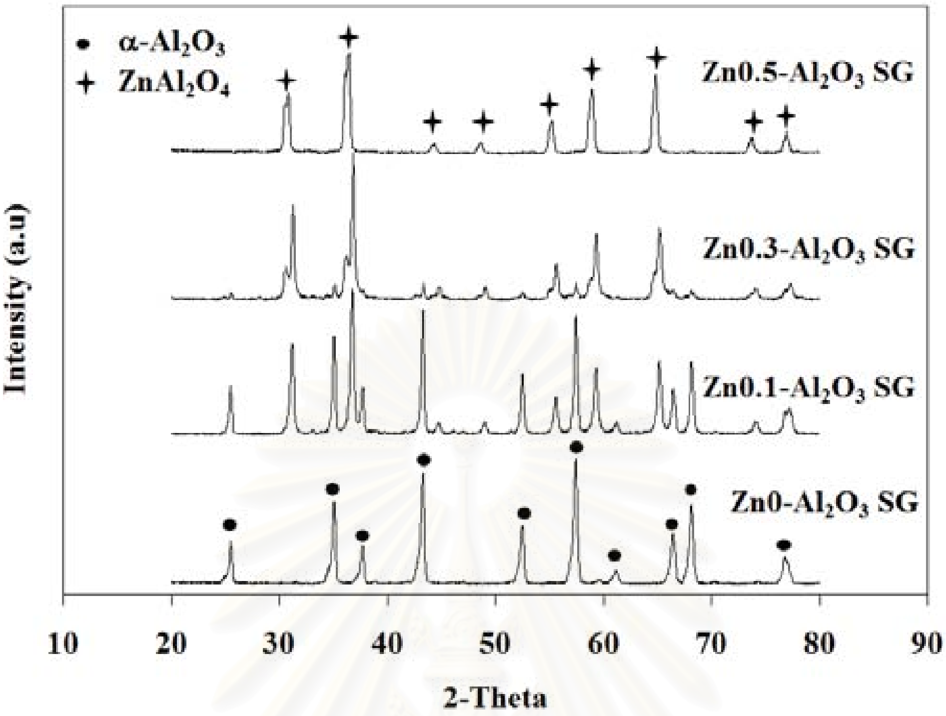
For nomenclature of the samples, the samples of Zn-modified Al_2O_3 with various molar ratios of Zn to Al 0, 0.1, 0.3, and 0.5 synthesized by sol-gel method were named as Zn0-Al_2O_3SG, Zn0.1-Al_2O_3SG, Zn0.3-Al_2O_3SG, and Zn0.5-Al_2O_3SG, respectively. The samples prepared by solvothermal method were named as Zn0-Al_2O_3SV, Zn0.1-Al_2O_3SV, Zn0.3-Al_2O_3SV, and Zn0.5-Al_2O_3SV, respectively. Pd catalysts supported on the corresponding Zn-modified Al_2O_3 were called as Pd/Zn0-Al_2O_3SG, Pd/Zn0.1-Al_2O_3SG, Pd/Zn0.3-Al_2O_3SG, Pd/Zn0.5-Al_2O_3SG, Pd/Zn0-Al_2O_3SV, Pd/Zn0.1-Al_2O_3SV, Pd/Zn0.3-Al_2O_3SV, Pd/Zn0.5-Al_2O_3SV, respectively.

5.2.1 Characterization of the Catalysts

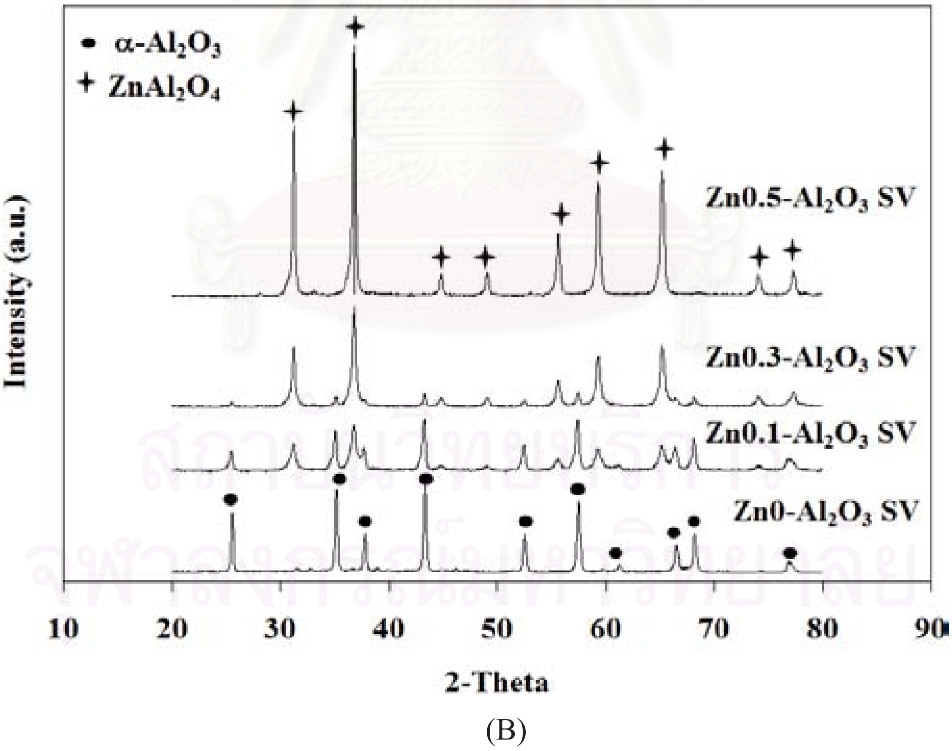
5.2.1.1 X-ray Diffraction (XRD)

The XRD patterns of the Al_2O_3 and Zn-modified Al_2O_3 supports with various molar ratios of Zn to Al prepared by sol-gel and solvothermal methods are shown in Figure 5.8.

As evident from XRD analysis, both the sol-gel and solvothermal synthesis exhibited similar results of characteristic peaks. For the unmodified Al_2O_3 supports (Zn0-Al_2O_3 SG and Zn0-Al_2O_3 SV), the characteristic peaks of α-Al_2O_3 structure were observed at 25.52°, 35.10°, 37.74°, 43.32°, 52.52°, 57.46°, 61.22°, 66.50°, 68.18°, and 77.86° 2θ (Mekasuwandumrong *et al.*,2006). In the case of Zn-modified Al_2O_3 supports, the diffraction lines of both spinel-type $ZnAl_2O_4$ structure and α-Al_2O_3 were apparent for the supports with molar ratios of Zn to Al was 0.1 and 0.3 (Zn0.1-Al_2O_3 SG, Zn0.1-Al_2O_3 SV, Zn0.3-Al_2O_3 SG, and Zn0.3-Al_2O_3 SV) while only the characteristic peaks of $ZnAl_2O_4$ at 30.88°, 36.48°, 44.44°, 48.76°, 55.24°, 58.96°, 64.88°, 73.80°, and 76.96° 2θ (Kanyanucharat *et al.*,2001) were present in the supports with molar ratios of Zn to Al 0.5 (Zn0.5-Al_2O_3 SG and Zn0.5-Al_2O_3 SV). From the experiments, it was found that Zn to Al ratio directly affected the crystalline phases of Al_2O_3 and formation of $ZnAl_2O_4$. XRD patterns of all the samples showed sharp peaks due to coarsening of the particles at higher temperatures (Wei *et al.*,2006).



(A)



(B)

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

5.2.1.2 Average Crystallite Size

The crystallite size of the Zn-modified Al_2O_3 supports with various molar ratios of Zn to Al prepared by sol-gel and solvothermal methods are shown in Table 5.4

Table 5.4 The average crystallite sizes of of Zn-modified Al_2O_3 supports with various molar ratios of Zn to Al synthesized by sol-gel and solvothermal methods.

Sample	Crystallite size (nm)
Zn0-Al_2O_3 SG	31.0^{Al}
Zn0.1-Al_2O_3 SG	40.4^{Al}, 28.0^{ZA}
Zn0.3-Al_2O_3 SG	38.4^{Al}, 37.8^{ZA}
Zn0.5-Al_2O_3 SG	14.7^{ZA}
Zn0-Al_2O_3 SV	69.5^{Al}
Zn0.1-Al_2O_3 SV	32.8^{Al}, 14.9^{ZA}
Zn0.3-Al_2O_3 SV	29.6^{Al}, 29.7^{ZA}
Zn0.5-Al_2O_3 SV	41.6^{ZA}

Al : α-Al_2O_3
ZA : $ZnAl_2O_4$

The average crystallite sizes of the α-Al_2O_3 prepared by sol-gel and solvothermal method were 31 and 69.5 nm, respectively. It was observed that the Zn-modified Al_2O_3 supports with molar ratios of Zn to Al 0.1 and 0.3 consisted of both α-Al_2O_3 and $ZnAl_2O_4$ structure while only $ZnAl_2O_4$ structure were present in the supports with molar ratios of Zn to Al was 0.5 as reported from XRD analysis. In the case of molar ratios of Zn to Al = 0.1 and 0.3, the crystallite sizes of $ZnAl_2O_4$ formed in the Zn-modified Al_2O_3 prepared by solvothermal method were smaller than those of the supports prepared by sol-gel method. While molar ratios of Zn to Al = 0.5, the crystallite sizes of $ZnAl_2O_4$ prepared by sol-gel method were smaller than those of supports prepared by solvothermal method.

5.2.1.3 BET Surface Areas

The BET surface areas of the Al_2O_3 and Zn-modified Al_2O_3 supports with various molar ratios of Zn to Al prepared by sol-gel and solvothermal methods are shown in Table 5.5.

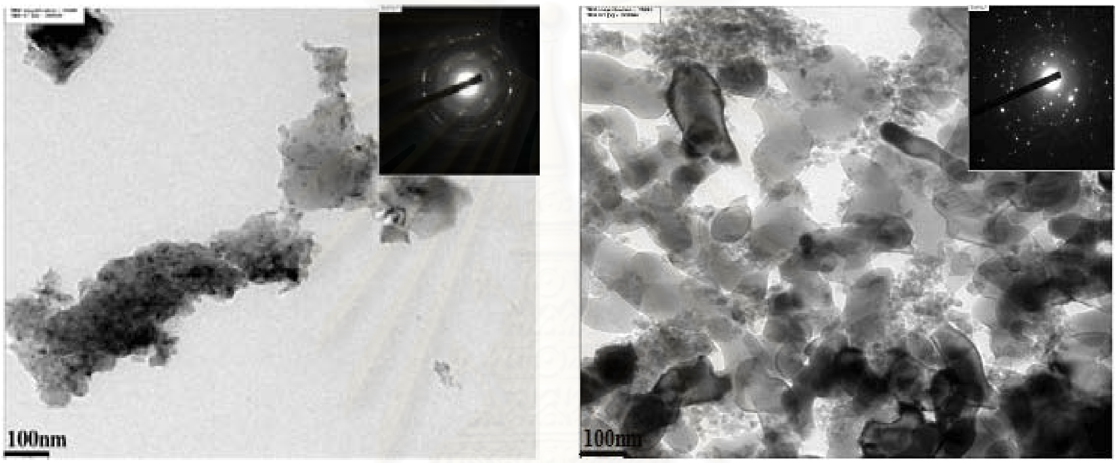
Table 5.5 BET surface areas of of Zn-modified Al_2O_3 supports with various molar ratios of Zn to Al synthesized by sol-gel and solvothermal methods.

Sample	BET Surface areas (m^2/g)
Zn0-Al_2O_3 SG	1.6
Zn0.1-Al_2O_3 SG	1.9
Zn0.3-Al_2O_3 SG	2.3
Zn0.5-Al_2O_3 SG	1.8
Zn0-Al_2O_3 SV	14.9
Zn0.1-Al_2O_3 SV	10.7
Zn0.3-Al_2O_3 SV	9.2
Zn0.5-Al_2O_3 SV	11.5

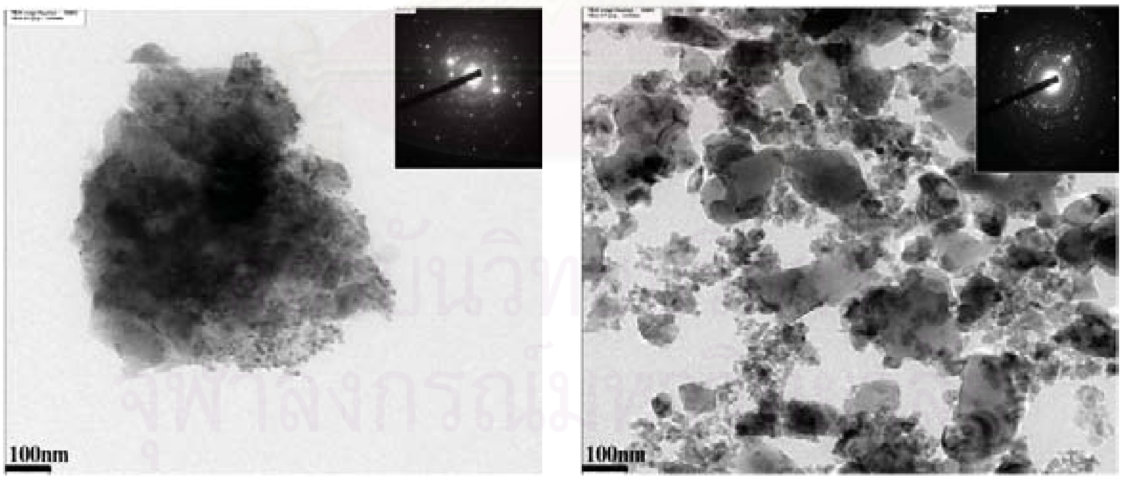
The surface areas of the supports prepared by sol-gel method were ranged from 1.6-2.3 m^2/g while those prepared by solvothermal were ranged from 9.2-14.9 m^2/g. Corresponding to the experiment, the modification of Zn on Al_2O_3 did not affect significantly the surface areas of the resulting samples. Moreover, the surface areas were quite low probably due to high agglomeration of these particles during calcinations at high temperature.

5.2.1.4 Transmission Electron Microscopy (TEM)

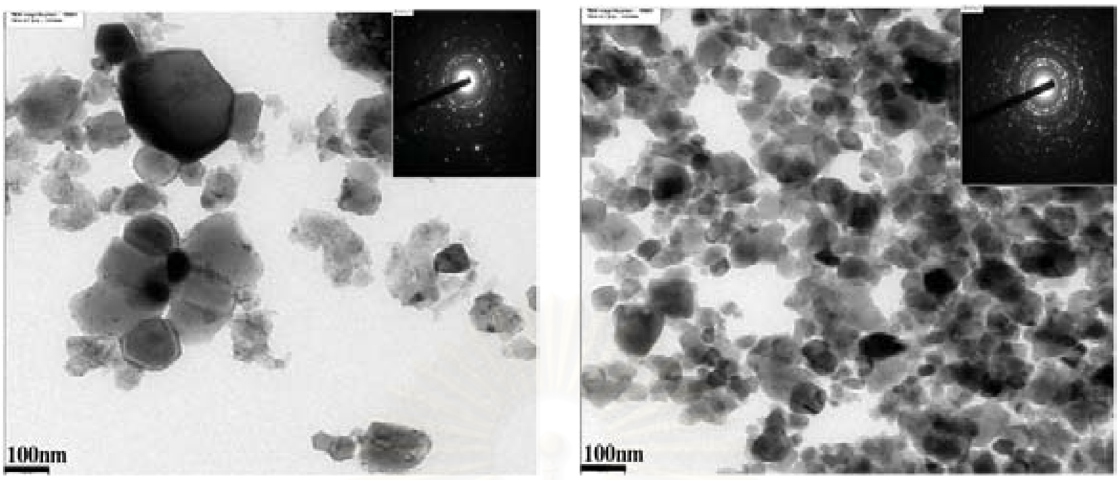
TEM micrographs with SAED patterns of Pd catalyst supported on Zn-modified Al_2O_3 with various molar ratios of Zn to Al prepared by sol-gel and solvothermal methods are shown in Figure 5.9.



(A) Pd/Zn0-Al_2O_3 SG (B) Pd/Zn0-Al_2O_3 SV



(C) Pd/Zn0.1-Al_2O_3 SG (D) Pd/Zn0.1-Al_2O_3 SV



(E) Pd/Zn0.5-Al_2O_3SG (F) Pd/Zn0.5-Al_2O_3SV

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

It can be seen that the sol-gel made catalysts (Pd/Zn0-Al_2O_3 SG and Pd/Zn0.1-Al_2O_3 SG) consisted of agglomerated particles with primarily irregular shape structure (average particle size around 0.5-1 μm) whereas for those prepared by solvothermal method (Pd/Zn0-Al_2O_3SV and Pd/Zn0.1-Al_2O_3SV), agglomeration of finger-like particles were observed. The finger-like α-Al_2O_3 particles were normally obtained by calcination of the solvothermal made α-Al_2O_3 powders at high temperature (Mekasuwandumrong *et al*.,2003, 2006). In case of Pd/Zn0.5-Al_2O_3SG and Pd/Zn0.5-Al_2O_3SV, the spherical shape particles were observed. For Pd/Zn-modified Al_2O_3, the corresponding selected area diffraction patterns shows rings match d-spacing for the $ZnAl_2O_4$ confirmed the structure of $ZnAl_2O_4$ (Mirosław *et al*.,2006). The large particles observed maybe the secondary particles formed by agglomeration of the primary nano-particles due to heat treatment during calcinations step. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5-10 nm were found to be deposited on both of the alumina supports.

5.2.1.5 Metal Active Sites

The metal active sites, the Pd dispersion, and the average Pd metal particle size from CO chemisorption experiment are summarized in Table 5.6.

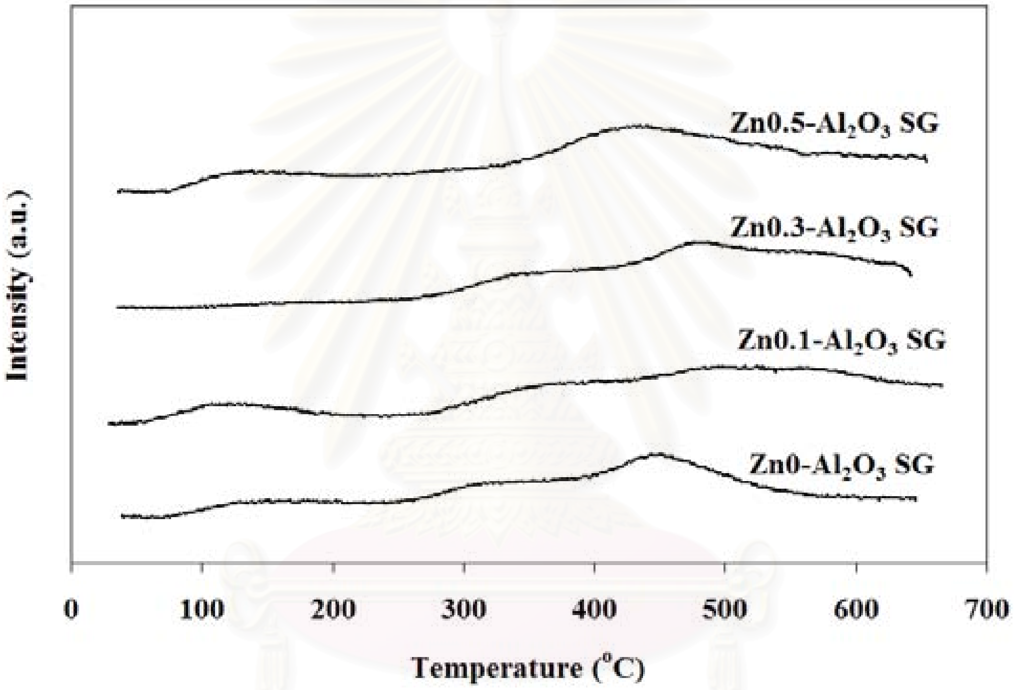
Table 5.6 Results from CO chemisorption of Pd supported on Zn-modified Al_2O_3 with various molar ratios of Zn to Al synthesized by sol-gel and solvothermal methods.

Sample	CO chemisorption $\times10^{17}$ (molecule CO/g cat.)	Pd dispersion (%)	d_P Pd^0 (nm)
Pd/Zn0-Al_2O_3 SG	11.3	8.8	13
Pd/Zn0.1-Al_2O_3 SG	4.9	3.9	29
Pd/Zn0.3-Al_2O_3 SG	10.0	8.1	14
Pd/Zn0.5-Al_2O_3 SG	8.3	6.3	18
Pd/Zn0-Al_2O_3 SV	32.8	20.7	5
Pd/Zn0.1-Al_2O_3 SV	22.7	16.5	7
Pd/Zn0.3-Al_2O_3 SV	12.2	10.4	11
Pd/Zn0.5-Al_2O_3 SV	30.03	23.3	4

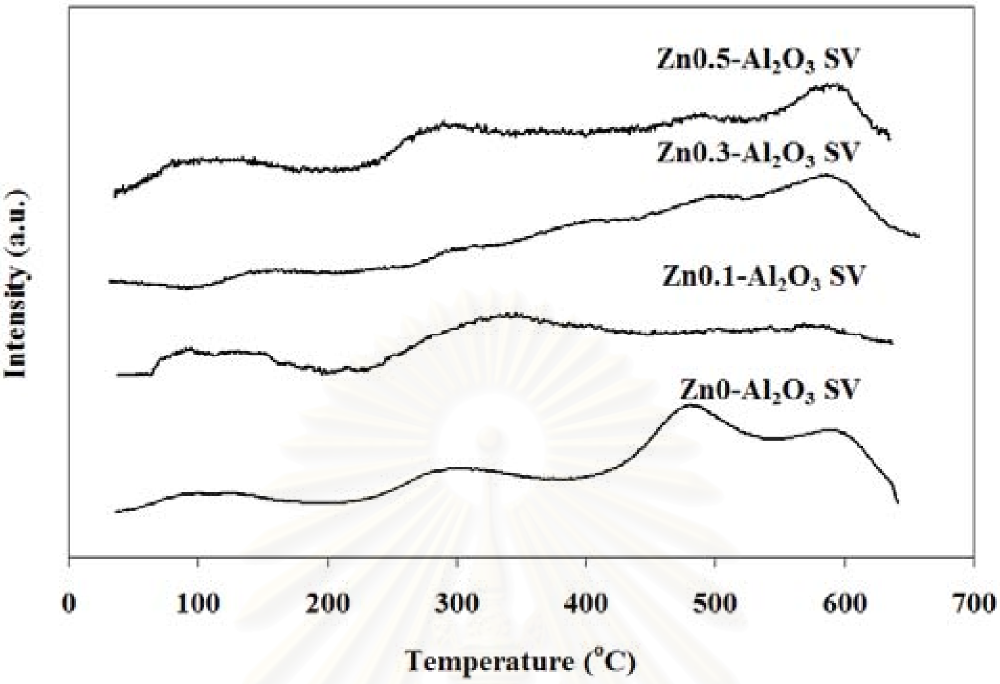
Without Zn addition on the Al_2O_3 supports, Pd/Zn0-Al_2O_3 SG and Pd/Zn0-Al_2O_3 SV possessed the amounts of Pd active sites 11.3 x 10^{17} and 32.8 x 10^{17} sites/g cat., respectively. The Pd active sites significantly decreased when the catalysts were supported on Zn-modified Al_2O_3 corresponding to the decreasing in Pd metal dispersion and increasing in the average Pd metal particle sizes. Comparing the samples prepared by different techniques, the catalysts prepared by sol-gel method showed lower amount of Pd active sites and Pd dispersion than the catalysts prepared by solvothermal method due probably to more agglomeration of the Al_2O_3 supports as noticed from TEM measurements. From the experiment, Pd/Zn0.1-Al_2O_3 SG showed the lowest Pd dispersion (3.9%). The average Pd metal particle sizes for the catalysts prepared by sol-gel were ranged from 13-29 nm while the catalysts prepared by solvothermal were ranged from 4-11 nm.

5.2.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

The temperature-programmed desorption profiles for the Al_2O_3 and Zn-modified Al_2O_3 supports are shown in Figure 5.10.



(A)



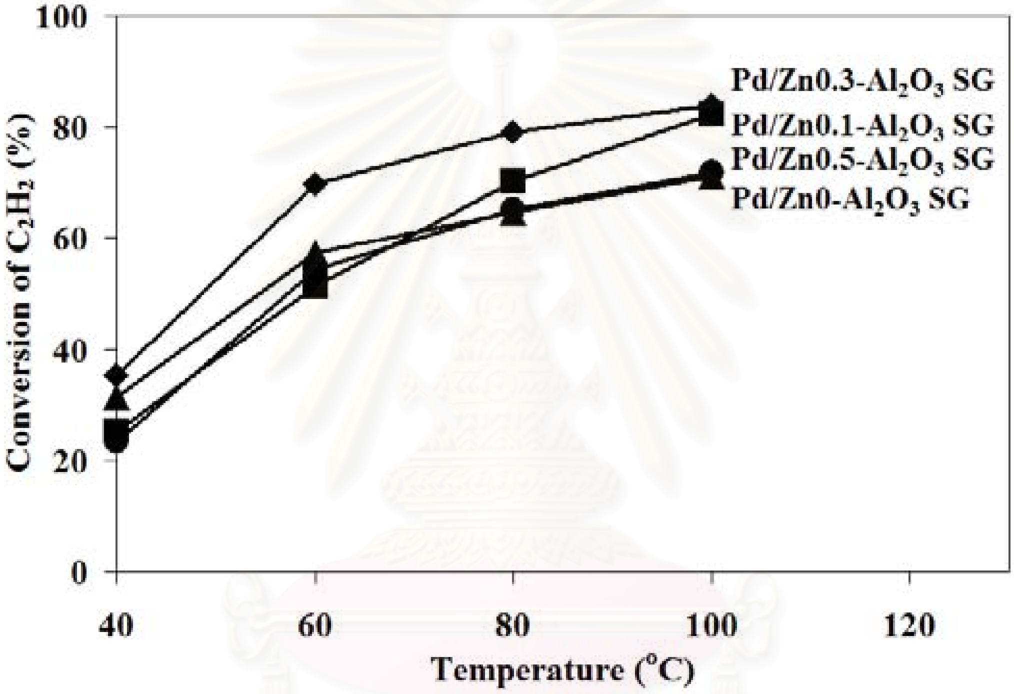
(B)

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

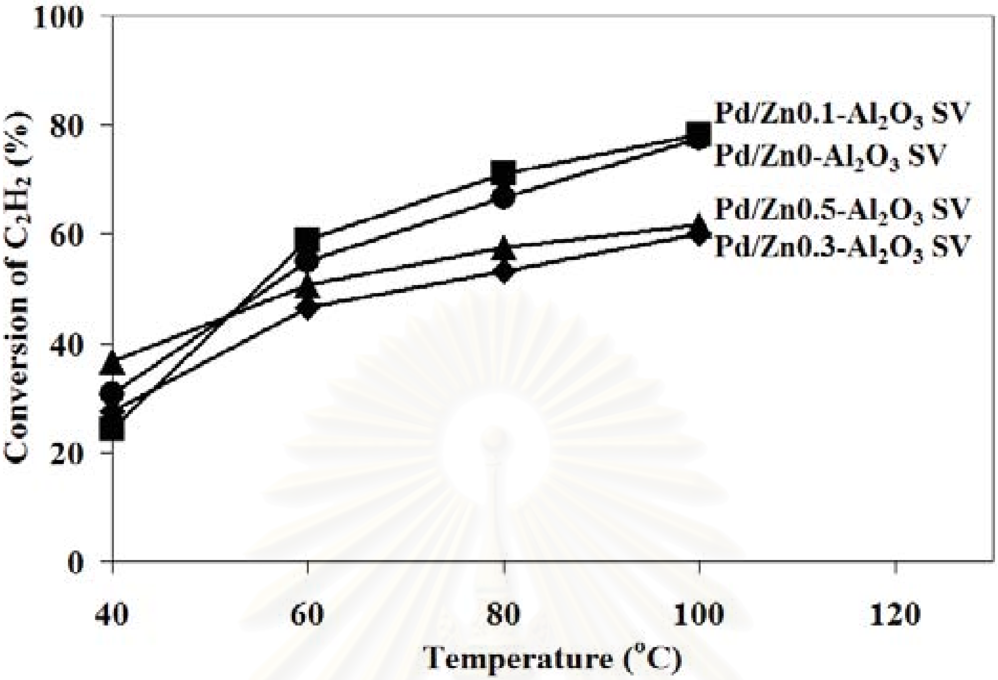
The desorption peak areas of all supports showed relatively lower acidity than other 'transition' alumina due to the dramatically decrease of the surface area after calcination at high temperature. However, desorption peaks could be still observed for all samples. From experimental, it was found that the desoprtion peak areas of the Al_2O_3 samples prepared by sol-gel method (Zn0-Al_2O_3 SG) were lower than that prepared by solvothermal method (Zn0-Al_2O_3 SV). Moreover, regardless of the preparation method used, the desorption peak areas of Zn-modified Al_2O_3 decreased. It was suggested that formation of $ZnAl_2O_4$ species resulted in a decrease of surface acidity of Al_2O_3. The results were in good agreement with those reported by Otero *et al.* They suggested that increasing of Zn content on the Al_2O_3 samples resulted in a decrease of surface acidity because it formed $ZnAl_2O_4$ species (Otero *et al.*,1997).

5.2.2 Catalytic Performance of the Catalysts

The catalytic properties of Pd/Zn-modified Al_2O_3 catalysts were evaluated in the selective hydrogenation of acetylene using a fixed bed flow reactor with a GHSV of 16901 h^{-1}. For study of temperature dependence of the catalysts on acetylene conversion and selectivity toward ethylene, the temperature range between 40-100°C and feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.) were used.



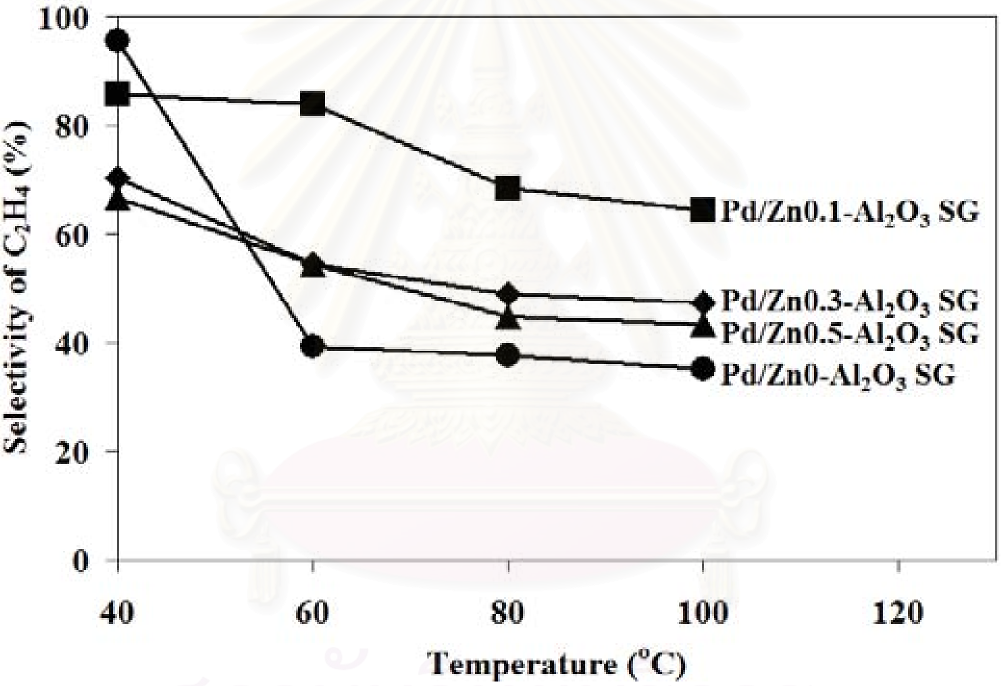
(A)



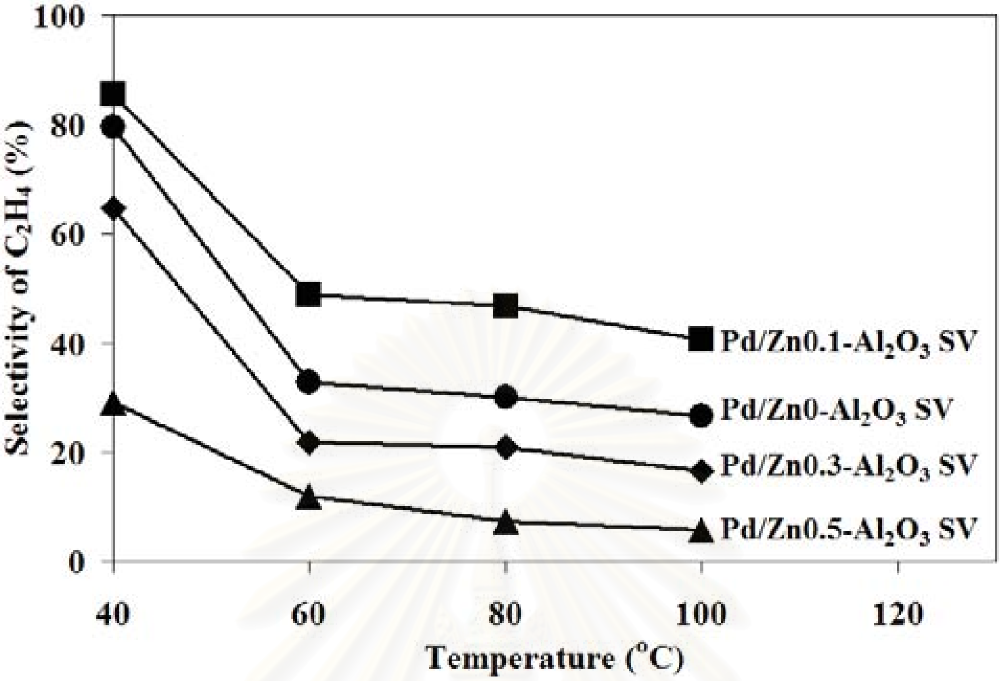
(B)

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

As shown in Figure 5.11., activity of all the catalysts directly increased with rising temperature as the kinetic energy of the system increased with increasing temperature. In case of the catalysts prepared by sol-gel method, all the modified catalysts exhibited higher activity than that of the unmodified catalyst with Pd/Zn0.3-Al_2O_3 SG showed the highest activity. Opposite to the catalysts prepared by sol-gel method, all the modified catalysts prepared by solvothermal showed lower activity than that of the unmodified catalyst except the Pd/Zn0.1-Al_2O_3 SV that showed higher activity from the unmodified catalyst. The selectivity of ethylene (Figure 5.12) observed over all the samples was declined when the temperature was increased due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction (Ngamsom *et al.*,2002). For the catalysts prepared by sol-gel method, with respect to the unmodified catalyst, the catalysts modified by Zn showed higher selectivity of ethylene with Pd/Zn0.1-Al_2O_3 SG catalyst exhibited the highest selectivity of ethylene. It was clearly seen that modification of Pd/Al_2O_3 catalyst with Zn by sol-gel method resulted in significantly improvement of ethylene selectivity. Opposite to the catalysts prepared by sol-gel method, all the modified catalysts presented lower selectivity of ethylene than that of the unmodified catalyst except Pd/Zn0.1-Al_2O_3 SV that showed higher selectivity. Comparing the samples prepared by different techniques, the catalysts prepared by sol-gel method showed better catalytic properties than the catalysts prepared by solvothermal method. Ethylene selectivity was found to improved in the order: Pd/Zn0.1-Al_2O_3 SG > Pd/Zn0.3-Al_2O_3 SG > Pd/Zn0.5-Al_2O_3 SG > Pd/Zn0.1-Al_2O_3 SV > Pd/Zn0-Al_2O_3 SG > Pd/Zn0-Al_2O_3 SV > Pd/Zn0.3-Al_2O_3 SV > Pd/Zn0.5-Al_2O_3 SV.



(A)

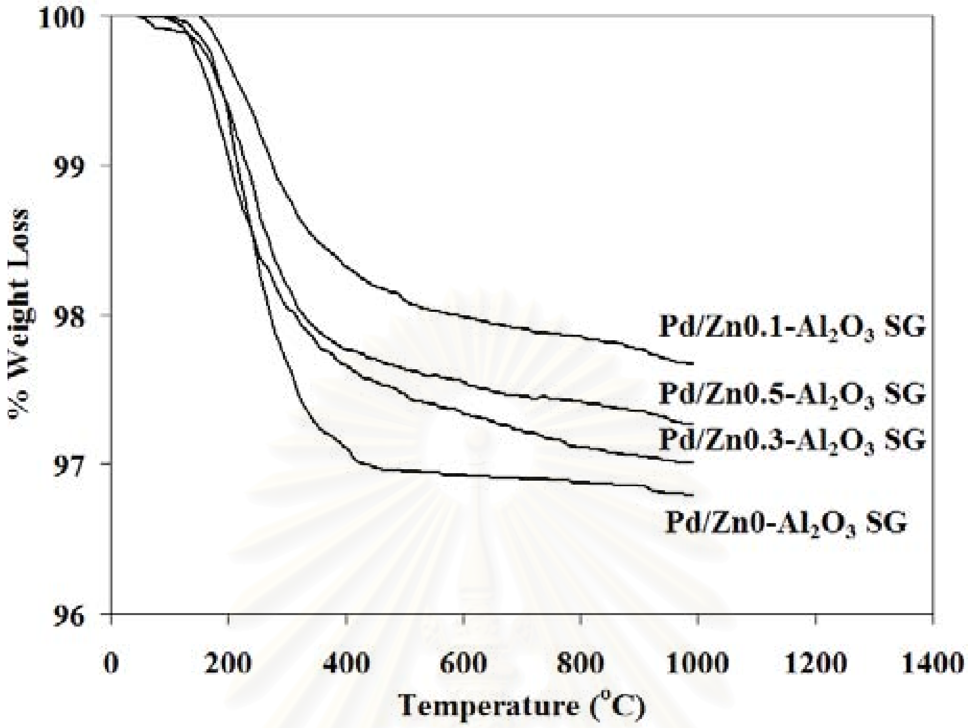


(B)

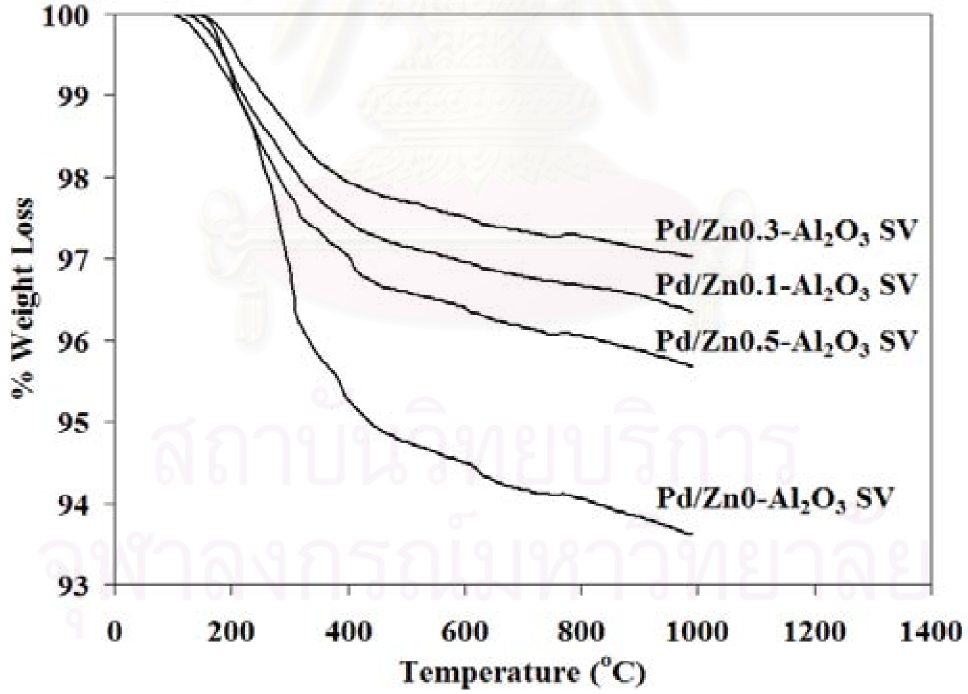
Figure 5.12 Temperature dependence of the catalytic performance (% selectivity of C_2H_4) of Pd/Zn-modified Al_2O_3 catalysts with various molar ratios of Zn to Al synthesized by (A) sol-gel and (B) solvothermal methods.

5.2.3 Characterization of the Spent Catalysts

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



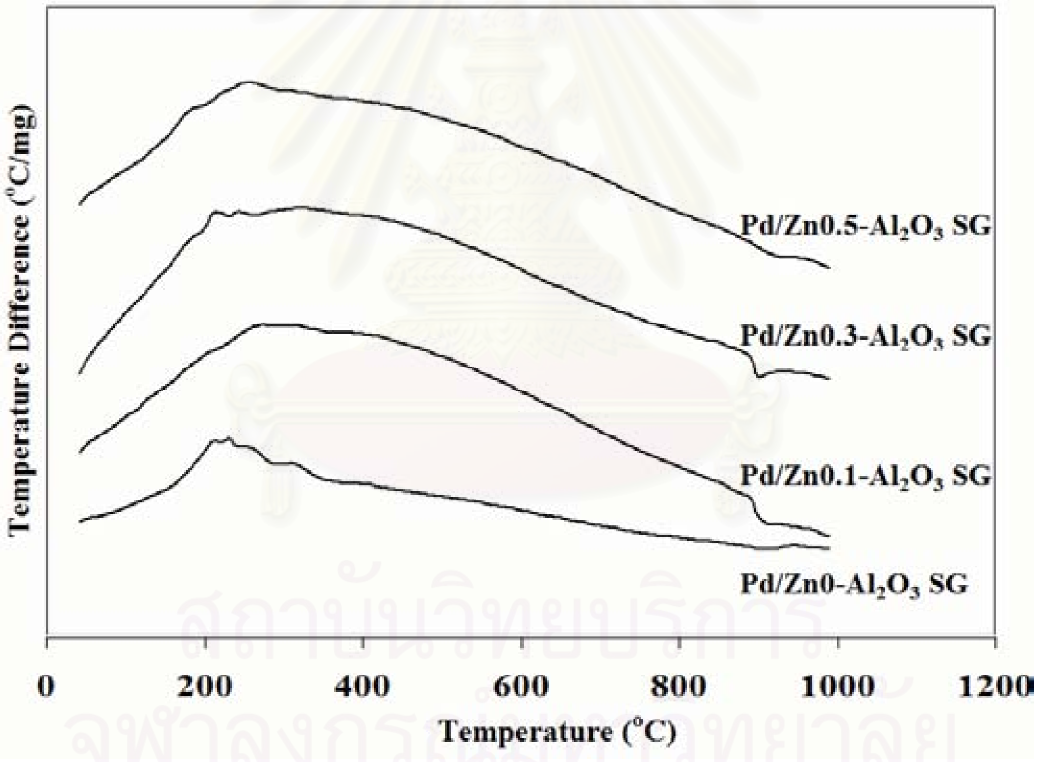
(A)



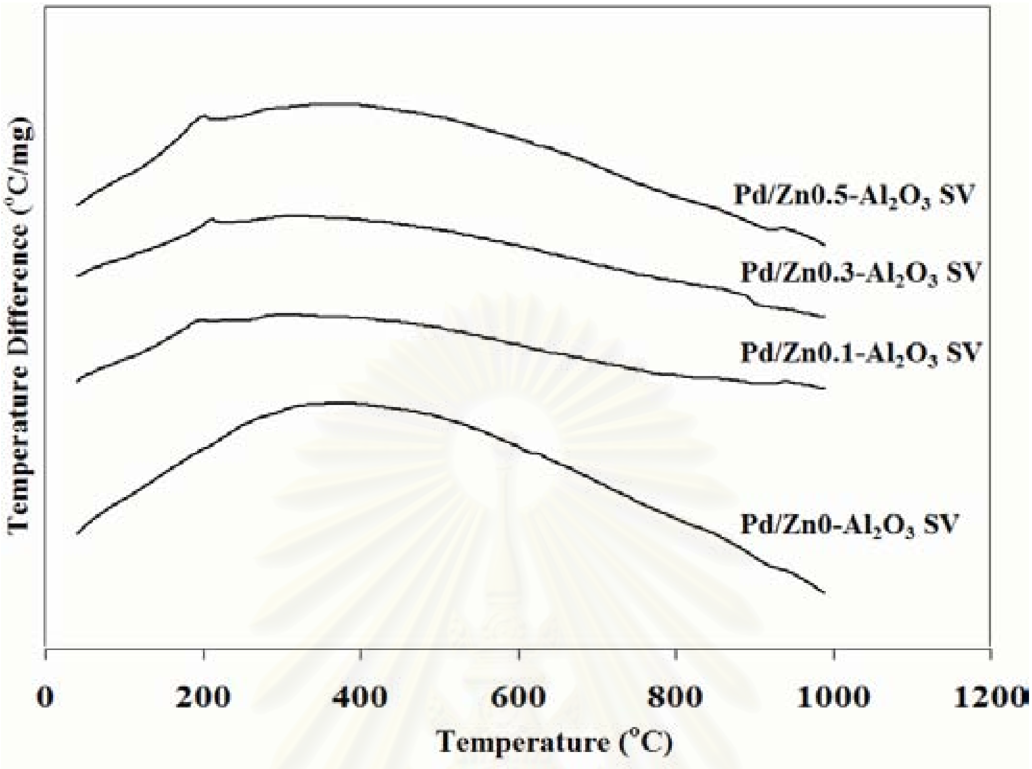
(B)

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

From Figure 5.12, the weight loss observed in the TGA profiles was due to oxidation of the carbonaceous deposited on the surface of used catalysts (Soares *et al.,* 1997). As shown by the exothermic peaks in Figure 5.13, the type of coke species occurred during reaction was probably “soft coke” since it could be removed from the used catalysts by oxidation at a relative lower temperature (~350°C) as suggested by Xiangjing *et al* (Xiangjing *et al.,*2006). Based on TGA results, the amount of coke deposits on the catalysts prepared by sol-gel method were lower than those prepared by solvothermal method with Pd/Zn0.1-Al_2O_3 SG showed the lowest value (2.33%wt) and Pd/Zn0-Al_2O_3 SV showed the highest valve (6.39%wt). The results were in good agreement with acidity of the Al_2O_3 supports measured from NH_3 TPD technique.



(A)



(B)

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

5.3 Effect of Ga- and Zn-modified Al_2O_3 on the Properties of Pd/Al_2O_3 Catalyst

From the experimental results in section 5.1 and 5.2, it was found that the Pd catalysts supported on the Ga- and Zn-modified Al_2O_3 prepared by sol-gel method exhibited higher performances than that of the unmodified Al_2O_3. Opposite to the catalysts prepared by sol-gel method, all the Pd catalysts supported on the Ga- and Zn-modified Al_2O_3 prepared by solvothermal method presented lower selectivity of ethylene than that of the unmodified catalyst except Pd/Zn0.1-Al_2O_3 SV that showed higher selectivity.

Based on the XRD analysis and TEM micrographs with SAED patterns, β-Ga_2O_3 and $ZnAl_2O_4$ were found in Ga- and Zn-modified Al_2O_3 supports, respectively. Their average crystallite sizes for all the samples were nanocrystalline (Prasitwuttisak *et al.*,2004). Thus, the presence of β-Ga_2O_3 and $ZnAl_2O_4$ structure in the Al_2O_3 supports may result in the differences of the interaction between Pd catalyst and the support i.e., Pd/α-Al_2O_3, Pd/β-Ga_2O_3-α-Al_2O_3, and Pd/$ZnAl_2O_4$. The changes in the interaction between Pd catalyst and the support has affected the catalyst activity as well as ethylene selectivity of the various Pd/Al_2O_3 catalysts.

From CO chemisorption and BET surface area results, the catalysts prepared by sol-gel method had lower surface area than the catalysts prepared by solvothermal so that the formation of surface oligomers and the undesirable hydrogenation of ethylene was decreased. In addition, the catalysts prepared by sol-gel possessed lower amount of Pd active sites and lower Pd dispersion than the catalysts prepared by solvothermal method due probably to more agglomeration of the supports as noticed from TEM measurements. This could also be the reason for selectivity enhancement for those prepared by sol-gel technique (Duca *et al.*,1996). Moreover, the Pd catalysts supported on the Ga- and Zn-modified Al_2O_3 supports prepared by sol-gel method exhibited higher activity than those prepared by solvothermal because of increasing in the average Pd metal particle size. It has been reported that the specific activity for selective hydrogenation reaction of alkynic compounds increased with increasing metal particle size (Molnár *et al.*,2001 and Sárkany *et al.*,1986).

According to the NH_3-TPD results, it was found that acidity of the Al_2O_3 supports prepared by sol-gel method was lower than that prepared by solvothermal method. Moreover, modification of Al_2O_3 supports by Ga and Zn decreased surface acidity of Al_2O_3 so that the catalysts exhibited less amount of carbonaceous deposits. The results were in good agreement with the amount of coke deposits on the catalysts measured from TGA.

From several previous investigations, it has been generally accepted that four main types of surface site were involved in Pd/Al_2O_3 catalyst in the selective acetylene hydrogenation. Three types of active sites locating on the Pd surface were responsible for selective hydrogenation of acetylene to ethylene, direct ethane formation from acetylene, and oligomer formation from acetylene. Another site located on the Al_2O_3 support surface involved the hydrogenation of ethylene to ethane (Lobo and Trimm,1973, Somorjai *et al.,* 1979, Moses *et al.*,1984, and, Lamb *et al.*,2004). It has been reported that the increase in ethylene hydrogenation (decrease in ethylene selectivity) was related to the amount of carbonaceous deposited on the catalyst surface. In other words, the carbonaceous deposit acted as a hydrogen bridge for the hydrogen spillover from Pd to support. It is also well known that acidity on Al_2O_3 surface promoted formation of carbonaceous deposited on catalyst surface. This study has shown that modification of Al_2O_3 supports by Ga and Zn can decrease surface acidity of Al_2O_3 so that the catalysts exhibited less amount of carbonaceous deposits and hydrogen spillover, thus selectivity of ethylene was much improved especially at high acetylene conversion.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions obtained from the experimental results of Pd catalysts supported on Ga- and Zn-modified Al_2O_3 with various molar ratios of Ga/Al and Zn/Al (0.1, 0.3, and 0.5) synthesized by sol-gel and solvothermal methods in selective acetylene hydrogenation in excess ethylene. Additionally, recommendations for future study are given in section 6.2.

6.1 Conclusions

1. The Pd catalysts supported on the Ga- and Zn-modified Al_2O_3 prepared by sol-gel method exhibited higher performances in selective hydrogenation of acetylene in excess ethylene than that of the unmodified Al_2O_3. Opposite to the catalysts prepared by sol-gel method, all the catalysts prepared by solvothermal method presented lower selectivity of ethylene than that of the unmodified catalyst except Pd/Zn0.1-Al_2O_3 SV that showed higher selectivity.

2. Differences in the catalyst activity as well as ethylene selectivity of the various Pd/Al_2O_3 catalysts may be due to the differences in (1) the interaction between Pd and the support i.e. Pd/α-Al_2O_3, Pd/β-Ga_2O_3-α-Al_2O_3, and Pd/$ZnAl_2O_4$, (2) the average Pd metal particle size, and (3) acidity of the supports.

3. Regardless of the preparation method used, modification of α-Al_2O_3 by Ga or Zn could decrease surface acidity of the Al_2O_3 so that less amount of carbonaceous deposits was formed during selective acetylene hydrogenation.

6.2 Recommendations

1. The effect of interaction between Pd catalyst and the support on the catalyst performance should be studied using more sophisticated techniques such as X-ray photoelectron spectroscopy.

2. The effect of Ga- and Zn-modified Al_2O_3 for selective hydrogenation of acetylene in excess ethylene over Pd catalyst should be studied for other phases of Al_2O_3 such as γ- Al_2O_3.

3. The other synthesis methods for Ga- and Zn-modified Al_2O_3 for selective hydrogenation of acetylene in excess ethylene over Pd catalyst such as precipitation and flame spray pyrolysis should be investigated.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calulation of support composition (Ga-Modified Al_2O_3)

Preparation of Ga-modified Al_2O_3 with various molar ratios of Ga 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 = 374.98 g/mol
- Aluminum isopropoxide ($((CH_3)_2CHO)_3Al$)
Molecular weight = 203.98 g/mol

Precursors: - Gallium (III) nitrate hydrate ($Ga(NO_3)_3$)
Molecular weight = 255.74 g/mol
- Gallium (III) acetylacetonate $[CH_3COCH{=}C(O)CH_3]_3Ga$
Molecular weight = 367.05 g/mol

Calculation:

Sol-gel method

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

$$\text{Aluminium} = (26.98 \times 24.0735)/374.98 = 1.7322 \text{ g}$$
$$= 1.7322/26.98 = 0.0642 \text{ mol}$$

For Ga/Al = 0.1, 0.0642 mole of aluminium

$$\text{Gallium required} = 0.0642 \times 0.1 = 0.00642 \text{ mol}$$
$$= 0.00642 \times 69.72 = 0.4476 \text{ g}$$

Gallium 0.4476 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72 mol

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of } Ga(NO_3)_3 \times \text{gallium required}}{\text{MW of Ga}}$$
$$= (255.74/69.72) \times 0.4476 = 1.6420 \text{ g}$$

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.98×24.0735)/374.98 = 1.7322 g

= 1.7322/26.98 = 0.0642 mol

For Ga/Al = 0.3, 0.0642 mole of aluminium

Gallium required = 0.0642×0.3 = 0.01926 mol

= 0.01926×69.72 = 1.343 g

Gallium 1.343 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72 mol

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of } Ga(NO_3)_3 \times \text{gallium required}}{\text{MW of Ga}}$$

= (255.74/69.72)×1.343 = 4.9262 g

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.98×24.0735)/374.98 = 1.7322 g

= 1.7322/26.98 = 0.0642 mol

For Ga/Al = 0.5, 0.0642 mole of aluminium

Gallium required = 0.0642×0.5 = 0.0321 mol

= 0.0321×69.72 = 2.2380 g

Gallium 2.2380 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72 mol

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of } Ga(NO_3)_3 \times \text{gallium required}}{\text{MW of Ga}}$$

= (255.74/69.72)×2.2380 = 8.2092 g

Solvothermal method

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Ga/Al = 0.1, 0.0735 mole of aluminium

Gallium required = 0.0735×0.1 = 0.00735 mol

= 0.00735×69.72 = 0.5120 g

Gallium 0.5120 g was prepared from $[CH_3COCH=C(O)CH_3]_3Ga$ and molecular weight of Ga is 69.72 mol

Thus, $[CH_3COCH=C(O)CH_3]_3$ required

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_3Ga \times \text{gallium required}}{\text{MW of Ga}}$$

= (367.05/69.72)×0.5120 = 2.6955 g

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Ga/Al = 0.3, 0.0735 mole of aluminium

Gallium required = 0.0735×0.3 = 0.022032 mol

= 0.022032×69.72 = 1.5361 g

Gallium 1.5361 g was prepared from $[CH_3COCH=C(O)CH_3]_3Ga$ and molecular weight of Ga is 69.72 mol

Thus, $[CH_3COCH=C(O)CH_3]_3$ required

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_3Ga \times \text{gallium required}}{\text{MW of Ga}}$$

= (367.05/69.72)×1.5361 = 8.0868 g

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Ga/Al = 0.5, 0.0735 mole of aluminium

Gallium required = 0.0735×0.5 = 0.03675 mol

= 0.03675×69.72 = 2.5622 g

Gallium 2.5622 g was prepared from $[CH_3COCH{=}C(O)CH_3]_3Ga$ and molecular weight of Ga is 69.72 mol

Thus, $[CH_3COCH{=}C(O)CH_3]_3$ required

$$= \frac{\text{MW of } [CH_3COCH{=}C(O)CH_3]_3Ga \times \text{gallium required}}{\text{MW of Ga}}$$

$$= (367.05/69.72) \times 2.5622 \quad = \quad 13.4775 \text{ g}$$

Calulation of support composition (Zn-Modified Al_2O_3)

Preparation of Zn-modified Al_2O_3 with various molar ratios of Zn 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 = 374.98 g/mol

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

Molecular weight = 203.98 g/mol

Precursors: - Zinc (II) nitrate hexahydrate ($(Zn(NO_3)_2).6H_2O$)

Molecular weight = 297.37 g/mol

- Zinc (II) acetylacetonate $[CH_3COCH{=}C(O)CH_3]_2Zn$

Molecular weight = 263.59 g/mol

Calculation:

Sol-gel method

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

$$\text{Aluminium} = (26.98 \times 24.0735)/374.98 = 1.7322 \text{ g}$$

$$= 1.7322/26.98 = 0.0642 \text{ mol}$$

For Zn/Al = 0.1, 0.0642 mole of aluminium

$$\text{Zinc required} = 0.0642 \times 0.1 = 0.00642 \text{ mol}$$

$$= 0.00642 \times 65.37 = 0.4079 \text{ g}$$

Zinc 0.4079 g was prepared from $Zn(NO_3)_2.6H_2O$ and molecular weight of Zn is 65.37 mol

$$Zn(NO_3)_2.6H_2O\ \text{required} = \frac{\text{MW of } Zn(NO_3)_2.6H_2O \times \text{zinc required}}{\text{MW of Zn}}$$

$$= (297.37/65.37)\times 0.4079 \quad = 1.9098\ \text{g}$$

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.98×24.0735)/374.98 = 1.7322 g

= 1.7322/26.98 = 0.0642 mol

For Zn/Al = 0.3, 0.0642 mole of aluminium

Zinc required = 0.0642×0.3 = 0.01926 mol

= 0.00642×65.37 = 1.2590 g

Zinc 1.2590 g was prepared from $Zn(NO_3)_2.6H_2O$ and molecular weight of Zn is 65.37 mol

$$Zn(NO_3)_2.6H_2O\ \text{required} = \frac{\text{MW of } Zn(NO_3)_2.6H_2O \times \text{zinc required}}{\text{MW of Zn}}$$

$$= (297.37/65.37)\times 1.2590 \quad = 5.7293\ \text{g}$$

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

Aluminium = (26.98×24.0735)/374.98 = 1.7322 g

= 1.7322/26.98 = 0.0642 mol

For Zn/Al = 0.5, 0.0642 mole of aluminium

Zinc required = 0.0642×0.5 = 0.0321 mol

= 0.0321×65.37 = 2.0984 g

Zinc 2.0984 g was prepared from $Zn(NO_3)_2.6H_2O$ and molecular weight of Zn is 65.37 mol

$$Zn(NO_3)_2.6H_2O\ \text{required} = \frac{\text{MW of } Zn(NO_3)_2.6H_2O \times \text{zinc required}}{\text{MW of Zn}}$$

$$= (297.37/65.37)\times 2.0984 \quad = 9.5492\ \text{g}$$

Solvothermal method

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Zn/Al = 0.1, 0.0735 mole of aluminium

Zinc required = 0.0735×0.1 = 0.00735 mol

= 0.00735×65.37 = 0.4800 g

Zinc 0.4800 g was prepared from $[CH_3COCH=C(O)CH_3]_2Zn$ and molecular weight of Zn is 65.37 mol

Thus, $[CH_3COCH=C(O)CH_3]_2$ required

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_2Zn \times \text{zinc required}}{\text{MW of Zn}}$$

= (263.59/65.37)×0.4800 = 1.9358 g

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Zn/Al = 0.3, 0.0735 mole of aluminium

Zinc required = 0.0735×0.3 = 0.0220 mol

= 0.0220×65.37 = 1.4400 g

Zinc 1.4400 g was prepared from $[CH_3COCH=C(O)CH_3]_2Zn$ and molecular weight of Zn is 65.37 mol

Thus, $[CH_3COCH=C(O)CH_3]_2$ required

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_2Zn \times \text{zinc required}}{\text{MW of Zn}}$$

= (263.59/1.4400)×65.37 = 5.8074 g

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

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = (26.98×15)/203.98 = 1.9840 g

= 1.9840/26.98 = 0.0735 mol

For Zn/Al = 0.5, 0.0735 mole of aluminium

Zinc required = 0.0735×0.5 = 0.03672 mol

= 0.03672×65.37 = 2.4003 g

Zinc 2.4003 g was prepared from $[CH_3COCH{=}C(O)CH_3]_2Zn$ and molecular weight of Zn is 65.37 mol

Thus, $[CH_3COCH{=}C(O)CH_3]_2$ required

$$= \frac{\text{MW of } [CH_3COCH{=}C(O)CH_3]_2Zn \times \text{zinc required}}{\text{MW of Zn}}$$

= (263.59/65.37)×2.4003 = 9.6790 g

Calculation of palladium loading

Preparation of 0.3%wt Pd on supports by the incipient wetness impregnation method is shown as follows:

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

Molecular weight = 338.42

- Support: - Al_2O_3
  - Ga-modified Al_2O_3
  - Zn-modified Al_2O_3

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

Palladium = 0.3 g

Alumina = 100-0.3 = 99.7 g

For 1 g of Al_2O_3 support

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

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

= (338.42/106.42)×0.003 = 0.0095 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 α-Al_2O_3 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 = 57.44^o

θ = 28.72^o

λ = 1.5418 Å

The crystallite size = $\dfrac{0.9 \times 1.5418}{0.00553 \cos 28.72}$ = 309.88 Å

= 31.0 nm

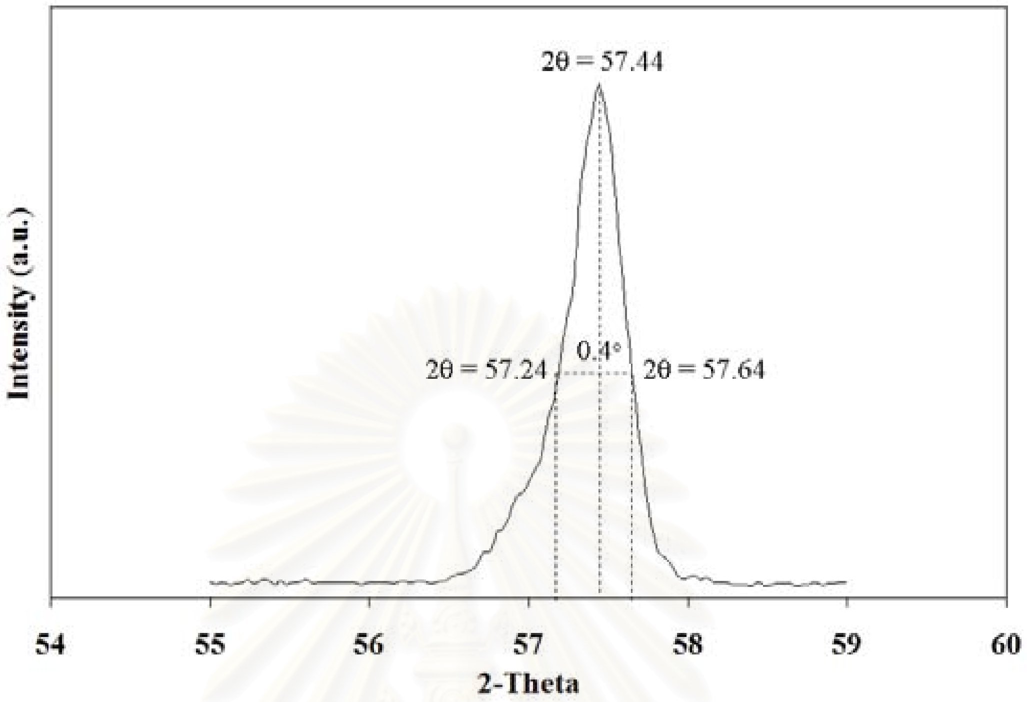


Figure B.1 The measured peak of α-Al_2O_3 prepared by sol-gel method to calculate the crystallite size.

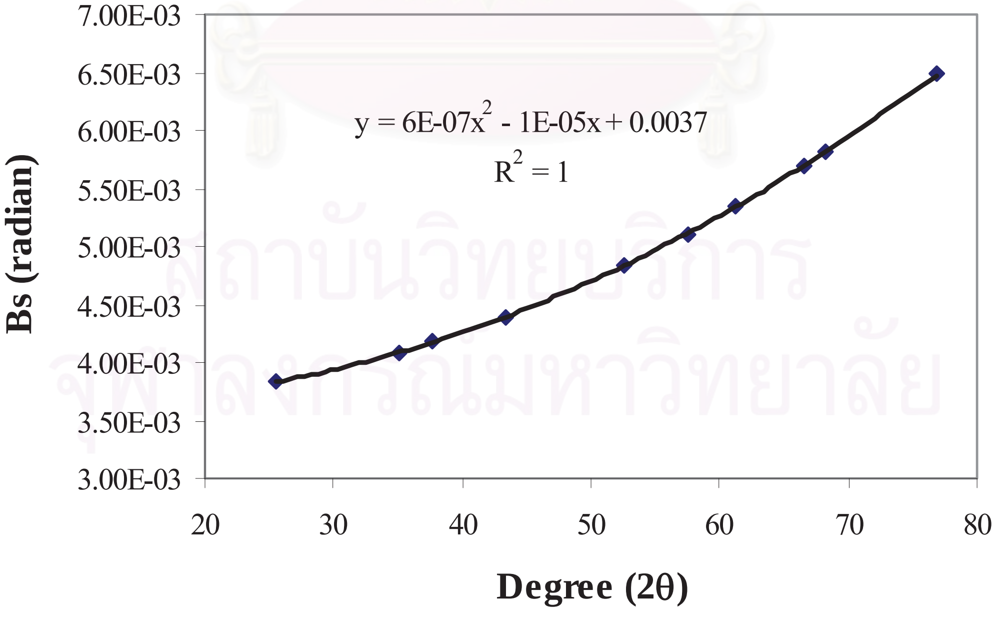


Figure B.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α-alumina as standard

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 = $100\times[(B-A)/B]$ 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

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

Metal active sites

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

Molecules of Pd loaded

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

Metal dispersion (%)

$$= 100\times[\text{molecules of Pd from CO adsorption/molecules of Pd loaded}]$$

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.

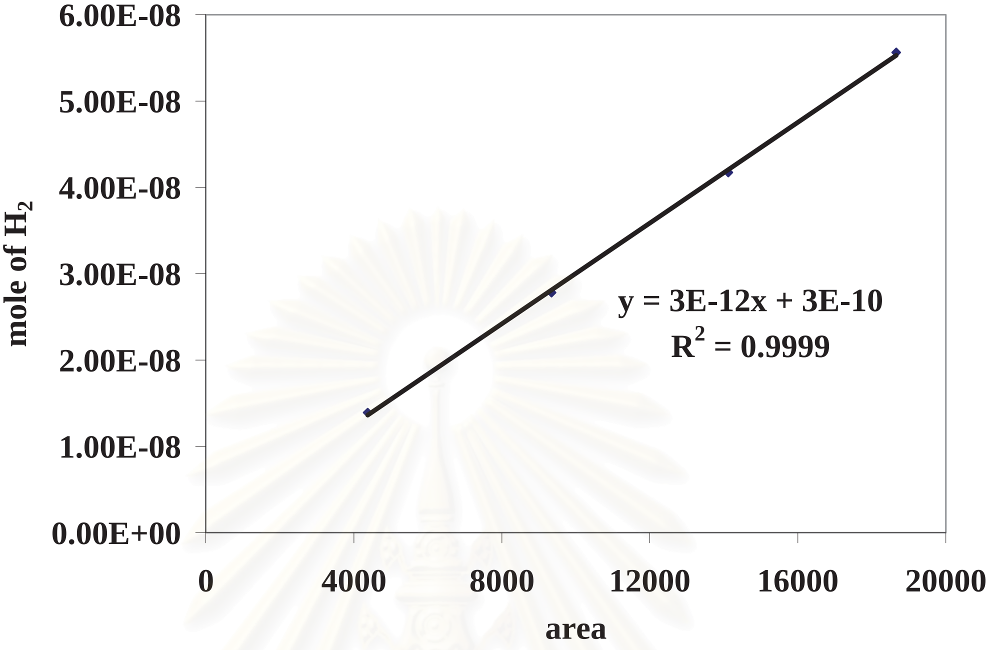


Figure D.1 The calibration curve of hydrogen from TCD of GC-8A.

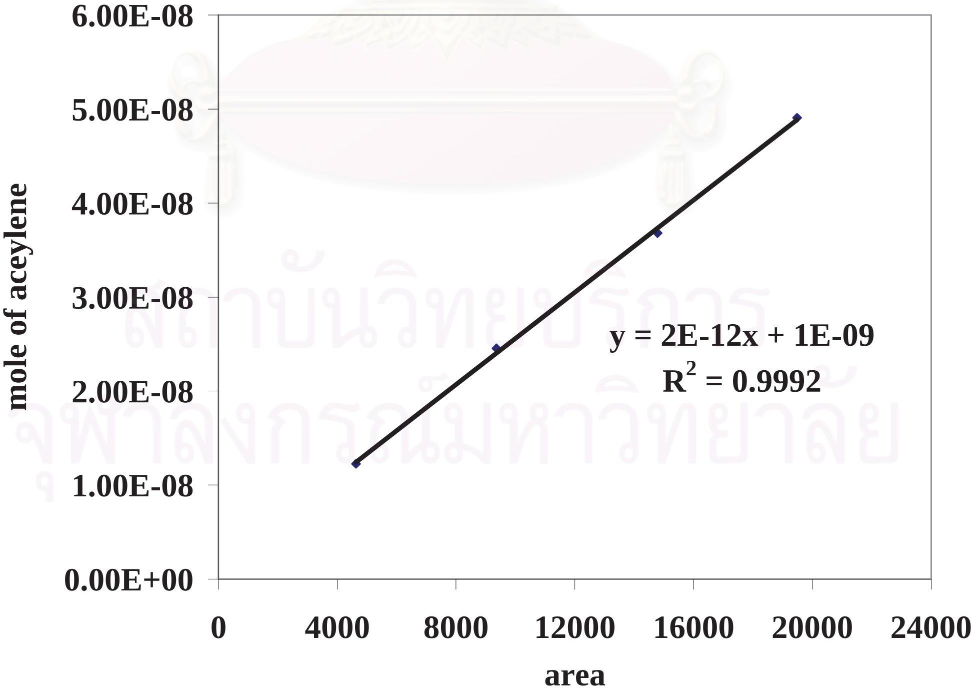


Figure D.2 The calibration curve of acetylene from FID of GC-9A.

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.

$$C_2H_2 + H_2 \xrightarrow{\qquad\qquad} C_2H_4 \qquad (E.1)$$

$$C_2H_4 + H_2 \xrightarrow{\qquad\qquad} C_2H_6 \qquad (E.2)$$

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.,

$$\text{mole of } C_2H_2 = (\text{area of } C_2H_2 \text{ peak from integrator plot on GC-9A}) \times 2.0 \times 10^{-12} \qquad \text{(ii)}$$

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.,

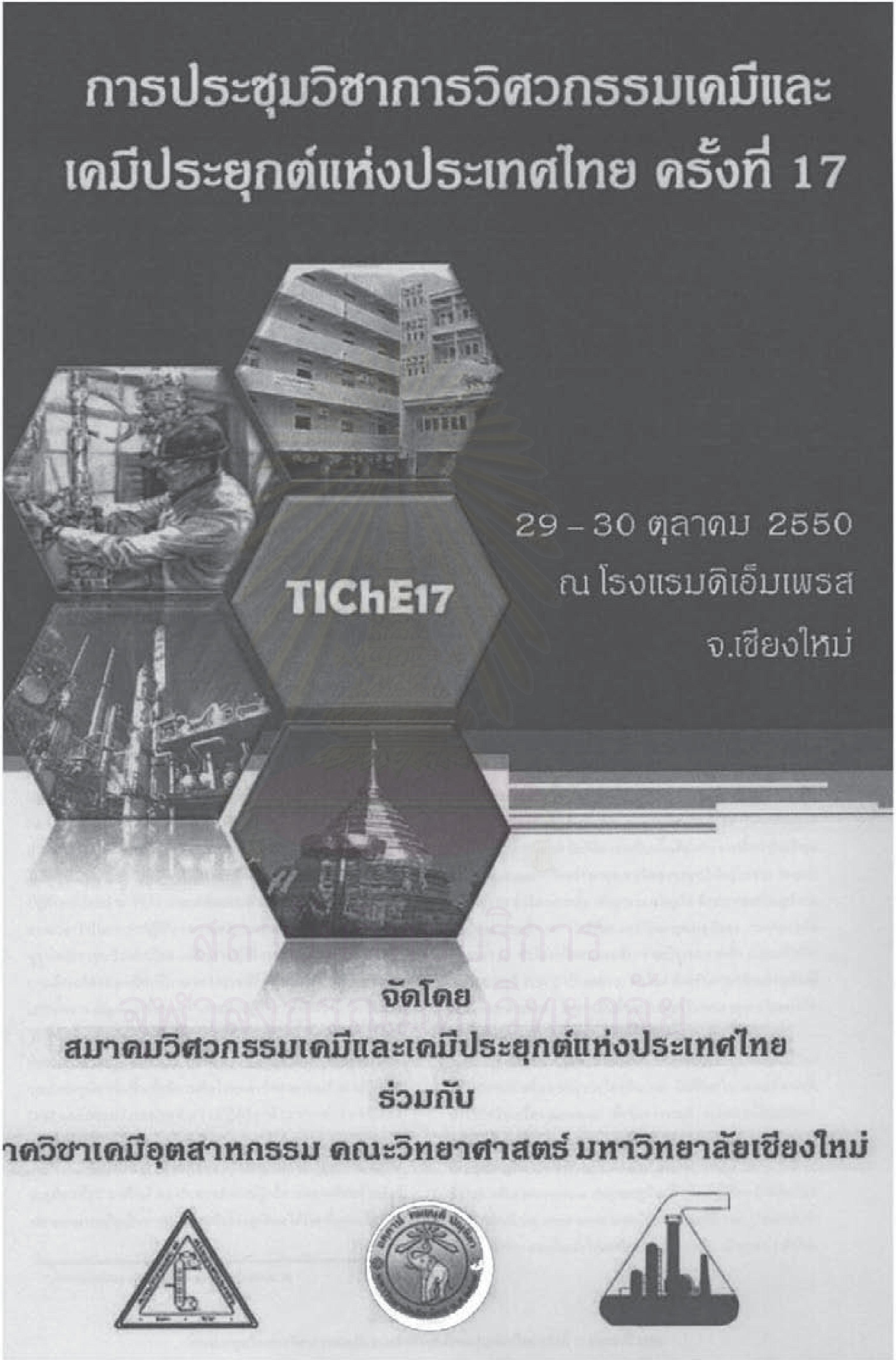
$$\text{mole of } H_2 = (\text{area of } H_2 \text{ peak from integrator plot on GC-8A}) \times 3.0 \times 10^{-12} \qquad \text{(vi)}$$

APPENDIX F

LIST OF PUBLICATIONS

1. Suthana Chinayon, Joongjai Panpranot, and Piyasan Praserthdam, “Effect of Zn-modified Al_2O_3 on the properties of Pd/Al_2O_3 catalyst in selective acetylene hydrogenation”, Proceeding of the 17th Thailand Chemical Engineering and Applied Chemistry Conference, Chiang Mai Thailand, October, 2007.

2. Chinayon, S., Mekasuwandumrong, O., Praserthdam, P., and Panpranot, J., Selective Hydrogenation of Acetylene over Pd Catalysts Supported on Nanocrystalline α-Al_2O_3 and Zn-Modified α-Al_2O_3. Catalysis Communications (2008), In Press.



การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 17

29 – 30 ตุลาคม 2550
ณ โรงแรมดิเอ็มเพรส
จ.เชียงใหม่

จัดโดย
สมาคมวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย
ร่วมกับ
าควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

KCF3_1

ผลของอะลูมินาที่ปรับสภาพด้วยซิงค์ต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

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ศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย เขตพญาไท กรุงเทพฯ 10330

บทคัดย่อ

งานวิจัยนี้ ศึกษาผลของอะลูมินาที่ปรับสภาพด้วยซิงค์ที่อัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมต่างๆ ซึ่งเตรียมโดยวิธีโซลเจลและวิธีโซลโวเทอร์มอลต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน พบว่าการนำอะลูมินาที่ปรับสภาพด้วยซิงค์ซึ่งเตรียมโดยวิธีโซล-เจลมาเป็นตัวรองรับตัวเร่งปฏิกิริยาแพลเลเดียม ช่วยเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาให้สูงขึ้น โดยอัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมเท่ากับ 0.1 ให้ค่าเลือกเกิดของอะทิลีนสูงที่สุด ในขณะที่การใช้วิธีโซลโวเทอร์มอลเตรียมตัวรองรับ ไม่ได้ช่วยให้ประสิทธิภาพของตัวเร่งปฏิกิริยาสูงขึ้น ผลวิเคราะห์การกระเจิงรังสีเอ็กซ์แสดงให้เห็นว่าปริมาณต่างๆของซิงค์ที่เติมลงไปมีผลต่อโครงสร้างของตัวรองรับอะลูมินาและเกิดสารประกอบซิงค์อะลูมิเนตผสมกับอะลูมินา ผลวิเคราะห์การสลายตัวทางความร้อนของตัวเร่งปฏิกิริยาที่ใช้แล้วพบว่าการปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์สามารถลดการเกิดโค้กที่สะสมบนพื้นผิวตัวเร่งปฏิกิริยา

คำสำคัญ: โซเจล, โซลโวเทอร์มอล, ตัวรองรับ, อะลูมินา, อะเซทิลีน

1. บทนำ

เอทิลีนเป็นวัตถุดิบสำคัญของอุตสาหกรรมการผลิตพอลิเอทิลีน โดยทั่วไปแล้วสารป้อนเอทิลีนที่ได้จากหน่วยแยกแนฟทา จะมีอะเซทิลีนปะปนมากับสารป้อนเอทิลีนในปริมาณร้อยละ 0.1 ถึง 1 โดยน้ำหนัก ซึ่งการมีอะเซทิลีนปะปนมากับสารป้อนเอ ทิลีนจะส่งผลเสียต่อกระบวนการพอลิเมอร์ไรเซชันของเอทิลีน เนื่องจากอะเซทิลีนจะไปเกาะอยู่บนตำแหน่งที่ว่องไวของตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาพอลิเมอร์ไรเซชันของเอทิลีน ทำให้ผลิตภัณฑ์พอลิเอทิลีนที่ได้มีคุณภาพลดลง[1] ดังนั้นอะเซทิลีนต้องถูกกำจัดออกให้อยู่ในระดับ 1-5 ppm สำหรับวิธีที่นิยมใช้ในภาคอุตสาหกรรม คือการทำปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีนไปเป็นเอทิลีน[2] โดยตัวเร่งปฏิกิริยาที่นิยมนำมาใช้คือ แพลเลเดียมบนตัวรองรับอะลูมินาเนื่องจากมีความว่องไวในการทำปฏิกิริยา ความสามารถในการเลือกเกิดเป็นเอทิลีนสูง และมีความเป็นกรดน้อย แต่ตัวเร่งปฏิกิริยาชนิดนี้ก็มีข้อจำกัดคือ ค่าการเลือกเกิดลดลงเมื่อปริมาณของอะเซทิลีนที่เข้าทำปฏิกิริยามากขึ้น และเกิดสาร oligomer ขึ้นระหว่างการทำปฏิกิริยา ดังนั้นจึงมีการค้นคว้าวิธีที่จะเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาชนิดนี้ โดยจากงานวิจัยที่ผ่านมาพบว่าประสิทธิภาพของตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับอะลูมินาเพิ่มขึ้นเมื่อมีการเติมโลหะตัวที่สองลงบนตัวเร่งปฏิกิริยา[3-8] และการปรับสภาพตัวเร่งปฏิกิริยาด้วยสารประกอบของออกซิเจน[9]

ดังนั้นในงานวิจัยนี้จึงสนใจศึกษาผลของการปรับสภาพอะลูมินาเพื่อนำมาเป็นตัวรองรับของตัวเร่งปฏิกิริยาแพลเลเดียมด้วยซิงค์ เพราะสามารถเกิดเป็นสารประกอบซิงค์อะลูมิเนตได้ง่าย ซึ่งการเกิดซิงค์อะลูมิเนตส่งผลดีคือเพิ่มความเสถียรภาพทางความร้อน ทนทานต่อสภาพความเป็นกรด และป้องกันการเกิด sintering กับโลหะได้[10,11]

2. อุปกรณ์และวิธีการทดลอง

2.1 การเตรียมตัวรองรับอะลูมินาและอะลูมินาที่ปรับสภาพด้วยซิงค์

ตัวรองรับอะลูมินาและอะลูมินาที่ปรับสภาพด้วยซิงค์เตรียมโดยวิธีโซล-เจลและวิธีโซลโวเทอร์มอล

สำหรับวิธีโซล-เจล, อะลูมิเนียมไนเตรท โนนาไฮเดรต ละลายในเอทานอล 50 มิลลิลิตรจนเป็นเนื้อเดียวกัน จากนั้นนำไปเข้าชุด reflux-condenser โดยรักษาอุณหภูมิของระบบให้อยู่ในช่วง 70-80°C เป็นเวลา 18 ชั่วโมง จากนั้น เติมสารละลายยูเรีย ซึ่งประกอบด้วยยูเรีย 60 กรัม และ น้ำกลั่น 50 มิลลิลิตร และรักษาอุณหภูมิของ ระบบเท่าเดิม เป็นเวลา 24 ชั่วโมงหรือจนกระทั่งกลายเป็นเจล จากนั้น นำเจลที่ได้ไปเผาที่อุณหภูมิ 1150°C เป็นเวลา 3 ชั่วโมง สำหรับการเตรียมอะลูมินาที่ปรับสภาพด้วยซิงค์, ในสารตั้งต้นจะใส่ซิงค์ไนเตรต เฮกซะไฮเดรตในปริมาณต่างๆลงไป และทำตามวิธีเดียวกันกับการเตรียมอะลูมินา

สำหรับวิธีโซลโวเทอร์มอล, อะลูมิเนียมไอโซโพรพอกไซด์ 15 กรัม ละลายในสารละลายโทลูอีน 100 มิลลิลิตรในบีกเกอร์ จากนั้นนำไปใส่ในเครื่อง autoclave ซึ่งช่องว่างระหว่างบีกเกอร์กับผนังของเครื่อง autoclave มีสารละลายโทลูอีน 40 มิลลิลิตรเติมอยู่ จากนั้น ทำการเพิ่มอุณหภูมิด้วยอัตรา 2.5°Cต่อนาที จนถึงอุณหภูมิ 300°C ทิ้งไว้ 2 ชั่วโมง หลังจาก autoclave ลดอุณหภูมิจนถึงอุณหภูมิห้อง นำผลิตภัณฑ์ที่ได้ไปล้างด้วยสารละลายเมทานอลโดยการเซนตริฟิวและ ปล่อยให้แห้งที่อุณหภูมิห้อง จากนั้น นำไปเผาที่อุณหภูมิ 1150°C เป็นเวลา 1 ชั่วโมง

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สำหรับการเตรียมอะลูมินาที่ปรับสภาพด้วยซิงค์, ในสารตั้งต้นจะใส่ซิงค์อะซิทิลอะซีโตเนตในปริมาณต่างๆลงไปตามลำดับ และทำตามวิธีเดียวกันกับการเตรียมอะลูมินา

2.2 การเตรียมตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับอะลูมินาและอะลูมินาที่ปรับสภาพด้วยซิงค์

เตรียมสารละลายแพลเลเดียมในเตรต และทำการฝังเคลือบลงบนตัวรองรับ (แพลเลเดียม 0.3 % โดยน้ำหนัก) ทิ้งไว้ที่อุณหภูมิห้องเป็นเวลา 6 ชั่วโมง จากนั้นนำไปอบที่อุณหภูมิ 110°C เป็นเวลา 12 ชั่วโมง นำตัวเร่งปฏิกิริยาที่เตรียมได้ไปเผาต่อในอากาศที่อุณหภูมิ 500°C เป็นเวลา 2 ชั่วโมง

2.3 การตรวจสอบคุณลักษณะของตัวเร่งปฏิกิริยา

เทคนิคต่างๆที่ใช้ทดสอบคุณลักษณะของตัวเร่งปฏิกิริยา อาทิ การกระเจิงรังสีเอ็กซ์ การดูดซับด้วยคาร์บอนมอนอกไซด์ การดูดซับทางกายภาพด้วยไนโตรเจน การสลายตัวทางความร้อน ฯลฯ

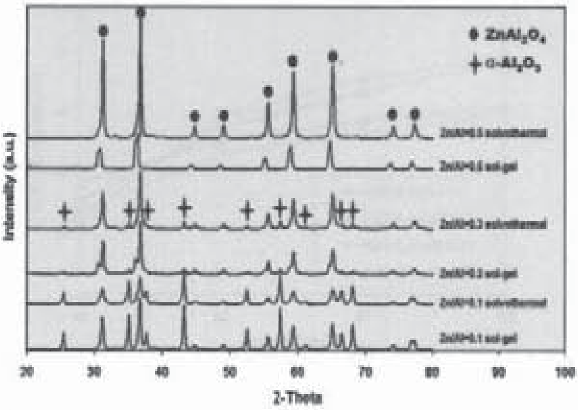
2.4 การศึกษาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

เตรียมตัวเร่งปฏิกิริยา 0.15 กรัม ติดตั้งเครื่องปฏิกรณ์เบดนิ่ง เปิดแก๊สไฮโดรเจนไหลผ่านที่อุณหภูมิ 150°C เป็นเวลา 2 ชั่วโมง จากนั้นลดอุณหภูมิลงที่ 40°C ความดัน 1 บรรยากาศ เปิดสารป้อน (อะเซทิลีนร้อยละ 1.5 ไฮโดรเจนร้อยละ 1.7 ในเอทิลีน) ไหลผ่านด้วยอัตรา 40 มิลลิลิตรต่อนาทีเพื่อทำปฏิกิริยา โดยทำปฏิกิริยาที่อุณหภูมิ 40, 60, 80 และ 100°C ทำการวิเคราะห์แก๊สผลิตภัณฑ์ด้วยเครื่องแก๊สโครมาโทกราฟี

3. ผลการทดลองและวิจารณ์ผล

งานวิจัยนี้แสดงให้เห็นถึงผลของการปรับสภาพอะลูมินาด้วยซิงค์เพื่อใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาแพลเลเดียมในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

ผลวิเคราะห์รังสีเอ็กซ์พบว่าเมื่อทำการปรับสภาพอะลูมินาด้วยซิงค์ที่อัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมต่างๆกันจะเกิดสารประกอบซิงค์อะลูมิเนตขึ้นทั้งวิธีโซล-เจล และโซลไวเทอร์มอล โดยอัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียม 0.1 และ 0.3 จะเกิดสารประกอบซิงค์อะลูมิเนตผสมอยู่กับอะลูมินา ขณะที่อัตราส่วน 0.5 จะเกิดสารประกอบซิงค์อะลูมิเนตเพียงอย่างเดียว



รูป 1 แสดงรูปแบบ XRD ของตัวรองรับอะลูมินาที่ปรับสภาพด้วยซิงค์ที่อัตราส่วนโดยโมลของ อะลูมิเนียมต่อซิงค์ต่างๆกันซึ่งเตรียมโดยวิธีโซล-เจลและโซลไวเทอร์มอล

ตารางที่ 1 แสดงขนาดผลึกของตัวรองรับอะลูมินาที่ปรับสภาพด้วยซิงค์โดยวิธีโซล-เจลและโซลไวเทอร์มอล (α : α-Al_2O_3 , Zn : $ZnAl_2O_4$)

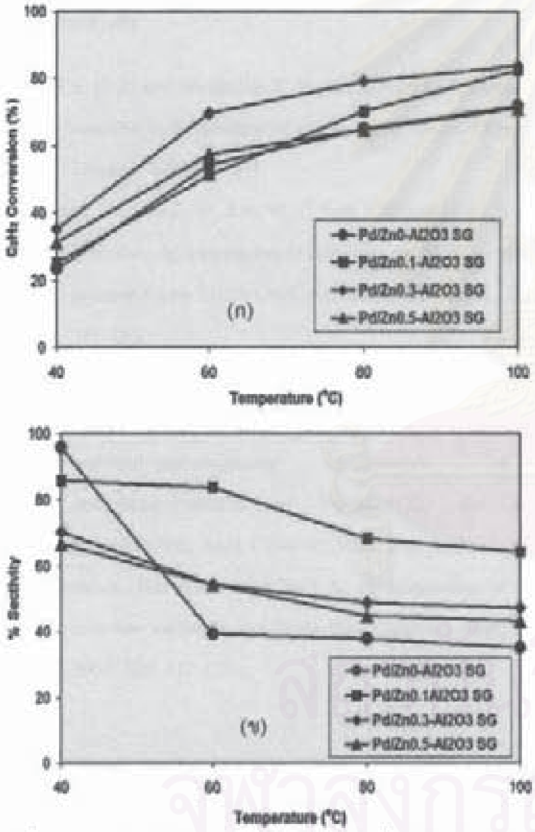
ตัวอย่าง	ขนาดผลึก (nm)
Zn0-Al_2O_3 SG	31.0^{α}
Zn0.1-Al_2O_3 SG	40.4^{α} , 28.0^{Zn}
Zn0.3-Al_2O_3 SG	38.4^{α} , 37.8^{Zn}
Zn0.5-Al_2O_3 SG	14.7^{Zn}
Zn0-Al_2O_3 SV	69.5^{α}
Zn0.1-Al_2O_3 SV	32.8^{α} , 14.9^{Zn}
Zn0.3-Al_2O_3 SV	29.6^{α} , 29.7^{Zn}
Zn0.5-Al_2O_3 SV	41.6^{Zn}

ขนาดผลึกคำนวณโดยสมการ Scherrer ของตัวรองรับต่างๆ แสดงดังตารางที่ 1 พบว่าขนาดผลึกของตัวรองรับอยู่ในระดับนาโนเมตร [12]

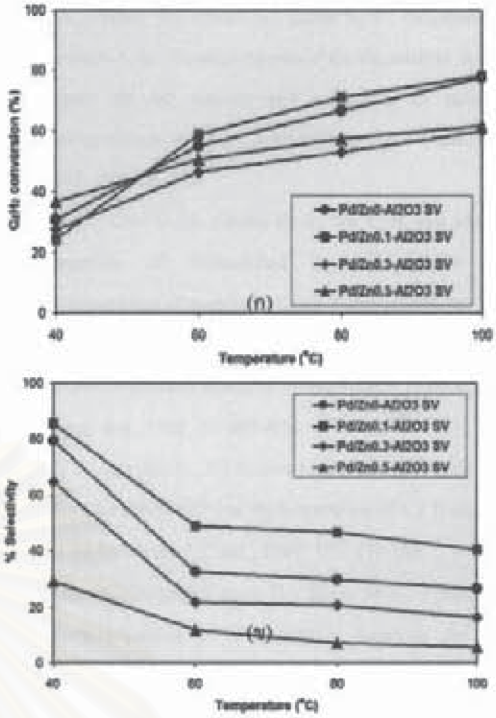
ผลการทดสอบตัวเร่งปฏิกิริยาซึ่งเตรียมโดยวิธีโซล-เจลและโซลไวเทอร์มอล ในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีนในสภาวะที่มีเอทิลีนมากเกินพอ โดยทำปฏิกิริยาที่อุณหภูมิ 40, 60, 80 และ 100°C แสดงดังรูปที่ 2 สำหรับวิธีโซล-เจล, จากรูปที่ 2.ก พบว่าความว่องไวของตัวเร่งปฏิกิริยาในการกำจัดอะเซทิลีนเพิ่มขึ้นเมื่ออุณหภูมิสูงขึ้น และการปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์ทำให้ตัวเร่งปฏิกริยามีความว่องไวเพิ่มขึ้น สำหรับค่าการเลือกเกิดของเอทิลีนแสดงดังรูปที่ 2.ข พบว่าการปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์สามารถเพิ่มค่าเลือกเกิดของเอทิลีนได้ โดยอัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมเท่ากับ 0.1 ให้ค่าเลือกเกิดของเอทิลีนสูงที่สุด

สำหรับวิธีโซลไวเทอร์มอลแสดงดังรูปที่ 3, จากรูปที่ 3.ก พบว่าการปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์ทำให้ตัวเร่งปฏิกิริยามีความว่องไวลดลง สำหรับค่าการเลือกเกิดของเอทิลีนแสดงดังรูปที่ 3.ข พบว่าการ

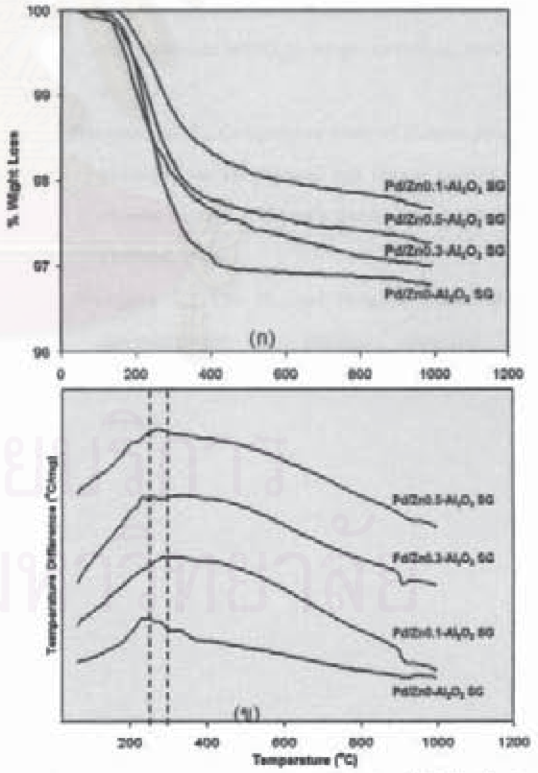
ปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์ไม่สามารถเพิ่มค่าเลือกเกิดของเอทีลีนได้ ยกเว้นที่อัตราส่วนโดยโมลของซิงค์ต่ออะลูมิเนียมเท่ากับ 0.1 ที่ปรับสภาพแล้วมีความว่องไวมากขึ้น แต่ไม่มากเท่ากับการเตรียมโดยวิธีโซลเจล ภายหลังการทำปฏิกิริยา อาจเกิดโค้กสะสมบนพื้นผิวตัวเร่งปฏิกิริยาส่งผลให้ตัวเร่งปฏิกิริยามีความว่องไวลดลง จากผล TGA ของตัวเร่งปฏิกิริยาที่ใช้แล้ว,น้ำหนักที่หายไปประหว่างการเผาตัวเร่งปฏิกิริยาด้วยออกซิเจนแสดงถึงปริมาณโค้กที่สะสมบนพื้นผิวของตัวเร่งปฏิกิริยา [13] จากรูปที่ 4 พบว่าการปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์สามารถลดการเกิดโค้กที่สะสมบนพื้นผิวตัวเร่งปฏิกิริยา โดยอัตราส่วนโดยโมล ของซิงค์ต่ออะลูมิเนียมเท่ากับ 0.1 ซึ่งเตรียมโดยวิธีโซล-เจล มีปริมาณโค้กสะสมบนพื้นผิวของตัวเร่งปฏิกิริยาน้อยที่สุด และจากผล DTA พบ exothermic peak ที่อุณหภูมิประมาณ 300°C แสดงว่าโค้กที่เกิดขึ้นเป็น soft-coke เนื่องจากสามารถกำจัดได้โดยเผาที่อุณหภูมิต่ำกว่า 350°C[13]



รูปที่ 2 แสดงประสิทธิภาพของตัวเร่งปฏิกริยาซึ่งเตรียมโดยวิธีโซล-เจลต่ออุณหภูมิในการทำปฏิกริยา: (ก) อะเซทิลีนที่เข้าทำปฏิกริยา (ข) ค่าเลือกเกิดของเอทีลีน



รูปที่ 3 แสดงประสิทธิภาพของตัวเร่งปฏิกริยาซึ่งเตรียมโดยวิธีโซลโวเทอร์มอลต่ออุณหภูมิในการทำปฏิกริยา: (ก) อะเซทิลีนที่เข้าทำปฏิกริยา (ข) ค่าเลือกเกิดของเอทีลีน



รูป 4 แสดงผล TGA-DTA ของตัวเร่งปฏิกริยาที่ใช้แล้ว ซึ่งเตรียมโดยวิธีโซล-เจล: (ก) ในเทอมของอุณหภูมิกับน้ำหนัก (ข) ในเทอมของอุณหภูมิกับอุณหภูมิที่เปลี่ยนแปลง

4. สรุปผลการทดลอง

การศึกษาคุณลักษณะของตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับอะลูมินาที่ปรับสภาพด้วยซิงค์ในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน พบว่าปริมาณของซิงค์ที่เติมเข้าไปมีผลต่อโครงสร้างของตัวรองรับอะลูมินาและสามารถเกิดเป็นสารประกอบซิงค์อะลูมิเนต เมื่อเปรียบเทียบวิธีในการสังเคราะห์ตัวรองรับระหว่างวิธีโซล-เจล และโซลโวเทอร์มอล พบว่าเมื่อนำอะลูมินาที่ปรับสภาพด้วยซิงค์ซึ่งเตรียมโดยวิธีโซล-เจลมาเป็นตัวรองรับตัวเร่งปฏิกิริยาแพลเลเดียมจะช่วยเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาให้สูงขึ้น นอกจากนี้การปรับสภาพตัวรองรับอะลูมินาด้วยซิงค์สามารถลดการเกิดโค้กที่สะสมบนพื้นผิวตัวเร่งปฏิกิริยา

5. กิตติกรรมประกาศ

ขอบคุณสภาวิจัยแห่งชาติและบัณฑิตวิทยาลัยจุฬาลงกรณ์มหาวิทยาลัยที่ให้ทุนสนับสนุนงานวิจัยนี้

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Selective hydrogenation of acetylene over Pd catalysts supported on nanocrystalline α-Al_2O_3 and Zn-modified α-Al_2O_3

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ABSTRACT

The catalytic performance of Pd catalysts supported on nanocrystalline α-Al_2O_3 and Zn-modified α-Al_2O_3 prepared by sol–gel and solvothermal methods was studied in the selective hydrogenation of acetylene. Acidity of the nanocrystalline α-Al_2O_3 was significantly decreased by incorporation of Zn atoms in the α-Al_2O_3. Both of acetylene conversions and ethylene selectivities were improved in the order: Pd/Zn-modified α-Al_2O_3-sol–gel > Pd/Zn-modified α-Al_2O_3-solvothermal > Pd/α-Al_2O_3-sol–gel ≈ Pd/α-Al_2O_3-solvothermal >> Pd/α-Al_2O_3-commerical. As revealed by thermal gravimetric and differential temperature analysis (TG-DTA), Pd catalysts on the nanocrystalline Zn-modified α-Al_2O_3 also showed less deactivation by coke formation.

1. Introduction

Pd-based catalyst supported on Al_2O_3 with low Pd loading (0.1–0.3 wt.%) is typically employed for selective hydrogenation of acetylene in ethylene feedstock [1–3]. Removal of acetylene is a crucial process in polyethylene production since acetylene poisons the polymerization catalysts [4,5]. The Al_2O_3 used as Pd catalyst support in this reaction contains mostly the α-phase Al_2O_3 since it possesses relatively low specific surface area and low acidity compared to other 'transition' alumina (such as β-, γ-, η-, χ-, κ-, δ-, θ-phase Al_2O_3). With respect to selectivity changes, catalysts with low dispersion were suggested to give better selectivity toward ethylene [1,2].

In recent years, nanocrystalline materials have gained considerable interest in the field of catalysis because they show significant differences in terms of catalytic activity and selectivity compared with those synthesized in micron scale. Several techniques have been reported for preparation of nanocrystalline Al_2O_3 such as sol–gel method [6], hydrothermal synthesis [7], microwave synthesis [8], emulsion evaporation [9], precipitation from solution [10], and solvothermal synthesis [11]. The sol–gel method is widely used due to its simplicity, however, the precipitated powders obtained are amorphous in nature and further heat treatment is required for crystallization. Solvothermal method is an alternative route for one-step synthesis of nanocrystalline materials.

In the present study, nanocrystalline α-Al_2O_3 and Zn-modified α-Al_2O_3 have been synthesized via sol–gel and solvothermal methods and employed as supports for Pd catalysts for selective hydrogenation of acetylene. Modification of nanocrystalline α-Al_2O_3 with zinc is studied because it can form $ZnAl_2O_4$ spinel which is an interesting material with low acidity that can exhibit the strong metal-support interaction (SMSI) with noble metal [12–14]. Based on the work reported by Moon et al. [15], addition of TiO_2 to Pd/SiO_2 catalysts has shown improvement in ethylene selectivity and less catalyst deactivation during selective acetylene hydrogenation. The origin of the improvement in catalyst performance was proposed to be due to strong interaction between the added TiO_2 and Pd. Thus, the presence of $ZnAl_2O_4$ in the Pd/α-Al_2O_3 catalyst may improve the catalytic performance in the selective acetylene hydrogenation as well. The molar ratio of Zn/Al = 0.1 was selected in order to avoid the formation of $ZnAl_2O_4$ alone so that surface area of the Zn-modified supports were not much different from that of the unmodified α-Al_2O_3. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, ammonia temperature program desorption (NH_3-TPD), CO chemisorption, transmission electron microscope (TEM), and thermal gravimetric and differential temperature analysis (TG/DTA).

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2. Experimental

2.1. Catalyst preparation

Nanocrystalline α-Al_2O_3 were prepared by sol–gel and solvothermal methods. In the sol–gel method, 24 g of aluminum nitrate was dissolved in 50 ml of ethanol at room temperature. The solution was then heated to 70–80 °C in the reflux-condenser reactor and held for 18 h, after which the urea solution 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 two 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 and held at that temperature for 3 h. The solvothermal-derived α-Al_2O_3 were prepared according to the method described in Ref. [16] using aluminum isopropoxide and toluene. For the preparation of Zn-modified α-Al_2O_3 by sol–gel and solvothermal method, an appropriate amount of zinc (II) nitrate hexahydrate and zinc (II) acetylacetonate (Zn/Al molar ratio = 0.1) were added to the precursor mixture of each method, respectively.

Approximately 0.3 wt.% Pd on α-Al_2O_3 and Zn-modified α-Al_2O_3 were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of $Pd(NO_3)_2$ (Aldrich). The catalysts were dried overnight at 110 °C and then calcined in N_2 flow 60 ml/min with a heating rate of 10 °C/min until the temperature reached 500 °C and them in air flow 100 ml/min at 500 °C for 2 h. For comparison purposes, a commercial α-Al_2O_3 (JRC-ALO2) was also employed as Pd catalyst support.

2.2. Catalyst characterization

X-ray diffraction patterns of the catalyst samples were obtained with a SIEMENS D5000 X-ray diffractometer using Cu Kα radiation with a Ni filter. The BET surface area measurements were carried out by nitrogen adsorption in a Micromeritic Chemisorb 2750 system. Each sample was degassed at 200 °C for 2 h. The analysis gas consisting of 30% N_2 in helium was adsorbed on the samples at low temperature by dipping cell into liquid nitrogen dewar. Ammonia temperature program desorption (NH_3-TPD) was performed in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Approximately 0.1 g of catalyst was placed in a quartz tube in a temperature-controlled oven. The amounts of CO chemisorbed on the catalyst were measured using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior to chemisorption, the sample was reduced in a H_2 flow at 150 °C for 2 h then cooled down to ambient temperature in a He flow. The distribution of palladium on catalyst supports were observed using JEOL Model JEM-2010 transmission electron microscope operated at 200 keV. Thermal gravimetric and differential temperature analysis (TG/DTA) were performed using an SDT Analyzer Model Q600 from TA Instruments, USA.

2.3. Reaction study

Selective acetylene hydrogenation was performed in a pyrex tube reactor (i.d. 10.1 mm). Prior to the start of each experimental run, the catalyst was reduced in H_2 at 150 C for 2 h. Then the reactor was purged with Ar and cooled down to the reaction temperature. Feed gas was composed of 1.5% C_2H_2, 1.7% H_2 and balanced C_2H_4 (TIG Co., Ltd.) with a GHSV of 16,901 h^{-1}. The composition of products and feeds were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). The temperature dependence of the catalytic performance was observed during the range of 40–100 C in 20 C increments.

Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. However, due to 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) was used. The ethylene being hydrogenated to ethane is the difference between all the hydrogen consumed and all the acetylene totally hydrogenated.

$$\text{Selectivity of } C_2H_4\ (\%) = \frac{100 \times [dC_2H_2 - (dH_2 - dC_2H_2)]}{dC_2H_2} \qquad (1)$$

where dC_2H_2 = mole of acetylene in feed – mole of acetylene in product, dH_2 = mole of hydrogenation in feed – mole of hydrogen in product.

3. Results and discussion

The XRD patterns of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 are shown in Fig. 1. The diffraction patterns were not different from those of the corresponding unmodified α-Al_2O_3 and Zn-modified α-Al_2O_3 supports. The characteristic peaks of α-Al_2O_3 were evident for Pd/α-Al_2O_3 samples while the diffraction lines of both spinel-type $ZnAl_2O_4$ structure and α-Al_2O_3 were apparent for the Pd/Zn-modified α-Al_2O_3 catalysts. The average crystallite sizes of each crystal phase were calculated from the Scherrer equation and are given in Table 1. The crystallite sizes α-Al_2O_3 and $ZnAl_2O_4$ were calculated from the full width at half maximum of the XRD peaks at 2θ = 43° and 37°, respectively. The average crystallite sizes of the α-Al_2O_3 prepared by sol–gel and solvothermal method were 31 and 69.5 nm, respectively while the crystallite sizes of $ZnAl_2O_4$ formed in the Zn-modified Al_2O_3 prepared by sol–gel and solvothermal method were 28 and 14.9 nm, respectively. The surface areas of the catalysts prepared by sol–gel were ranged from 1.6 to 2.3 m^2/g while those prepared by solvothermal were ranged from 10.5 to 14.9 m^2/g. The surface areas were quite low probably due to high agglomeration of these nanocrystalline particles during calcination at high temperature. The nitrogen adsorption–desorption isotherms and the pore size distribution plots are shown in Figs. 2 and 3, respectively. Based on the nitrogen adsorption–desorption isotherms at 77 K, all the samples exhibited Type IV adsorption isotherms according to Brunauer Deming, Deming and Teller (BDDT) classification [17]. The sol–gel Al_2O_3, however, pos-

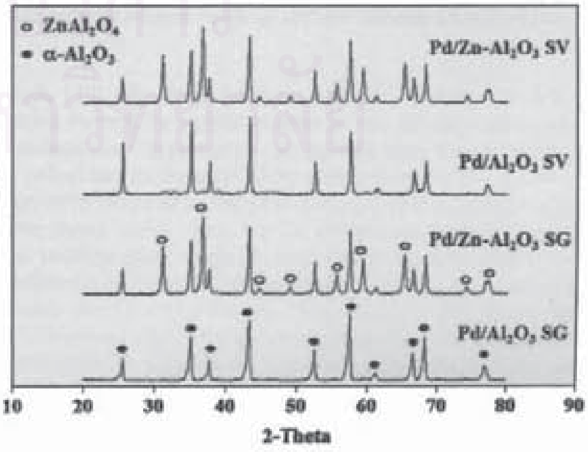

Fig. 1. XRD patterns of the Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 supports prepared by sol-gel (SG) and solvothermal (SV) methods.

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Table 1
Characteristics of the various Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts

Sample	Crystallite size (nm)		BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Pd active sites ($\times 10^{-17}$ molecule CO/g cat.)	Pd dispersion (%)	d_p Pd^0 (nm)
	α-Al_2O_3	$ZnAl_2O_4$						
Pd/Al_2O_3 SG	31.0	n.d.[a]	1.6	0.011	20.4	11.3	8.8	13
Pd/Zn–Al_2O_3 SG	40.4	28	1.9	0.020	11.8	4.9	3.9	29
Pd/Al_2O_3 SV	69.5	n.d.	14.9	0.075	13.6	32.9	20.8	5
Pd/Zn–Al_2O_3 SV	32.8	14.9	10.7	0.100	22.4	22.8	16.6	7

[a] n.d. = not determined.

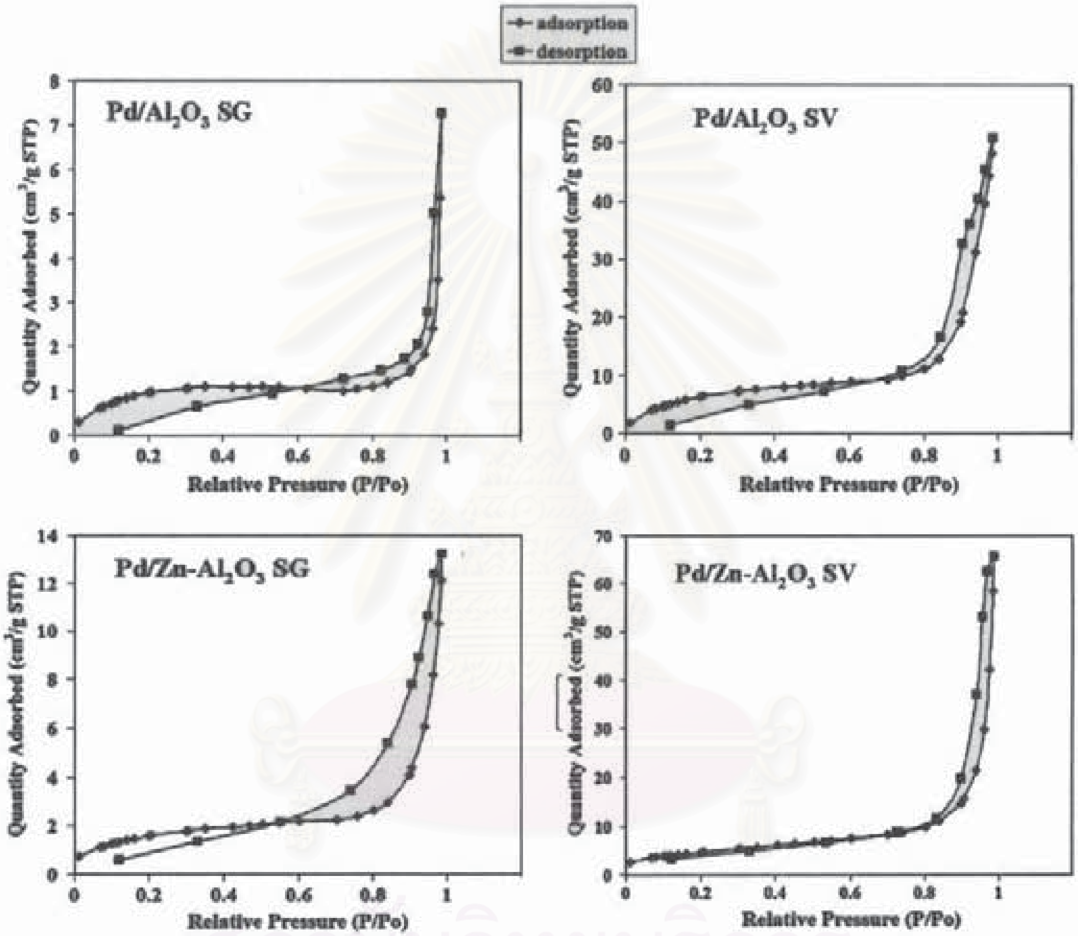

Fig. 2. N_2 adsorption–desorption isotherms of the Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 supports prepared by sol–gel (SG) and solvothermal (SV) methods.

sessed much less pore volume than the samples prepared by the solvothermal method. Incorporation of Pd particles by impregnation did not alter the textural properties of the supports as shown by similar pore size distributions in Fig. 3.

Fig. 4 shows the TEM micrographs with SAED patterns of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 prepared by sol–gel and solvothermal methods. It can be seen that the sol–gel made catalysts consisted of agglomerated particles with primarily irregular shape structure (average particle size around 0.5–1 μm) whereas for those prepared by solvothermal method, agglomeration of finger-like particles were observed. The finger-like α-Al_2O_3 particles are normally obtained by calcination of the solvothermal-made α-Al_2O_3 powders at high temperature [18,19]. For Pd/Zn-modified α-Al_2O_3, the corresponding selected area diffraction patterns shows rings match d-spacing for the $ZnAl_2O_4$ confirmed the structure of $ZnAl_2O_4$ [20]. The large particles observed maybe the secondary particles formed by agglomeration of the primary nano-particles due to heat treatment during calcinations step. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5–10 nm were found to be deposited on both of the alumina supports.

The metal active sites, the Pd dispersion, and the average Pd metal particle sizes from CO chemisorption experiment are also summarized in Table 1. The technique is based on the assumption that only one CO molecule adsorbed on one metal active site [21] and it is known that CO did not chemisorb on Al_2O_3 support [22–24]. Without Zn addition on the Al_2O_3 supports, Pd/Al_2O_3 sol–gel and Pd/Al_2O_3 solvothermal possessed the amounts of Pd active sites 11.3 × 10^{17} and 32.8 × 10^{17} sites/g cat., respectively. The Pd active sites significantly decreased when the catalysts were supported on Zn-modified α-Al_2O_3. The Pd/Zn–Al_2O_3 SG and Pd/Zn–

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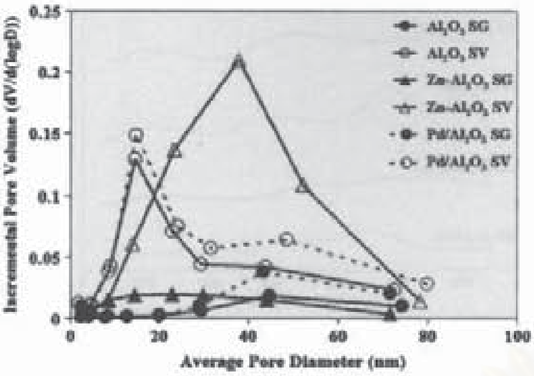

Fig. 3. Pore size distributions of the α-Al_2O_3, Zn-modified α-Al_2O_3, and Pd/α-Al_2O_3.

Al_2O_3 SV possessed the amounts of Pd active sites 4.86×10^{17} and 22.7×10^{17} sites/g cat., respectively. Thus, the catalysts on Zn-modified Al_2O_3 had lower Pd dispersion and larger Pd particle size (as determined from CO chemisorption experiments). Comparing the samples prepared by different techniques, the catalysts prepared by sol–gel method showed lower amount of Pd active sites and Pd dispersion than the catalysts prepared by solvothermal method due probably to more agglomeration of the α-Al_2O_3 supports as noticed from TEM measurements.

NH_3 temperature program desorption was a commonly used technique for the titration of surface acid sites [25]. The strength of an acid site could be related to the corresponding desorption temperature, while the total amount of ammonia desorption after saturation coverage permits quantification of the number of acid sites at the surface. The temperature-programmed desorption profiles for the nanocrystalline α-Al_2O_3 and Zn-modified α-Al_2O_3 supports are shown in Fig. 5. It was found that the desoprtion peak areas of the α-Al_2O_3 samples prepared by sol–gel method were lower that prepared by solvothermal method. Moreover, regardless of the preparation method used, the desorption peak areas of Zn-modified α-Al_2O_3 decreased. It is suggested that formation of $ZnAl_2O_4$ species resulted in a decrease of surface acidity of α-Al_2O_3 [26].

The catalytic properties of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts were evaluated in the selective hydrogenation of acetylene using a fixed bed flow reactor with a GHSV of 16,901 h^{-1}. Study of temperature dependence of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts on acetylene conversion and selectivity toward ethylene in the temperature range between 40 and 100 °C are shown in Fig. 6. For comparison purposes, selective acetylene hydrogenation using Pd catalysts supported commercial

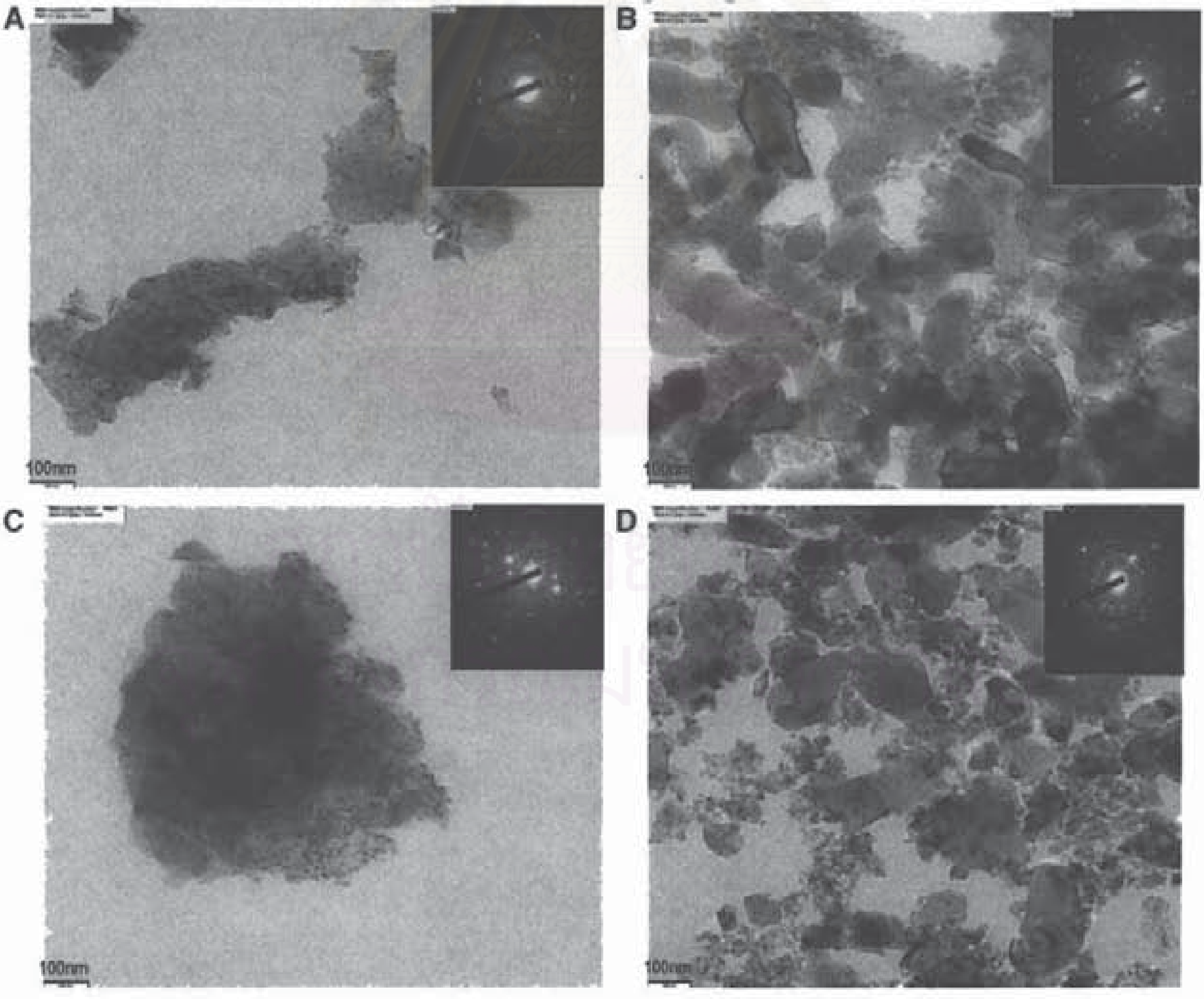

Fig. 4. TEM micrographs of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts prepared by sol–gel (SG) and solvothermal (SV) methods with SAED pattern: (A) Pd/Al_2O_3 SG (B) Pd/Al_2O_3 SV (C) Pd/Zn–Al_2O_3 SG (D) Pd/Zn–Al_2O_3 SV.

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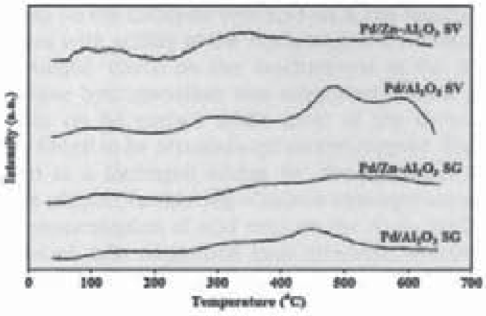

Fig. 5. NH_3 temperature program desorption profiles for the Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 supports prepared by sol–gel (SG) and solvothermal (SV) methods.

α-Al_2O_3 was also carried out. In all cases, acetylene conversion increased with increasing temperature while ethylene selectivity decreases due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. Acetylene conversion as well as ethylene selectivity was found to be in the order: Pd/Zn-modified α-Al_2O_3-sol–gel > Pd/Zn-modified α-Al_2O_3-solvothermal > Pd/α-Al_2O_3-sol–gel ≈ Pd/α-Al_2O_3-solvothermal >> Pd/α-Al_2O_3-commerical. It was clearly seen that the use of nanocrystalline α-Al_2O_3 prepared by sol–gel or solvothermal method resulted in much better catalyst performance compared to the commercial one. It can be noticed that Pd/Al_2O_3-SV had the largest Pd active sites; however, it exhibited the lowest activity. This can probably be explained by the dependent of acetylene hydrogenation activity on Pd particle size. Many researchers have shown that the specific activity of Pd decreased by an order of magnitude when the size of palladium particles were very small (1–5 nm) [27–29]. Modification of Pd/α-Al_2O_3 catalysts with Zn, however, resulted in significantly improvement of both acetylene conversion and ethylene selectivity. Comparing the samples prepared by the different techniques, the catalysts prepared by sol–gel method showed better catalytic properties than the catalysts prepared by solvothermal method.

After reaction, the amounts of carbonaceous deposits on the catalyst samples were measured by thermal gravimetric analysis and the results are shown in Fig. 7. A small weight loss (<1%) observed in the TGA profiles (Fig. 5A) below 200 °C was probably due to the removal of physisorbed water and/or chemisorbed hydroxyl groups. The weight loss at higher temperature was due to oxidation of the carbonaceous deposited on the surface of used catalysts [30]. As shown by the exothermic peaks in Fig. 5B, the type of coke species occurred during reaction was probably "soft coke" since it could be removed from the used catalysts by oxidation at a relative lower temperature (~350 °C) as suggested by Xiangjing et al. [31]. Based on TGA results, the amount of coke deposits on the catalysts prepared by sol–gel method were lower than those prepared by solvothermal method while Pd/Zn-modified α-Al_2O_3 prepared by sol–gel method showed the lowest value (2.33 wt.%) and Pd/α-Al_2O_3 prepared by solvothermal method showed the highest valve (6.39 wt.%). For Pd/α-Al_2O_3-commerical, the amount

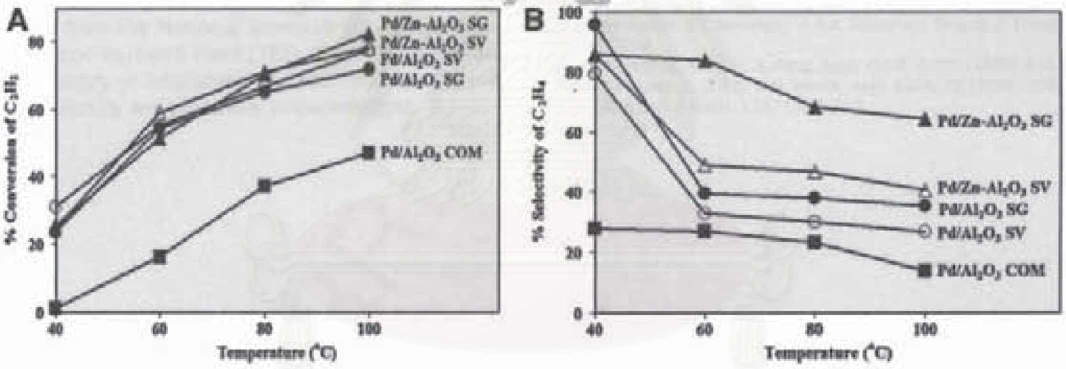

Fig. 6. Temperature dependence of the catalytic performance of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts; (A) in terms of % conversion of C_2H_2 (B) in terms of % selectivity of C_2H_4.

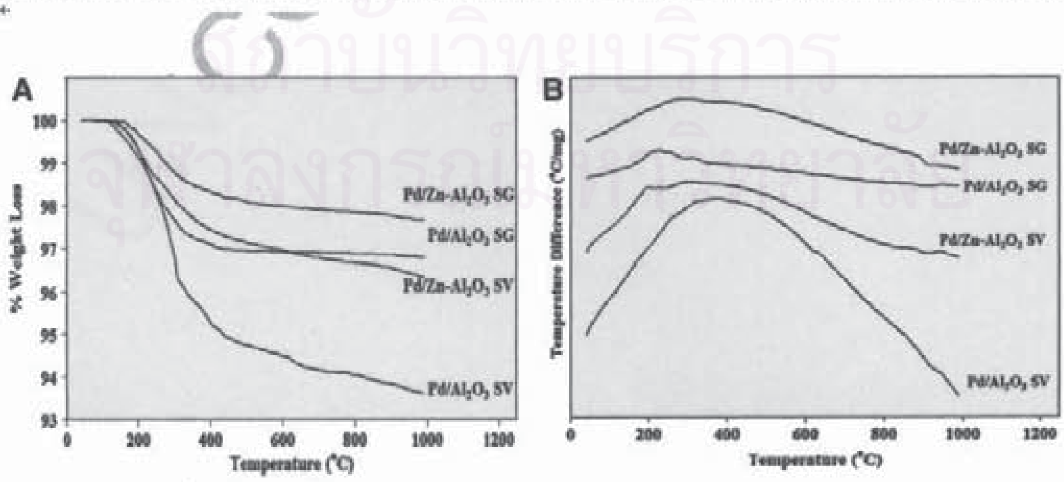

Fig. 7. Thermal gravimetric and differential temperature analysis (TG/DTA) of Pd/α-Al_2O_3 and Pd/Zn-modified α-Al_2O_3 catalysts after reaction: (A) in terms of temperature (°C) and weight loss (%), (B) in terms of temperature (°C) and temperature difference (°C/mg).

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of coke deposits on the catalysts was 3.53 wt.% The results were in good agreement with acidity of the Al_2O_3 supports measured from NH_3 TPD technique. Based on the mechanisms in the literature [32,33], acetylene hydrogenation was suggested to take place on the active sites on Pd surface while most of the carbonaceous deposits were found to be accumulated on the support. The carbon deposits acted as a hydrogen bridge for the hydrogen spillover from Pd to the support facilitating ethylene hydrogenation to ethane. The low concentration of acid sites on the Al_2O_3 surface considerably reduced coke deposition thus ethylene selectivity was improved.

4. Conclusions

Modification of α-Al_2O_3 supports by Zn drastically decreased surface acidity of Al_2O_3 due to formation of $ZnAl_2O_4$ species. When used as the supports for Pd catalysts in selective acetylene hydrogenation, the catalysts exhibited lower Pd dispersion and larger Pd particle size (as determined from CO chemisorption experiments) compared to those on the unmodified ones. The Pd/Zn-modified α-Al_2O_3 catalysts showed higher acetylene conversion and ethylene selectivity and less amount of carbonaceous deposits than Pd on the unmodified and commercial α-Al_2O_3. Comparing the samples prepared by the different techniques, the catalysts prepared by sol–gel method showed better catalytic properties than those prepared by solvothermal method due to larger Pd particle size and lower amount of acid sites obtained.

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