ผลของการปรับสภาพอะลูมินาด้วยนิกเกิลต่อสมบัติของตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาในปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน

นายนิติกร ว่องวรานนท์

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EFFECT OF Ni-MODIFIED Al_2O_3 ON THE PROPERTIES OF Pd/Al_2O_3 CATALYST IN SELECTIVE ACETYLENE HYDROGENATION

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งานวิจัยนี้ ศึกษาผลของอะลูมินาที่ปรับสภาพด้วยนิกเกิลที่อัตราส่วนโดยโมลของนิกเกิลต่ออะลูมิเนียมต่างๆ ซึ่งเตรียมโดยวิธีโซล-เจลและวิธีโซลโวเทอร์มอลต่อสมรรถนะตัวเร่งปฏิกิริยาแพลเลเดียมบนอะลูมินาสำหรับปฏิกิริยาไฮโดรจิเนชันแบบเลือกเกิดของอะเซทิลีน พบว่าสมรรถนะตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับตัวเร่งปฏิกิริยาที่ปรับสภาพด้วยนิกเกิลให้ผลที่ดีกว่าตัวเร่งปฏิกิริยาแพลเลเดียมบนตัวรองรับแอลฟาอะลูมินาในอุตสาหกรรม โดยตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีโซล-เจล ที่อัตราส่วนโดยโมลของนิกเกิลต่ออะลูมิเนียมเท่ากับ 1 ให้ค่าเลือกเกิดของเอทิลีนสูงสุด ในขณะที่ตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีโซลโวเทอร์มอลอัตราส่วนโดยโมลของนิกเกิลต่ออะลูมิเนียมเท่ากับ 0.3 ให้ค่าเลือกเกิดของเอทิลีนสูงที่สุด ที่อัตราส่วนโดยโมลของนิกเกิลต่ออะลูมิเนียมเท่ากัน (0.5) ค่าเลือกเกิดของเอทิลีนของตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีโซล-เจลให้ค่าสูงกว่าตัวอย่างตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีโซลโวเทอร์มอล ผลวิเคราะห์จากการกระเจิงรังสีเอ็กซ์แสดงให้เห็นว่าอัตราส่วนโดยโมลของนิกเกิลต่ออะลูมิเนียมมีผลต่อโครงสร้างผลึกของตัวรองรับตัวเร่งปฏิกิริยาอะลูมินาและการเกิดสารประกอบระหว่างอะลูมินาและนิกเกิล จากการวิเคราะห์โดยการดูดซับแอมโมเนียแบบโปรแกรมอุณหภูมิแสดงให้เห็นว่าการเกิดผลึกนิกเกิลอะลูมิเนต ส่งผลต่อการลดความเป็นกรดของตัวรองรับตัวเร่งปฏิกิริยาอะลูมินาและลดการเกิดโค้กที่สะสมบนพื้นผิวตัวเร่งปฏิกิริยา นอกจากนี้ยังอาจส่งผลต่อสมบัติของพื้นผิวแพลเลเดียมทำให้ค่าเลือกเกิดของเอทิลีนสูงขึ้น

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NITIKON WONGWARANON: EFFECT OF Ni-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., 118 pp.

In this study, the effect of Ni-modified Al_2O_3 prepared by sol-gel and solvothermal methods with varying Ni/Al molar ratios on catalytic performances of supported Pd catalysts for selective hydrogenation of acetylene has been studied. It was found that catalytic performances of the Pd catalyst supported on Ni-modified Al_2O_3 were superior compared to those of Pd-supported on commercial α-Al_2O_3. For the sol-gel-made samples, when Ni/Al ratio was 1, the highest ethylene selectivity was achieved whereas for the solvothermal-made samples, the utmost ethylene selectivity was obtained when Ni/Al ratio was 0.3. For a similar Ni/Al ratio (0.5), ethylene selectivity of the sol-gel-made samples was higher than that of solvothermal-made. From X-ray diffraction, it is suggested that varying Ni/Al ratio directly affected the crystalline phases of alumina supports and formation of nickel-alumina compounds. A revealed by NH_3 temperature programmed desorption studies, 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. Moreover, formation of $NiAl_2O_4$ could modify the properties of Pd surface so that high ethylene selectivities were obtained.

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CHAPTER I

INTRODUCTION

1.1 Rationale

Ethylene is light hydrocarbon which does not occur in nature. Ethylene can be prepared by dehydration of ethanol with sulfuric acid at about 180°C or derived from natural gas and petroleum, by cracking and fractional distillation. Ethylene is an important raw material in the synthesis of many chemicals. It is used in making polyethylene and saran, in the manufacture of ethanol and ethylene oxide, and as an anesthetic. Ethylene was called olefiant gas by the early chemists.

In general, ethylene production contains small proportions of acetylenic compounds. Ethylene stream from a naphtha cracker unit contains about 0.1-1 wt% of acetylene. 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, acetylene content in the ethylene feed has to be reduced to the low ppm-range. The methods used for removing trace amount of acetylene in ethylene stream are the selective catalytic hydrogenation of acetylene to ethylene and the adsorption acetylene from ethylene by zeolite, but the first method is more popular for the industrial process.

The selective catalytic hydrogenation reaction of acetylene to ethylene is usually performed on a supported palladium catalyst. Generally, the catalyst support must present a good stability at high temperature. 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 frequently studied support for palladium catalyst in selective acetylene hydrogenation is α-Al_2O_3.

Typically, α-Al_2O_3 has a relatively low surface area of approximately 0.1-3 m^2/g and Pd loading is around 0.001-1 wt%. Compared to Pd/γ-Al_2O_3, lower ethane is formed on Pd/α-Al_2O_3 catalyst due to the smaller amount of oligomers/deposits that can act as hydrogen reservoir for over hydrogenation of ethylene product (Sárkány *et al.*, 1986). Moreover, catalysts of low dispersion have been suggested to give better selectivity towards ethylene (Hub *et al.*, 1988 and Boitiaux *et al.*, 1983) since certain fraction of sites that are not covered by acetylene provides ethylene hydrogenation. Modification of palladium surface by promoting with a second metal especially the metal of group IB such as Ag (Praserthdam *et al.*, 2002 and Ngamsom *et al.*, 2004), K (Park *et al.*, 1992), Si (Shin *et al.*, 1998), Au (Sárkány *et al.*, 2002), Cu (Guczi *et al.*, 1999), and Co (Sárkány *et al.*, 1995) has been reported to improve the catalyst performance (Ryndin *et al.*, 1988 and Guczi *et al.*, 1994). Changing the electron density of palladium influences the relative adsorption strength of the reactant, intermediates, and hydrogen. Additionally, active site may be partly blocked by a second metal. However, modification of α-Al_2O_3 support in the Pd/α-Al_2O_3 catalyst has not been studied very often.

It is interesting to study the effect of Ni-modified α-Al_2O_3 on the properties of Pd/α-Al_2O_3 catalyst because it can easily from nickel aluminate ($NiAl_2O_4$) spinel which is a highly stable material that can have beneficial effect on the catalyst properties. As shown in the literature, Ni supported on $NiAl_2O_4$ is more resistant to deactivation by coke formation during the reforming of methane and acetylene hydrogenation processes than those deposited on other supports (Al-Ubaid *et al.*, 1988, Bhattacharyya *et al.*, 1994, and Murthy *et al.*, 1993).

The main purpose of this thesis is to investigate the characteristics and catalytic properties of Ni-modified Al_2O_3 supported Pd catalysts in selective hydrogenation of acetylene. The effects of preparation method such as sol-gel and solvothermal method as well as the Ni/Al ratio on the properties of the final Pd/α-Al_2O_3 catalysts were focused.

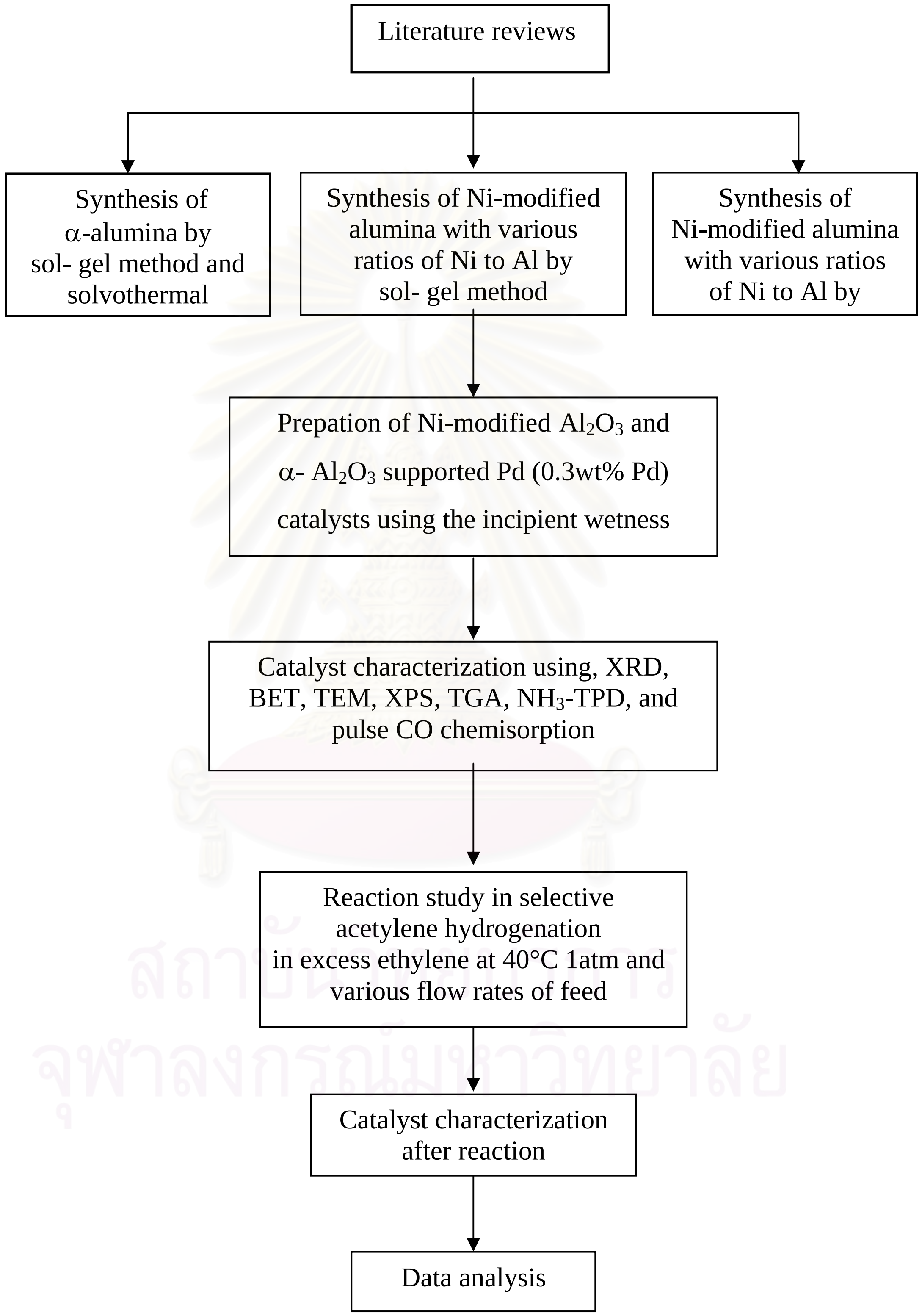
1.2 Objective

The objective of this research is to investigate the characteristics and catalytic properties of sol-gel and solvothermal derived Ni-modified α-Al_2O_3 supported Pd catalysts in selective acetylene hydrogenation in excess ethylene with various Ni/Al ratios.

1.3 Research Scopes

1. Preparation of α-Al_2O_3 by sol- gel and solvothermal methods.
2. Preparation of Ni-modified α-Al_2O_3 with various molar ratios of Ni to Al (0.3, 0.5 and 1) by sol-gel and solvothermal methods.
3. Preparation of α-Al_2O_3 and Ni-modified α-Al_2O_3 supported Pd catalysts (0.3 wt% Pd) using the incipient wetness impregnation method.
4. Characterization of the catalyst samples using X- ray diffraction (XRD), BET surface area analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), CO pulse chemisorption, and NH_3-temperature program desorption.
5. Study of the catalyst performance in selective acetylene hydrogenation using a fixed-bed quartz reactor.
6. Study of catalyst deactivation after performing acetylene hydrogenation using temperature program oxidation.

1.4 Research Methodology



CHAPTER II

LITERATURE REVIEWS

Selective hydrogenation of hydrocarbons with multiple unsaturation, i.e., dienes and acetylenes (alkynes) to achieve partial hydrogenation and to synthesise monoenes is of fundamental importance. Specifically, the selective hydrogenation of acetylene in ethylene rich stream is a crucial process in polyethylene production with the aim of the complete elimination of acetylene, which poisons the polymerization catalysts. Typically, supported palladium catalyst is employed for this process due to its good activity and selectivity. Nevertheless, various factors have shown to affect the performance of Pd catalysts for the selective hydrogenation of acetylene such as addition of a second metal and pretreatment with oxygen-containing compounds. This chapter summarizes the recent reports on (2.1) supported Pd catalysts in selective hydrogenation reaction and (2.2) Ni-modified catalyst in selective hydrogenation reaction. Comments on the previous studies are given in section (2.3).

.

2.1 Supported Pd Catalyst in Selective Hydrogenation Reaction

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

S. Asplund (1996) studied the catalyst aging by coke formation for the selective hydrogenation of acetylene in the presence of excess ethylene on supported palladium catalyst. He found that the deposited coke have a substantial influence on the effective diffusivity, which decreased about one order of magnitude during 100 h of operation. He also observed previously the selectivity for the undesired ethane was higher on aged catalysts, while the activity for acetylene hydrogenation was almost constant. However, these effects were strongly dependent on the catalyst particle size, although the behavior of fresh catalysts was unaffected by mass transfer limitations. When the catalyst used was Pd/Al_2O_3 the change in selectivity with aging could be explained solely as a consequence of the increased diffusion resistance. The mass transfer effects were important also on Pd/Al_2O_3, but on this catalyst there was an additional increase in ethane selectivity that could not be attributed to diffusion limitations. Calculations and experimental tests showed that the observed phenomena are relevant also for the shell-type catalysts normally used industrially. The coke formation itself was about four to five times faster on Pd/α-Al_2O_3 compared to the α-Al_2O_3 supported catalyst. The coke was generally concentrated towards the pellet periphery showing the influence of diffusion resistance also on the coke-forming reactions.

E. W. Shin *et al*. (1998) synthesized supported Pd catalysts modified with Si deposited on the support by silane decomposition when used in acetylene hydrogenation; the Si-modified catalysts show higher selectivity for ethylene and produce less amount of green oil than the unmodified Pd catalysts. They suggested that Si covers the Pd surface as Si or SiO_2 patches. The Pd surface is diluted with the deposited Si. However, the electronic property of the Pd surface seems to be unaffected by the Si species. They conclude that improved performance of the Si modified catalysts comes mostly from geometric modification of the Pd surface by Si.

J. H. Kang *et al.* (2000) studied the effect of transition-metal oxides as promoters of the Pd catalyst for acetylene hydrogenation. Transition-metal oxides added to Pd/SiO_2 improve significantly the activity and the ethylene selectivity of the catalyst in acetylene hydrogenation, which is caused by the interaction between the oxides and the Pd surface similar to the case of the oxide-supported catalysts. They confirmed that metal oxide spread on and modify both geometrically and electronically the Pd surface after the catalyst is reduced at 500^{o}C. Such a behavior of metal oxides in the catalyst is correlated well with their promotional effect on the catalyst performance. They found that the oxide on the Pd surface retard the sintering of the dispersed Pd particles, suppresses the adsorption of ethylene in the multiply-bound mode, and facilitates the desorption of ethylene produced by acetylene hydrogenation. Among the three metal oxides examined in this study, titanium oxide is found to have the most promotional effect.

Q. Zhang *et al.* (2000) studied an alloy of palladium and silver dispersed on Al_2O_3 for the selective hydrogenation of acetylene. They reported that the activity of Pd–Ag catalyst is lower than that of pure metal Pd catalyst. But the selectivity of Pd–Ag catalyst is higher and less impaired by temperature increase than that of Pd catalyst. They also found that metal Pd and Ag can form an alloy on the surface of alumina. There is a synergetic effect in the hydrogenation of acetylene over Pd–Ag catalyst. Addition of Ag to Pd catalyst decreases the quantity of absorption hydrogen, and reduces absorption hydrogen spill over from the bulk of the metals to react with acetylene, which increases the selectivity of acetylene hydrogenation to ethylene.

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 indicate that it is produced in smaller amounts and its average chain length is shorter on a Si-modified catalyst than on an unmodified one. The above findings are 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 is believed to arise from the geometric modification of the Pd surface with small clusters of the Si species.

2.2 Ni-Modified Catalyst in Selective Hydrogenation Reaction

J. A. Peña (1995) studied Ni/$NiAl_2O_4$ catalyst for the hydrogenation of acetylene to ethylene and ethane. They reported the evolution of activity and selectivity and coke behavior. These studies have been carried out on fresh catalyst and on catalyst samples subjected to an accelerated thermal aging process. The results show that the catalytic activity increases with time on stream (activation period), until a point is reached in which catalyst deactivation predominates (deactivation period). They also found that a few coking/regeneration cycles are enough to cause significant changes in the kinetic behavior of the catalyst. These changes are selective in nature and decrease the coke formation rate, while increasing the total observed rates of hydrogenation to ethane and ethylene. The net rate of active site generation is higher for the aged catalyst, and a faster apparent activation rate is obtained. Also, because of the lower deactivation rate, a greater number of active sites are present when the activation and deactivation rate are balanced, and therefore higher maximum hydrogenation yields are obtained with the aged catalyst.

J. C. Rodriguez and coworkers (1997) studied the influence of zinc addition on the catalytic performance and physicochemical properties of nickel-based catalyst used in selective hydrogenation of acetylene were investigated. They found that the activity and selectivity to ethylene of the nickel-based catalysts were positively modified by incoperation of zinc into their solid structure. The zinc-modified catalysts produced smaller amounts of coke and methane than those not containing zinc. Coke deposition had a strong effect on the ethylene selectivity. However, this influence was much more significant for zinc-modified catalysts than for non modified nickel-based solids. They also found that the case of zinc-modified catalyst, the metal nickel phase was interacting strongly and highly interdispersed in a non stoichiometric zinc aluminate spinel matrix. The high interdispersion of the metal nickel phase diminished the number of three-nickel-atom arrangements necessary for the formation of surface intermediates that led to coke and methane production. The non modified nickel-based solids, however, were composed of large metal crystallites on which coke and methane precursored of large metal crystallites on which coke and methane precursors were very easily formed. The high interaction between metal nickel particles and the zinc aluminate matrix prevented whisker formation to some extent. The low concentration of acid sites on the solid surface considerably reduced amorphous-like coke deposition.

V. Rives and coworkers (1998) studied Ni-containing catalysts for selective acetylene hydrogenation to ethylene have been prepared by controlled calcination of hydrotalcite-like precursors. They also found that in addition to Ni and Al, Cr and Zn were added to improve the catalytic performance. Despite addition of Zn hinders coke formation, the activity to gaseous products decreased as the Ni content is increased. An increase in coke concentration increases activity and selectivity to ethylene, specially in those samples with not too high Ni contents. The highest selectivity to ethylene is achieved for Zn/Ni = 4 (molar ratio).

C. Guimon and coworkers (2003) studied the effect of the support (silica and silica-alumina) and of the composition of Ni-based hydrogenation catalyst. They found support, silica has very weak interactions with the metal, which ispresent with oxidation states +3 (on upper surface) and +2 after calcineation. The pre-reduction induces a non-negligible sintering for the samples with high Ni content, and thus the formation of large size crystallites. The addition of alumina to silica leads to the existence of two types of Ni^{2+} crystallites, one presenting strong interaction with the support, the other with very weak interaction (or none). The amount of the latter increased with the Ni content. This addition has a positive effect on the formation of coke, which is mainly related to the hydrogenolytic (naked) metallic sites corresponding to the metal without interaction with the support. The TPO experiment have shown the existence of at least three types of coke, which are, ordering them according to their oxidability, filamentous carbon, amorphous coke, and strongly adsorbed hydrogenated carbon. The formation of the latter is facilitated by the acidity of silica-alumina, while filamentous carbon is generated by the sites with weak metal-support interactions and amorphous coke is formed by those with strong metal-support interactions. Although the production of coke is relatively high, particularly in the case of Ni/SiO_2, it does not alter the desired selectivity (hydrogenation of acetylene to ethylene). On the contrary, for Ni/SiO_2-Al_2O_3 catalysts with high Ni contents, it improves the initial selectivity because the coke deactivates the hydrogenolytic sites which are active for the side reactions (production of saturated hydrocarbons), while the hydrogenating sites, active for the main reaction, and should be covered by a monolayer of ethylidene that is a precursor of ethane.

2.3 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 addtion of a second metal such as Ag in the catalysts. The commonly used support for palladium is α-Al_2O_3. Formation of nickel aluminate spinel has been reported in other catalyst systems such as Ni/$NiAl_2O_4$ and Ni-Zn-Al mixed oxide and has shown an improvement on the catalyst performances. Moreover, commercial catalysts that are highly resistant to deactivation have been developed by stabilizing with nickel on the support. Therefore, it is interesting to study the properties of Ni-modified alumina supported Pd catalysts in selective hydrogenation of acetylene. $NiAl_2O_4$ can provide a stabilizing effect due to its good properties such as high resistance to acids, low surface acidity, high melting points, and better diffusion.

CHAPTER III

THEORY

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

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

Like other group VIII metals, palladium can be used for hydrogenation of unsaturated hydrocarbons. Palladium shows the highest selectivity of these metals in heterogeneously catalyzed semi-hydrogenation of alkynes and dienes to the corresponding alkenes (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”).

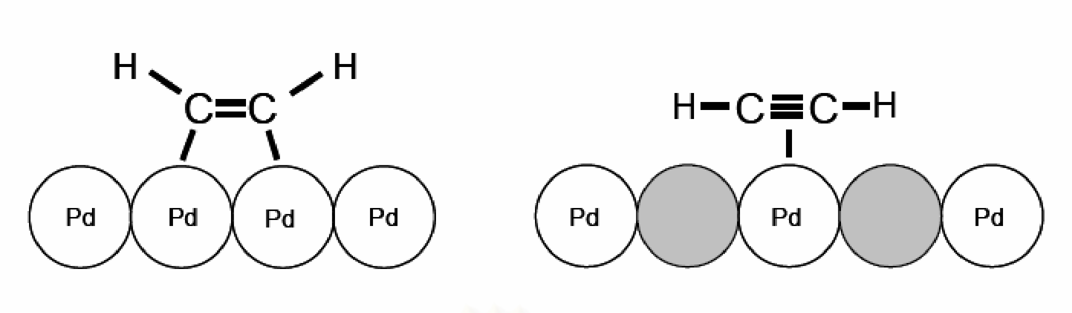


Figure 3.1 Di-σ bonded acetylene molecule to two neighbouring Pd atoms (left) and a weakly π-bonded acetylene molecule to an isolated Pd atom (right). Only the π-bonded acetylene is hydrogenated in high selectivity to ethylene.

3.2 Aluminium Oxides or Alumina (Al_2O_3)

The structure of α-alumina consists of close packed planes of the large oxygen ions stacking in A-B-A-B sequence, thus forming hexagonal close packed array of anions. The aluminium cations are located at octahedral sites of this basic array and from another type of close packed planes between the oxygen layer. To maintain neutral charge, however, only two third of the available octahedral sites are filled with cation. Figure 3.2 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

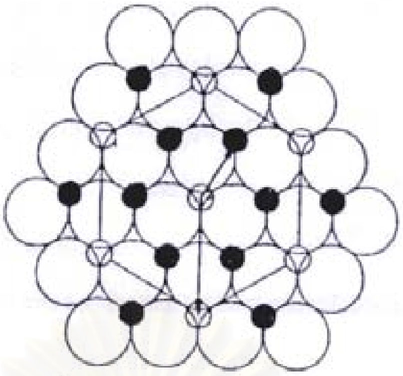


Figure 3.2 Illustration of Al and O atom packing in the basal plan

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 800ºC due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000ºC when the crystallization to the thermodynamically stable α- alumina occurs.

3.3 Nikel Aluminate and Nickel oxide

A negative ion are usually given the formula $AlO_2^-$and derived from aluminum hydroxide. Solution of aluminate is strongly basic.

- Nickel aluminate ($NiAl_2O_4$)

$NiAl_2O_4$ is a binary oxide consisting of nickel oxides and aluminum oxides that crystallize in spinel structure. The unit cell of spinel is represented by formula of AB_2O_4. The Ni^{2+} ions occupy the tetrahedrally coordinated A site and Al^{3+} ions occupy the octahedrally coordinated B site. The structure of nickel aluminate is shown in Figure 3.3

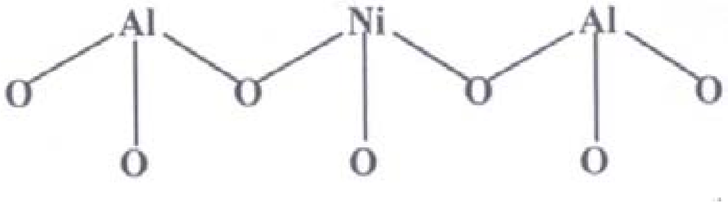


Figure 3.3 Structure of nickel aluminate

- Nickel oxide (NiO)

Nickel oxide (NiO) is a green cubic crystally compound, mp 2090^{o}C, density 7.45 g/cm^3, the properties of which are related to its method of preparation. Green nickel oxide is prepared by firing a mixture of water and pure nickel powder in air at 1000^{o}C or by firing a mixture of high purity nickel powder, nickel oxide and water in air. Whereas this temperature is required for full development of the crystal, the temperature is high enough that an equilibrium leading to dissociation back to the element is established. Consequently, it is virtually impossible to obtain green nickel oxide made by high temperature firing that does not have traces of nickel metal.

Black nickel oxide, a microcrystalline from, results from calcinnation of the carbonate or nitrate at 600ºC. This incompletely annealed product typically has more oxygen than its formula indicates, ie, 76-77 wt.% nickel compared to the green from, which has 78.5% nickel content. This results from chemisorption of oxygen on the surface of the crystal defects. Black nickel oxide composition are chemically reactive and from simple nickel (II) salt when heated with mineral acid. Both black and green nickel oxide can be converted to the metal by heating the carbonmonoxide, or hydrogen. Both green and black nickel oxide fuse with potassium hydroxide at 700ºC to from potassium nickelate, K_2NiO_2. Other nickel oxide, e.g., Ni_2O_3, density 4.84 g/cm^3, NiO_2 and Ni_3O_4 have been reported.

3.4 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 (200-300ºC) 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 (200-300ºC) 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 250ºC yielded glycol derivative of boehmite. In 1992, they have found that the reaction of aluminum isopropoxide (AIP) in toluene at 300ºC resulted in λ-alumina. Mekasuwandumrong, et al., (2003) have reported that thermal decomposition of aluminum isopropoxide in ineral oil at 250-300ºC over 2 h resulted in λ-alumina powder having high thermal stability and clued be transformed directly to α-alumina at temperature higher than 1000ºC.

3.5 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.

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

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

3.6 Acetylene Hydrogenation Reaction

Ethylene for the polymerization to polyethylene is produced by cracking of light alkanes in a steam cracker. The ethylene stream has to be purified and one step in the purification process is the selective hydrogenation of acetylene to ethylene.

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad \Delta H = -172 \text{ kJ/mol}, \Delta S = -111 \text{ J/K·mol (298 K)}$$

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, and Arnold *et al.*, 1997). Following reactions occur in an acetylene hydrogenation reactor.

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

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

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

The first reaction (3.1) is the most wanted 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”.

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

An additional essential parameter affecting the selectivity of the system is the ratio between hydrogen and acetylene (H_2:C_2H_2). Hypothetically, the H_2:C_2H_2 ratio would be 1:1, which would mean that no hydrogen would remain for the side reaction (eq. 3.2) after acetylene hydrogenation (eq. 3.1). However, in practice, the catalyst is not 100% selective and the H_2:C_2H_2 ratio is usually higher than 1:1 to get complete conversion of the acetylene. As hydrogen is one of the reactants, the overall acetylene conversion will increase with increasing hydrogen concentration. Increasing the H_2:C_2H_2 ratio from SOR to EOR can help offset the decline in catalyst activity with time on stream. However, this increased acetylene conversion with a higher H_2:C_2H_2 ratio can have a cost in selectivity which leads to ethylene loss. Typically, the H_2:C_2H_2 ratio is between 1.1 and 2.5 (Derrien *et al*., 1986 and Molnár *et al*., 2001).

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

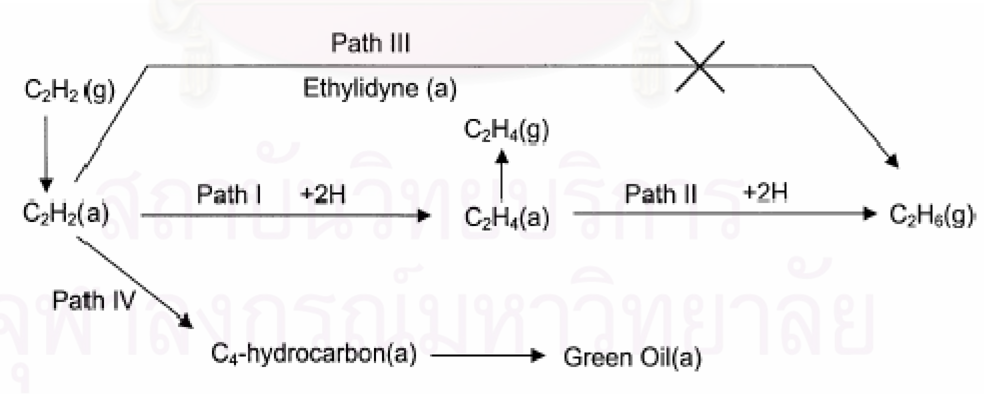


Figure 3.4 Major reaction path of acetylene hydrogenation (Kang *et al*., 2002)

Accordingly, 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).

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 definded as moles of acetylene converted with respect to acetylene in the feed:

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

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

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

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

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

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

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

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

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

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

CHAPTER IV

EXPERIMENTAL

.

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

4.1 Chemicals

The chemicals used in this experiment are specified as follows:

1. Aluminium nitrate (98%) ($Al(NO_3)_3.9H_2O$) available from Aldrich Chemical Company, USA.
2. Urea (99.5%) available from Univar, Australia.
3. Ethyl alcohol absolute anhydrous available from Mallinckrodt Baker Co., Ltd.
4. Aluminium Isopropoxide (AIP, $[(CH_3)_2CHO]_3Al$) available from Aldrich, 98%+
5. Palladium (II) nitrate hydrate from Aldrich.
6. Nickel (II) acetyacetonate $[CH_3COCH=C(O-)CH_3]_2Ni$ available from Aldrich, 95%
7. Nickel nitrate-6-hydrate ($Ni(NO_3)_2.6H_2O$) available from Riedel-de Haën
8. Toluene ($C_6H_5CH_3$) available from Carlo Erba Reagenti, 99.5%

4.2 Catalyst Preparation

4.2.1 Preparation of α-Al_2O_3 by Sol-gel Method

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

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

4.2.2 Preparation of Ni-modified Alumina by Sol-gel Method

For the preparation of Ni-modified alumina, a mixture of aluminium nitrate nonahydrate and ethanol used as starting solution was prepared by dissolving 24 g of aluminium nitrate in 50 cc of ethanol at room temperature. $Ni(NO_3)_2.6H_2O$ was added to the starting solution at the Ni/Al molar ratio = 0.3, 0.5 and 1.0 and then followed the same procedures as that of α-Al_2O_3 by sol-gel.

4.2.3 Preparation of α-Al_2O_3 by Solvothermal Method

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

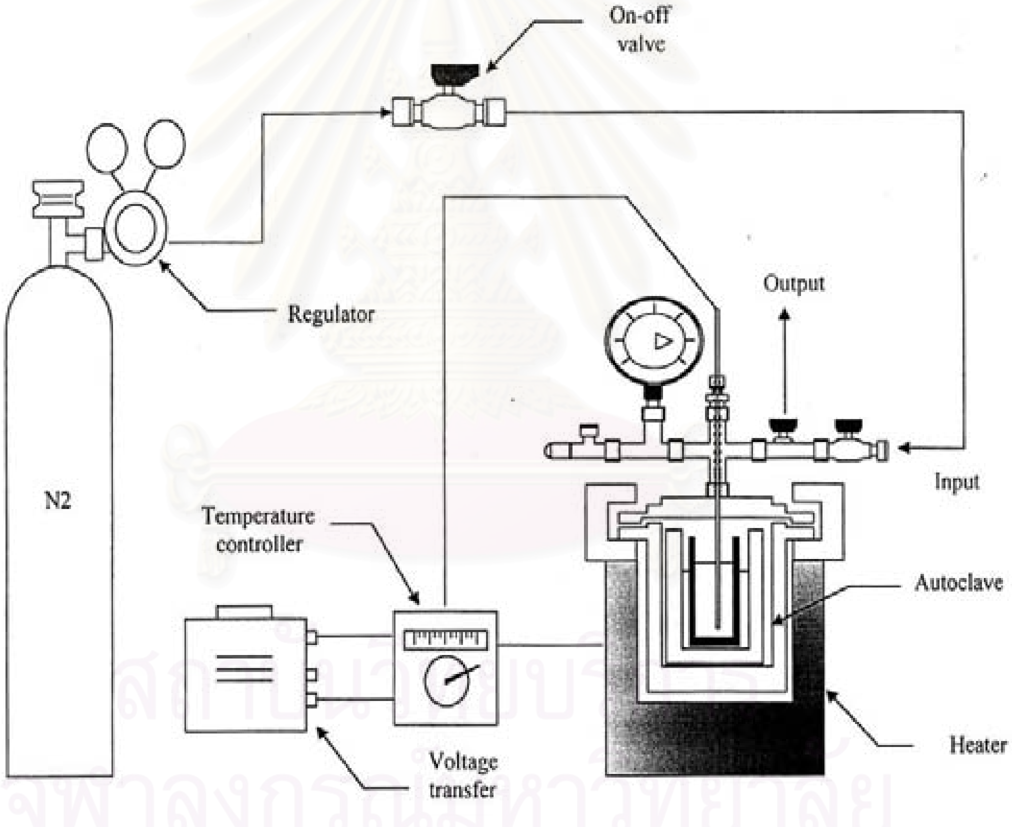


Figure 4.1 Diagram of the reaction equipment for the catalyst preparation.

4.2.4 Preparation of Ni-modified Alumina by Solvothermal Method

Ni-modified alumina was prepared by mixture of aluminum isopropoxide 15.0 grams and appropriate amount of nickel (II) acetylacetonate (Ni/Al molar ratio = 0.3, 0.5 and 1.0). The starting materials were suspended in 100 ml of toluene in beaker, and then set up in 300 ml autoclave. In the gap between the beaker and autoclave wall, 40 ml of toluene was added and then followed the same procedures as that of α-Al_2O_3 by solvothermal.

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4.2.5 Palladium Loading

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

1. α-Al_2O_3 and Ni-modified Al_2O_3 supports were impregnated with a solution of palladium by the incipient wetness technique. Using the water capacity measurement obtained previously for α-Al_2O_3 and Ni-modified Al_2O_3 particles, a sufficient amount of the palladium salt was added to obtain a 0.3% weight of palladium.
2. The impregnated support was left to stand for 6 hours to assure adequate distribution of metal complex. The support was subsequently dried at 110°C in air overnight.
3. The dried impregnated support was calcined under 60 mL/min nitrogen with the heating rate of 10°C/min until the temperature reached 500°C. A 100 mL/min of flowing air was then switched into the reactor to replace nitrogen and the temperature was held at 500°C for 2 hours.
4. The calcined sample was finally cooled down and stored in a glass bottle in a desicator for later use.

4.3 Catalyst Characterization

4.3.1 X-ray Diffraction (XRD)

XRD will be 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 0.02°.

4.3.2 BET Surface Area Analysis

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 $200^{o}C$ for 2 h 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 satuated with nitrogen and desorbed nitrogen at room temperature by moved 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 catalyst supports were observed using AJEM-200CX transmission electron microscope operated at 160 kV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University..

4.3.4 Temperature Programmed Desorption (TPD)

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

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

4.3.5 Metal Active Site Measurement

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

Approximately 0.2 g 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

150°C and held at this temperature for 1 h 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. Calculation details of %metal dispersion are given in Appendix C.

4.3.6 X-ray Photoelectron Spectroscopy (XPS)

The XPS analysis was performed originally using an AMICUS spectrometer equipped with a Mg Ka X-ray radiation. For a typical analysis, the source was operated at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10^{-5} Pa. The AMICUS system is computer controlled using the AMICUS "VISION 2"software.

4.3.7 Thermal Gravimetric Analysis (TGA)

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

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

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

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

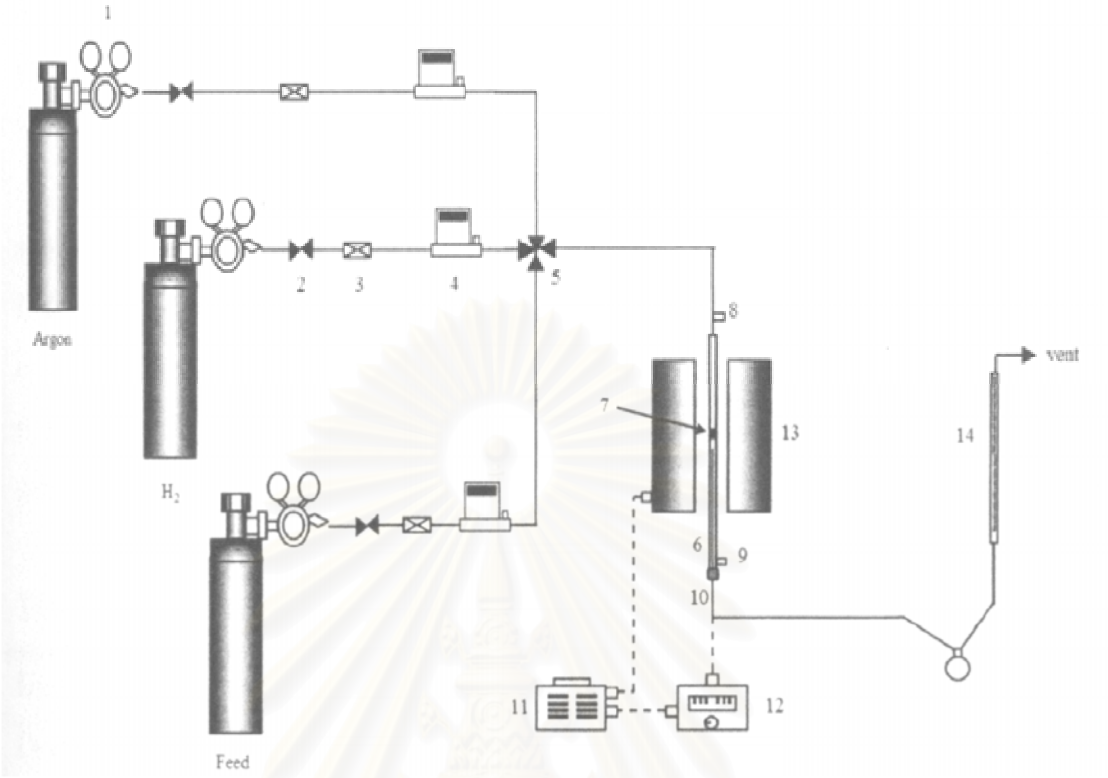
4.4 Reaction Study in Acetylene Hydrogenation

Catalytic performance of the catalysts was studied in selective hydrogenation of acetylene. The experiment was performed in a quartz tube reactor (i.d. 10.1 mm). Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.), a GHSV of 39435, 24433, 16901 and 9288 h^{-1} were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). The operating conditions for each instrument are summarized in Table 4.1

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

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

Approximately 0.15 g of catalyst was packed in quartz tubular down flow reactor. The catalyst bed length was about 0.25 cm. The reactor was placed into the furnace and argon was introduced into the reactor in order to remove remaining air. Prior to reaction, the catalyst was reduced with 100 ml/min hydrogen flow at a temperature of 150°C and held at that temperature for 2 h. Afterwards, argon was switched in to replace hydrogen for cooling down to the reaction temperature, 40ºC. The reactant was introduced at elevated temperature from 40 ºC, 1 atm and flowed 20 to 100 ml/min, sampling was undertaken when the steady state of the system was reached, which was approximately within 2 h. Effluent gases were sampled to analyze the concentration of CH_4, C_2H_2, C_2H_4 and C_2H_6 using GC-9A equipped with a carbosieve S-II column, whereas H_2 concentration was analyzed by GC-8A equipped with a molecular sieve 5A column. System of acetylene hydrogenation is shown in Figure 4.2. The Details of the calculation of the catalyst activity to convert acetylene and the selectivity are given in Appendix E



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

Figure 4.2 A schematic of acetylene hydrogenation system

CHAPTER V

RESULTS AND DISCUSSION

This thesis was conducted in order to investigate the characteristics and catalytic properties of α-Al_2O_3 and Ni-modified Al_2O_3 supported Pd catalysts in selective hydrogenation of acetylene. In this chapter, the experimental results and discussions are described. The results and discussions are divided into four main sections. The characteristics of the catalysts synthesized by sol-gel, solvothermal, and commercial catalyst are described in section 5.1, 5.2, and 5.3, respectively and effect of nickel aluminate formation on the properties Pd catalysts supported on sol-gel and solvothermal derived Ni-modified α-Al_2O_3 are discussed in section 5.4.

5.1 Sol-gel Derived Al_2O_3 and Ni-modified Al_2O_3 Supported Pd Catalysts

The samples of Ni-modified Al_2O_3 with various molar ratios of Ni to Al (0, 0.3, 0.5 and 1) synthesized by sol-gel were named as Ni0-Al_2O_3SG, Ni0.3-Al_2O_3SG, Ni0.5-Al_2O_3SG, and Ni1-Al_2O_3SG, respectively. Pd catalysts supported on Ni-modified Al_2O_3 were called Pd/Ni0-Al_2O_3SG, Pd/Ni0.3-Al_2O_3SG, Pd/Ni0.5-Al_2O_3SG, and Pd/Ni1-Al_2O_3SG, respectively.

5.1.1 Characterization of the Catalysts Prepared by Sol-gel Method

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

5.1.1.1 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 sol-gel catalyst supports are shown in Table 5.1.

Table 5.1 BET surface areas of Ni-modified Al_2O_3 with various molar ratios of Ni to Al

Sample	Ni/Al ratio	BET S.A. (m^2/g)
Ni0-Al_2O_3SG (α- Al_2O_3)	0	1.5
Ni0.3-Al_2O_3SG	0.3	1.5
Ni0.5-Al_2O_3SG	0.5	1.8
Ni1-Al_2O_3SG	1	3.9

The BET surface areas of the Ni-modified Al_2O_3 were ranged from 1.5-3.9 m^2/g which were quite low but typical for the α-Al_2O_3 supports. There were no significantly differences in the BET surface area of the Ni-modified Al_2O_3 with various Ni/Al ratios, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature (Prasitwuttisak, 2004).

5.1.1.2 X-ray Diffraction (XRD)

Catalyst structure of the oxides in the catalyst samples was characterized by X-ray diffraction technique. The XRD patterns of Pd catalysts supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al are shown in Figure 5.1. For the alpha alumina (α-Al_2O_3-sol-gel), XRD peaks at 25.52º, 35.10º, 37.74º, 43.32º, 52.52º, 57.46º, 61.22º, 66.50º, 68.18º and 77.86º 2θ were evident (Prasitwuttisak, 2004). While the XRD peaks for nickel aluminte spinel appeared at 19.08º, 31.42º, 37.02º, 45.02º, 55.94º, 59.68º, 65.60º and 78.84º 2θ (Kanyanucharat, 2001). Additional peaks corresponding to NiO were also presented at 43.3°, 44.8° and 62.9° 2θ (Peña *et al.*, 1995).

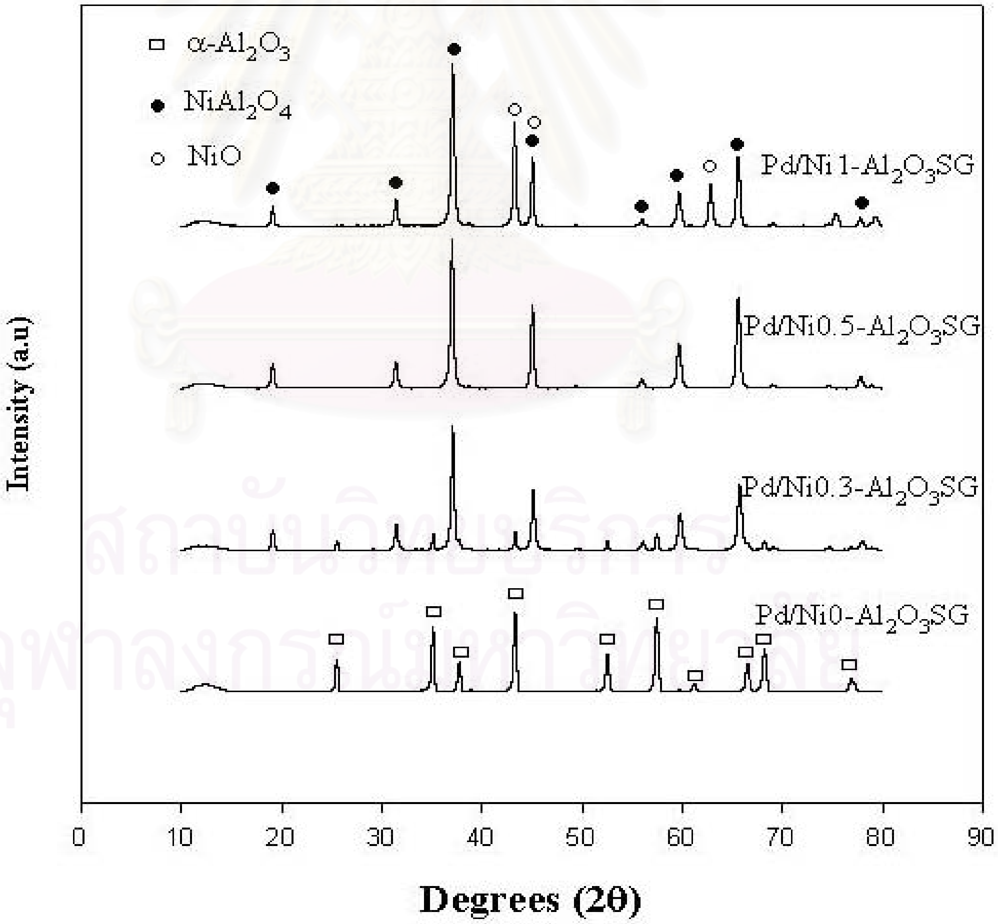


Figure 5.1 The XRD patterns of Pd catalyst supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al by sol-gel

It is shown that without Ni modification (Pd/Ni0-Al_2O_3SG), only XRD characteristic peaks of α-Al_2O_3 were observed. For Pd/Ni0.3-Al_2O_3SG, both α-Al_2O_3 and $NiAl_2O_4$ XRD peaks were apparent and for Pd/Ni0.5-Al_2O_3SG, only XRD peaks of $NiAl_2O_4$ spinel were found. Increasing Ni/Al ratio to 1 (Pd/Ni1-Al_2O_3SG) resulted in the mixed $NiAl_2O_4$ and NiO crystalline phases. The spinel structure is a non-tolerant structure concerning an excess of Ni. If Ni/Al is higher than 0.5, free NiO is present on spinel and favors the reduction of nickel at low temperature. Stoichiometric spinel seems difficult to obtain as pure phase and forms easily small zones of free nickel oxide. If the Ni/Al ratio is lower than 0.5, a solid solution of Al_2O_3 and $NiAl_2O_4$ is formed is obtained (Sahli *et al.*, 2006). However, the XRD characteristic peaks associated with Pd^0 ($2\theta = 40.2^o$ and 46.7^o) or PdO ($2\theta = 33.9^o$) phase were not observed in all the samples. This was probably due to the very low amount of Pd present and/or a very good dispersion of Pd phase on all the catalyst supports (Kontapakdee, 2005).

5.1.1.3 Average Crystallite Size

The average crystallite size of each crystal phase was calculated from the Scherrer equation. The crystallite size of α-Al_2O_3, $NiAl_2O_4$ and NiO in the Pd supported on Ni-modified α-Al_2O_3 with various molar ratios of Ni to Al prepared by sol-gel are shown in Table 5.2

The average crystallite sizes of all catalysts were ranged nanocrystalline (Prasitwuttisak, 2004). For Pd/Ni0-Al_2O_3SG, the crystallite size of α-Al_2O_3 was 34 nm. For Pd/Ni0.3-Al_2O_3SG, crystallite sizes of α-Al_2O_3 and $NiAl_2O_4$ were 94 and 31 nm, respectively. While Ni/Al ratio to 0.5 (Pd/Ni0.5-Al_2O_3SG), crystallite size of $NiAl_2O_4$ was 27 nm and for Pd/Ni1-Al_2O_3SG, it was found that crystallite sizes of $NiAl_2O_4$ and NiO were 25 and 38 nm, respectively. In all cases, the average crystallite sizes of $NiAl_2O_4$ were smaller than those of α-Al_2O_3. The results suggest that crystal growth rate for $NiAl_2O_4$ was slower than that of α-Al_2O_3.

Table 5.2 Crytsallite size of catalysts prepare by sol-gel

Sample	Crystallite size (nm)
Pd/Ni0-Al_2O_3SG	34^{α}
Pd/Ni0.3-Al_2O_3SG	94^{α}, 31^{NA}
Pd/Ni0.5-Al_2O_3SG	27^{NA}
Pd/Ni1-Al_2O_3SG	25^{NA}, 38^{N}

$^{\alpha}$ α-Al_2O_3

^{NA} $NiAl_2O_4$

^{N} NiO

5.1.1.4 Metal Active Sites

The metal active sites measurement is based on CO chemisorption techniqueon the assumption that one CO molecule adsorbs on one palladium site (Anderson *et al.*, 1985, Mahata *et al.*, 2000, Ali and Goodwin, 1998 and Sales *et al.*, 1999). The amounts of CO chemisorption on the catalysts reduced at 150ºC and the percentages of palladium dispersion are given in Table 5.3. The details for calculation of Pd dispersion and average Pd^0 particle size are given in Appendix C. Addition of Ni to α-Al_2O_3 supported (0-0.5 Ni/Al ratio) resulted in a slight decrease in the CO chemisorption from 7.51 to 5.37×10^{17} molecule CO/g catalyst and Pd dispersion from 4.42-3.16%. However, the addition of Ni into α-Al_2O_3 with Ni/Al ratio = 1 gives the highest CO chemisorption and %Pd dispersion compared with other synthesized catalysts. Since NiO was reduced to metallic nickel at the reduction temperatures range 400-450ºC (Sharath *et al.*, 2006). Therefore, this catalyst which was reduced at 150ºC might exist in NiO form. Hence, the increase of CO chemisorption and %Pd dispersion mentioned above probably due to the CO adsorption of NiO. The average Pd^0 particle sizes for Pd/Ni0-Al_2O_3SG, Pd/Ni0.3-

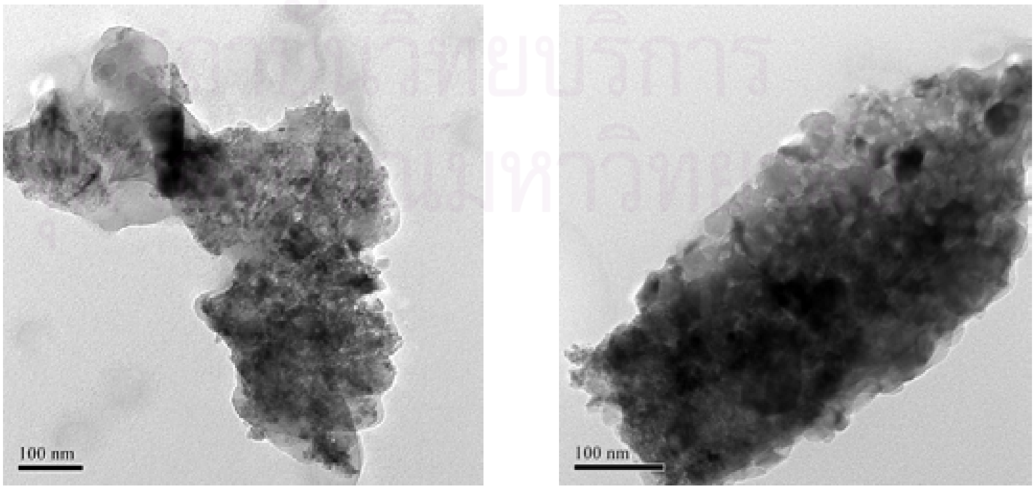
Al_2O_3SG and Pd/Ni0.5-Al_2O_3SG were ranged from 25-35 nm. For Pd/Ni1-Al_2O_3SG, average Pd^0 particle size is smaller than any other catalysts prepared by sol-gel.

Table 5.3 Results from CO chemisorption of Pd supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al by sol-gel

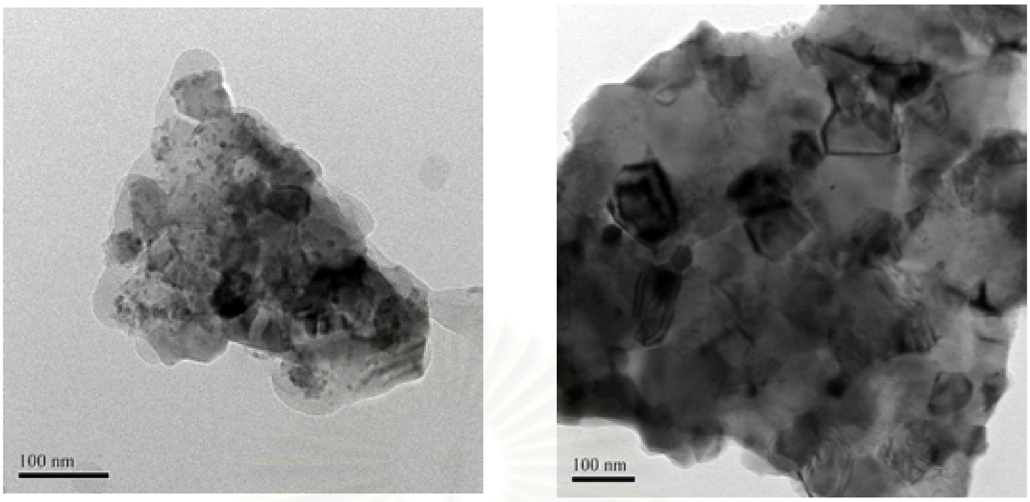
Sample	CO chemisorption $\times 10^{17}$ (molecule CO/g cat.)	Pd dispersion (%)	d_P Pd^0 (nm)
Pd/Ni0-Al_2O_3SG	7.51	4.42	25
Pd/Ni0.3-Al_2O_3SG	6.22	3.65	31
Pd/Ni0.5-Al_2O_3SG	5.37	3.16	35
Pd/Ni1-Al_2O_3SG	24.20	14.24	8

5.1.1.5 Transmission Electron Microscopy (TEM)

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



(A) (B)



(C) (D)

Figure 5.2 The TEM micrographs of (A) Pd/Ni0-Al_2O_3SG, (B) Pd/Ni0.3-Al_2O_3SG, (C) Pd/Ni0.5-Al_2O_3SG, (D) Pd/Ni1-Al_2O_3SG

It can be seen that the sol-gel made catalysts (Figure 5.2 (A) Pd/Ni0-Al_2O_3SG, (B) Pd/Ni0.3-Al_2O_3SG, (C) Pd/Ni0.5-Al_2O_3SG and (D) Pd/Ni1-Al_2O_3SG) were consisted of agglomerated particles with primarily irregular shape structure. The catalysts were no significantly difference in the TEM images, palladium particles/clusters with average particle size ca. 5-10 nm were found to be deposited on the catalyst supports.

5.1.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

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

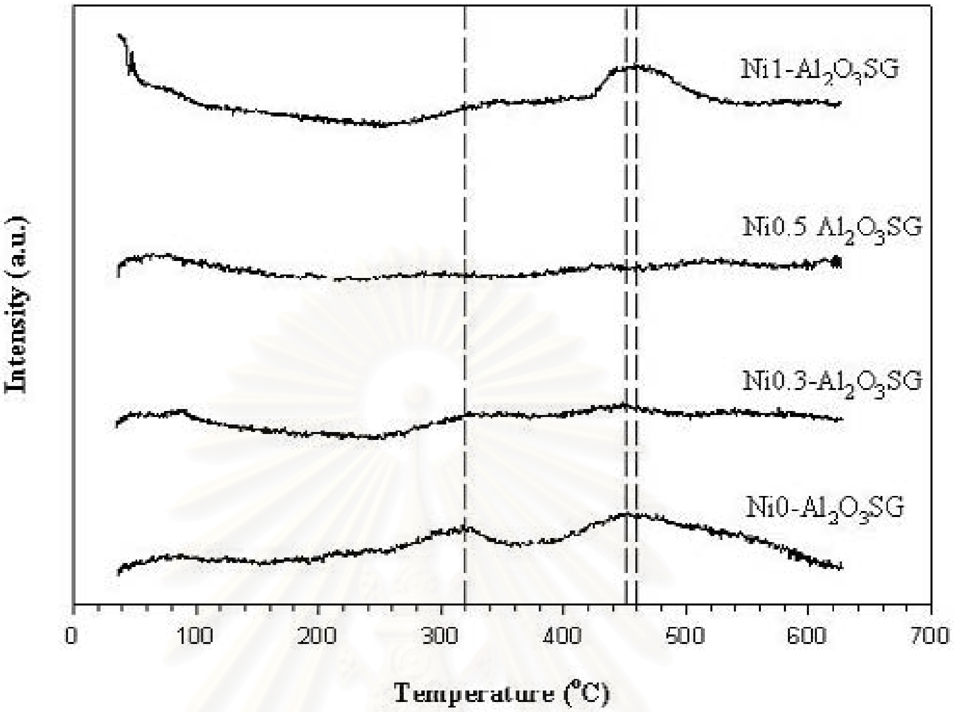


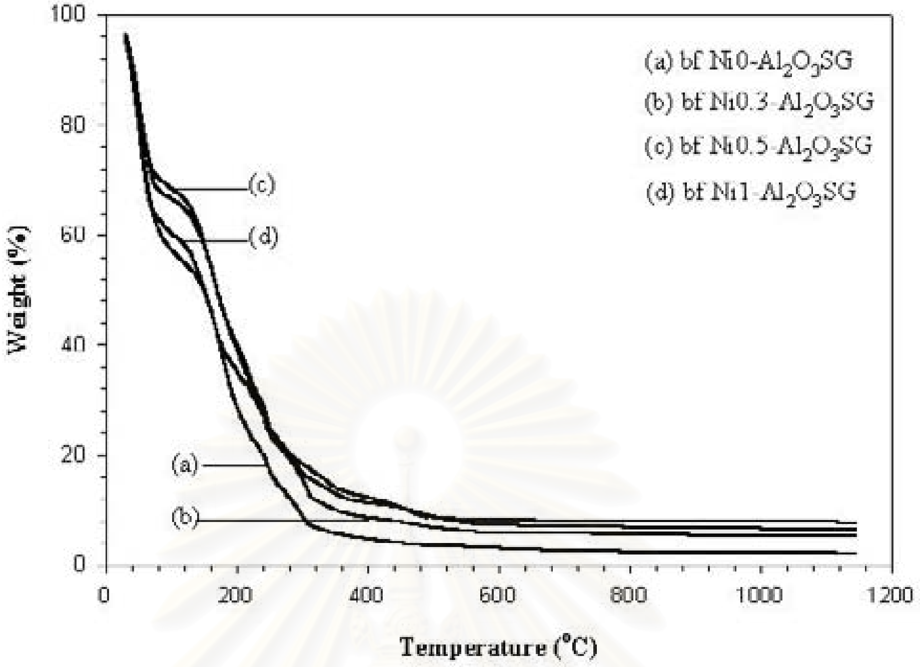
Figure 5.3 NH_3 temperature programmed desorption of Ni-modified Al_2O_3 with various molar ratios of Ni to Al by sol-gel

This Figure shows NH_3 temperature programmed desorption profiles for the sol-gel made α-Al_2O_3 and the Ni-modified α-Al_2O_3 supports. The peak areas of the α-Al_2O_3 powder (Ni0-Al_2O_3SG) showed relatively low acidity due probably to the dramatically decrease of the surface area after calcination at high temperature. However, two desorption peaks corresponding to different acid sites were still observed at ca. 320 and 450^{o}C. Ni0.3-Al_2O_3SG had lower acidity than Ni0-Al_2O_3SG because it formed both α-Al_2O_3 and $NiAl_2O_4$ species. The results are in good agreement with those reported by other researchers. For examples, Yingcheng (Yingcheng *et al.*, 2004) reported that the catalyst prepared with $MgAl_2O_4$ modified α-Al_2O_3 support showed less density and strength of acidity than that of the pure α-Al_2O_3 supported catalyst. For Ni0.5-Al_2O_3SG, no distinctive peaks were observed and the profile became flat. Such results indicate that acidity of the α-Al_2O_3 sample was drastically decreased by incorporation of Ni atoms. A small peak was observed at ca. 460ºC for Ni1-Al_2O_3SG due probably to the formation of NiO species which some acidity may be remained.

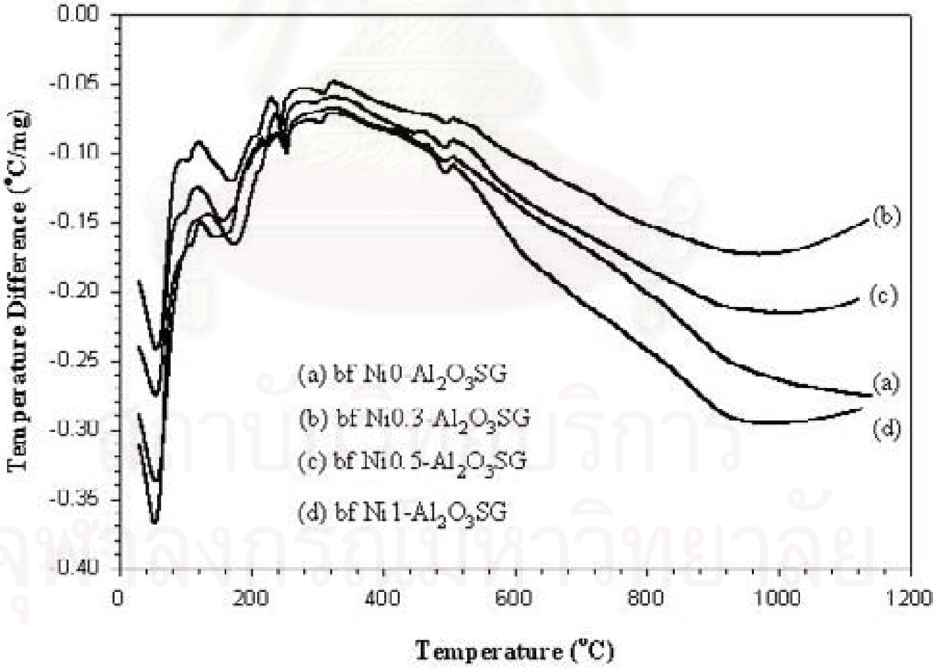
5.1.1.7 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was determined using a SDT Analyzer Model Q600 from TA Instruments. The analysis was performed with 2 steps heating rate. 3ºC/min from room temperature to 500^{o}C and continue heating at 5ºC/min to 1150 ºC. Then, temperature was hold for 3 h. Figure 5.4 shows TGA analysis of Ni-modified alumina prepared by sol-gel before calcined in air at temperature 1150ºC.

Results for thermal gravimetric analysis of the obtained gel are shown in Figure 5.4. Overall weight losses of all gel samples were essentially the same at around 95-98%. Three weight-decrease processes were detected, which were accompanied by three endothermic peaks in DTA. The first was observed below 100^{o}C and is due to the desorption of physisorbed water. The second and third weight decrease occurred at around 120-230^{o}C and 230-500^{o}C may be attributed to the combustion of organic complex forming in gel structure. The last endothermic DTA peaks without any weight loss were observed at around 520^{o}C which should be assigned to the crystallization of $NiAl_2O_4$ from amorphous gel. This is confirmed by the crystallization of $NiAl_2O_4$ by calcination of gel at 600^{o}C and higher (Sahli *et al.*, 2006).



(A)



(B)

Figure 5.4 Thermal gravimetric analysis (TGA) of Ni-modified alumina prepared by sol-gel before calcined: (A) in terms of temperature (ºC) and weight (%), (B) in terms of temperature (ºC) and temperature difference (ºC/mg)

5.1.2 Catalytic Performance of 0.3%Pd/Ni-modified Al_2O_3 Prepared by Sol-gel

The performance of the catalysts in selective hydrogenation of acetylene was determined 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 H_2 consumption increases until all of the acetylene is converted to ethane and none remains as ethylene. At that point, the selectivity is 0%. The selectivity can be measured by observing the change in ethane and ethylene from the inlet and the outlet. However, this is not practical since a change of 0.05% in the measurement would be a 10% change in selectivity for 0.5% of acetylene at the inlet. The selectivity in term of ethylene gain can also be measured by looking at the hydrogen consumed in the converter and the amount of acetylene converted. The performance of the catalysts in this study will therefore be reported in terms of acetylene conversion and ethylene gain observed from hydrogen and acetylene concentrations.

In this study, the performance of 0.3%Pd catalysts supported on Ni-modified Al_2O_3 with various Ni/Al ratios in acetylene hydrogenation was evaluated at the temperature 40ºC. Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.), a GHSV of 39435, 24433, 16901 and 9288 h^{-1} were used. Figure 5.5 shows catalytic performance of the catalysts prepared by sol-gel.

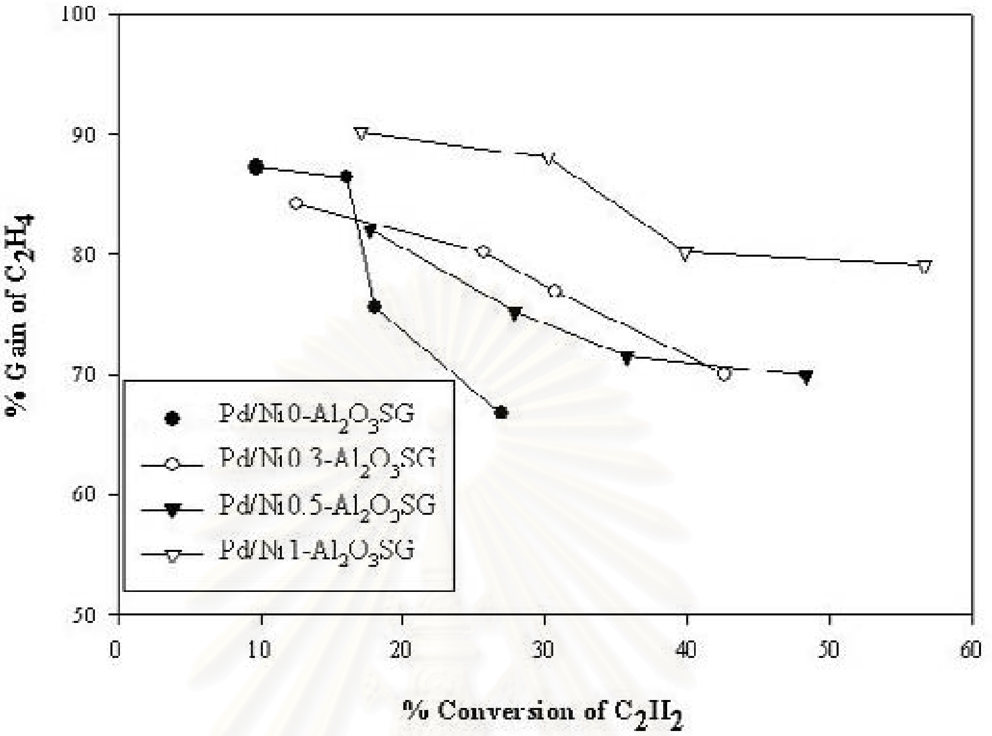
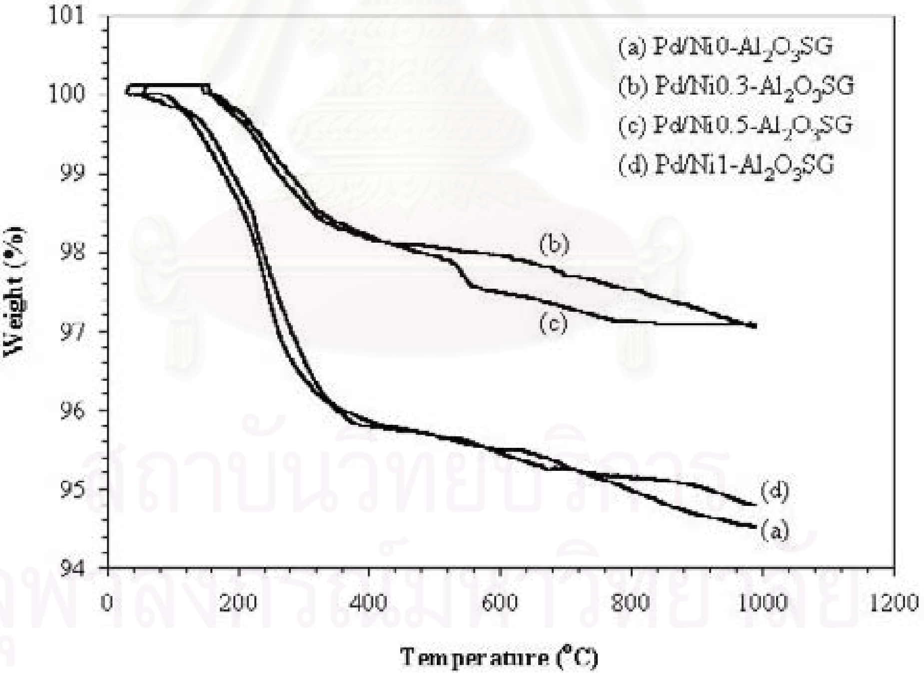


Figure 5.5 Catalytic performance of catalysts prepared by sol-gel

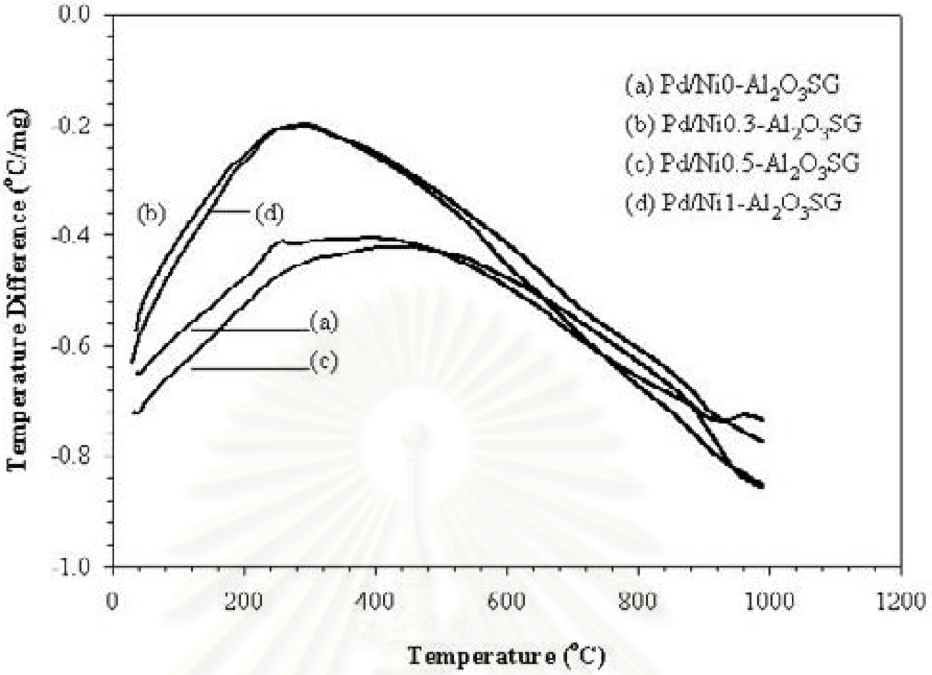
The catalyst performance in selective hydrogenation of acetylene to ethylene was studied for all the catalyst samples using a fixed bed flow reactor. Changing in ethylene gain with acetylene conversion for Pd/α-Al_2O_3 (Pd/Ni0-Al_2O_3SG) and Pd/Ni-modified α-Al_2O_3 catalysts (Pd/Ni0.3-Al_2O_3SG, Pd/Ni0.5-Al_2O_3SG, and Pd/Ni1-Al_2O_3SG) are shown in Figure 5.5. In general, ethylene gain decreases with increasing acetylene conversion due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction (Ngamsom, 2002, and Aungkapipattanachai, 2005). It was found that Ni/Al ratio = 1 (Pd/Ni1-Al_2O_3SG) exhibited higher ethylene gain than any other molar ratios. The catalytic performance of Pd/Ni0.3-Al_2O_3SG and Pd/Ni0.5-Al_2O_3SG are similar. The Pd/α-Al_2O_3 (Pd/Ni0-Al_2O_3SG) showed the lowest catalytic performance among the catalysts prepared by sol-gel method. The ethylene gain was improved in the order: Pd/Ni1-Al_2O_3SG > Pd/Ni0.3-Al_2O_3SG ≈ Pd/Ni0.5-Al_2O_3SG > Pd/Ni0-Al_2O_3SG. Such results indicate that Ni-modified Al_2O_3 via sol-gel method could improve catalytic performance of Pd/Ni-modified α-Al_2O_3 catalysts (Rives *et al.*, 1998). It is likely that formation of $NiAl_2O_4$ may enhance the catalytic performance of Pd/Ni-modified Al_2O_3 by reducing acidity of the α-Al_2O_3 support as shown by the NH_3-TPD results.

5.1.3 Catalyst Deactivation

After reaction, coke may deposit on the catalyst surface and cover the active metal resulting in loss of activity. The amount of carbonaceous deposits on the catalyst samples in selective hydrogenation of acetylene were measured by thermal gravimetric analysis and shown in Figure 5.6. The total amount of coke deposition was measured by TG/DTA on SDT Analyzer Model Q600. The analysis was carried out from room temperature to 1000ºC at a heating rate of 5ºC/min in oxygen.



(A)



(B)

Figure 5.6 Thermal gravimetric analysis (TGA) of Pd supported on Ni-modified alumina prepared by sol-gel after reaction: (A) in terms of temperature (ºC) and weight (%), (B) in terms of temperature (ºC) and temperature difference (ºC/mg)

The results of thermal gravimetric analysis made after reaction are presented in Figure 5.6. From this figure, the weight loss of Pd/Ni0-Al_2O_3SG and Pd/Ni1-Al_2O_3SG, the weight loss were ranged from 5-5.4 wt.%. The weight loss during temperature-programmed oxidation may indicate a higher rate of coke deposition on the surface of these samples (Pawelec *et al.,* 2006). For Pd/Ni0.3-Al_2O_3SG and Pd/Ni0.5-Al_2O_3SG were similar and were approximately 2.8 wt.%. Such results indicate that formation of $NiAl_2O_4$ when used as supports for Pd catalysts could reduce coke deposition on the catalyst surface (Bhattaacharyya *et al.*, 1994 and Rostrup-Nielses *et al.,* 1984) and the effect of coke on the selectivity to ethylene depends as well on the composition of the catalyst (Rives *et al.,* 1998). The exothermic peaks observed in temperature difference profiles of all catalysts corresponding to the oxidation of one type of coke ‘‘soft-type’’ (Xiangjing *et al.,* 2006 and Jovanovic *et al.,* 1997), were observed at 300ºC for Pd/Ni0.3-Al_2O_3SG and

Pd/Ni0.5-Al_2O_3SG and were observed at 400ºC for Pd/Ni0-Al_2O_3SG and Pd/Ni1-Al_2O_3SG.

5.2 Solvothermal Derived Al_2O_3 and Ni-modified Al_2O_3 Supported Pd Catalysts

The samples of Ni-modified Al_2O_3 with various molar ratios of Ni to Al (0, 0.3, 0.5 and 1) prepared by solvothermal method were named as Ni0-Al_2O_3SV, Ni0.3-Al_2O_3SV, Ni0.5-Al_2O_3SV, and Ni1-Al_2O_3SV, respectively. The Pd catalysts supported on Ni-modified Al_2O_3 were called Pd/Ni0-Al_2O_3SV, Pd/Ni0.3-Al_2O_3SV, Pd/Ni0.5-Al_2O_3SV, and Pd/Ni1-Al_2O_3SV, respectively.

5.2.1 Characterization of the Catalysts Prepared by Solvothermal Method

5.2.1.1 BET Surface Areas

The BET surface areas of catalyst supports prepared by solvothermal measured by N_2 physisorption measurement are shown in Table 5.4.

Table 5. 4 BET surface areas of Ni-modified Al_2O_3 with various molar ratios of Ni to Al by solvothermal

Sample	Ni/Al ratio	BET S.A. (m^2/g)
Ni0-Al_2O_3SV (α- Al_2O_3)	0	4.7
Ni0.3-Al_2O_3SV	0.3	1.8
Ni0.5-Al_2O_3SV	0.5	1.4
Ni1-Al_2O_3SV	1	1.7

The BET surface areas of all the catalyst supports prepared by solvothermal were ranged from 1.4-4.7 m^2/g. There were no significantly different and still quite low, which due probably to high agglomeration of particles by calcinations at high temperature (Kanyanucharat, 2001).

5.2.1.2 X-ray Diffraction (XRD)

The XRD patterns of 0.3%Pd catalysts supported on α-Al_2O_3 and Ni-modified Al_2O_3 with prepared by solvothermal are shown in Figure 5.7.

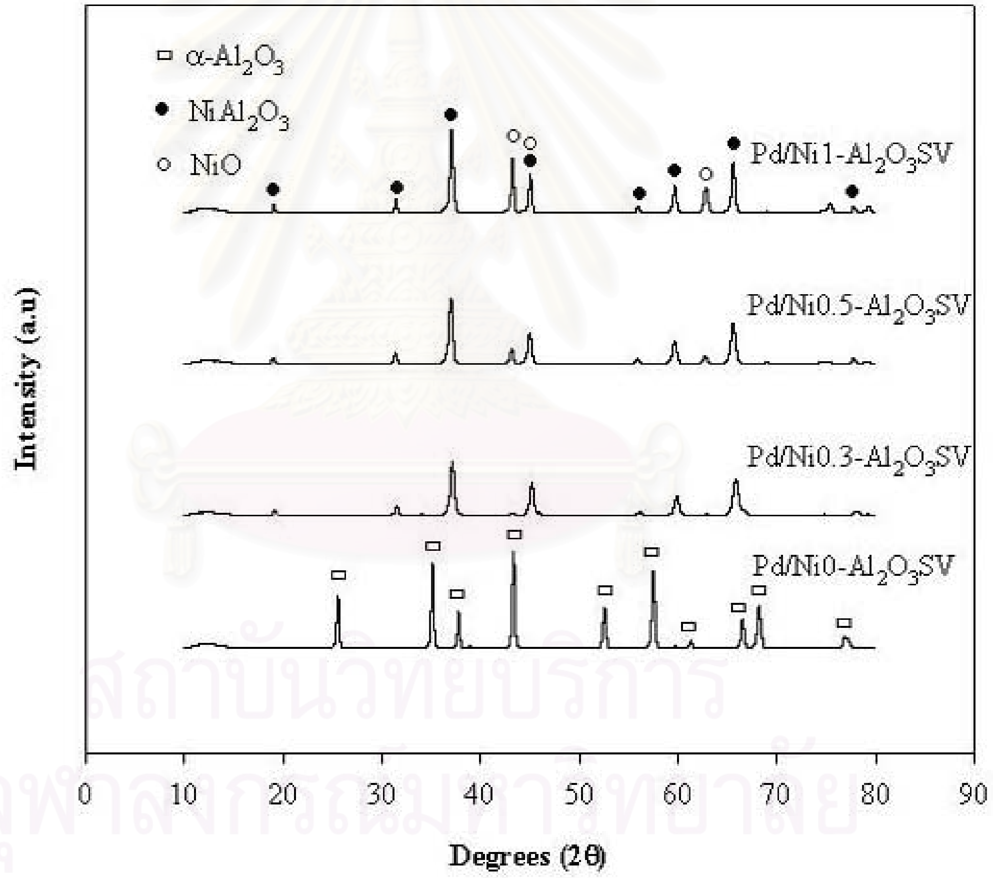


Figure 5.7 The XRD patterns of Pd catalysts supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al by solvothermal

The XRD peaks of Pd/Ni0-Al_2O_3SV indicate the presence of only α-Al_2O_3 (Prasitwuttisak, 2004). Mekasuwandumrong (Mekasuwandumrong, 1999) reported that the as-synthesized alumina powders via solvothermal method exhibit the typical characteristic peaks of the χ-alumina which transforms direcly to α-alumina after 1 h calcination at 1150ºC. Pd/Ni0.3-Al_2O_3SV showed only XRD peaks of $NiAl_2O_4$ spinel (Kanyanucharat, 2001) while Pd/Ni0.5-Al_2O_3SV and Pd/Ni1-Al_2O_3SV resulted in both $NiAl_2O_4$ and NiO crystalline phases (Peña *et al.*, 1995). The introduction of nickel into alumina may lead to different types of materials such as the formation of spinel compound or segregation of oxide phase or a mixture depending on the experimental conditions. The crystallinity of the spinel depends on the calcinations temperature and increases with the increase of calcination temperature (Chokkaram *et al.*, 1996). However, no XRD peaks for Pd^0 or PdO were observed due probably to the very low amount of Pd present and/or a very good dispersion of Pd phase on all the catalyst supports.

5.2.1.3 Crystallite Size

The average crystallite size of each crystal phase was calculated from the Scherrer equation. The crystallite size of 0.3%Pd catalyst supported on Ni-modified Al_2O_3 prepared by solvothermal are shown in Table 5.5.

Table 5.5 Crytsallite size of catalysts prepare by solvothermal

Sample	Crystallite size (nm)
Pd/Ni0-Al_2O_3SV	54^{α}
Pd/Ni0.3-Al_2O_3SV	24^{NA}
Pd/Ni0.5-Al_2O_3SV	23^{NA}, 26^{N}
Pd/Ni1-Al_2O_3SV	29^{NA}, 45^{N}

$^{\alpha}$ α-Al_2O_3

^{NA} $NiAl_2O_4$

^{N} NiO

The average crystallite size of each crystal phase was found to be in nano-scale (23-54 nm) (Kanyanucharat, 2001). The average crystallite size of α-Al_2O_3 for Pd/Ni0-Al_2O_3SV was 54 nm while the crystallite size of $NiAl_2O_4$ which formed in the Pd/Ni0.3-Al_2O_3SV was 24 nm. For Pd/Ni0.5-Al_2O_3SV, the crystallite size of $NiAl_2O_4$ and NiO were 23 and 26 nm, respectively. And for Pd/Ni1-Al_2O_3SV, the crystallite sizes of $NiAl_2O_4$ and NiO were 29 and 45 nm, respectively. For all the catalysts, the average crystallite sizes of $NiAl_2O_4$ were smaller than those of α-Al_2O_3. Such results suggest that crystal growth rate for $NiAl_2O_4$ was slower than that of α-Al_2O_3.

5.2.1.4 Metal Active Sites

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

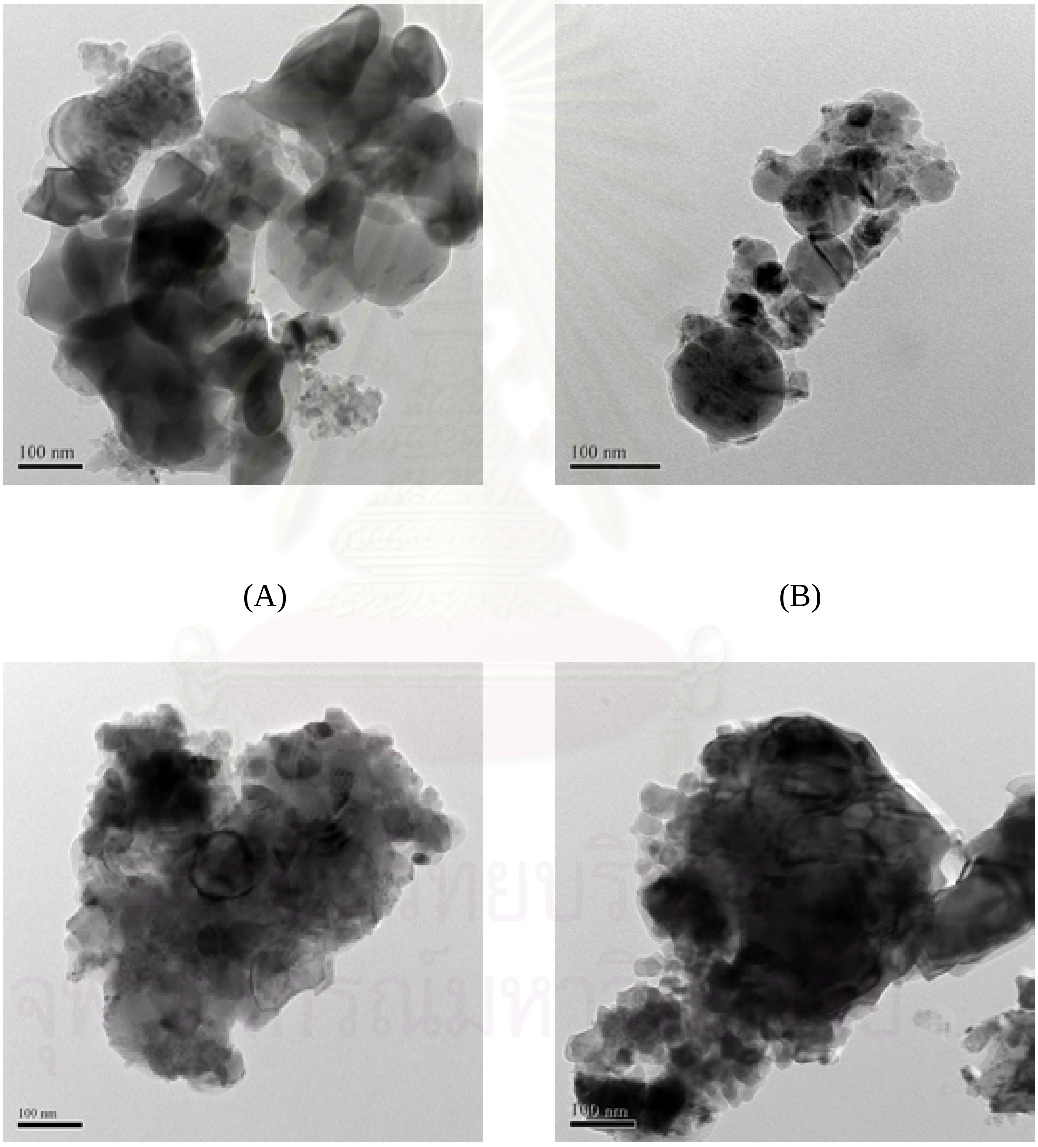
Table 5.6 Results from CO chemisorption of Pd supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al by solvothermal

Sample	CO chemisorption $\times 10^{17}$ (molecule CO/g cat.)	Pd dispersion (%)	$d_P{}^1$ Pd^0 (nm)
Pd/Ni0-Al_2O_3SV	8.10	4.76	24
Pd/Ni0.3-Al_2O_3SV	6.28	3.69	30
Pd/Ni0.5-Al_2O_3SV	7.35	4.32	26
Pd/Ni1-Al_2O_3SV	12.7	7.47	15

The pulse CO chemisorption technique was based on the assumption that one carbon monoxide molecule adsorbs on one palladium site (Anderson *et al.*, 1985, Mahata *et al.*, 2000, Ali and Goodwin 1998 and Sales *et al.*, 1999). The catalysts prepared by solvothermal with Ni/Al ratios 0-0.5 showed similar CO chemisorption, percent Pd dispersion and particle size of Pd^0. It was found that the amounts of chemisorped CO were ranged from 6.28 to 8.10×10^{17} molecule CO/g cat., the percent Pd dispersion were ranged from 3.69-4.76% and the calculated average particle size of Pd^0 metal were ranged from 24-30 nm. However, the catalyst (Ni/Al = 1) give the highest CO chemisorption and % Pd dispersion equal to 12.7×10^{17} molecule CO/g cat and 7.47%, respectively. These might be a result of the CO adsorption of NiO. Consequently, the calculated Pd^0 particle size was smaller (15 nm).

5.2.1.5 Transmission Electron Microscopy (TEM)

TEM micrographs were taken in order to physically measure the size of the palladium oxide particles and/or palladium clusters. TEM micrographs of Pd catalyst supported on Ni-modified Al_2O_3 with various molar ratios of Ni to Al by solvothermal are shown in Figure 5.8



(A) (B)

(C) (D)

Figure 5.8 The TEM micrographs of (A) Pd/Ni0-Al_2O_3SV, (B) Pd/Ni0.3-Al_2O_3SV, (C) Pd/Ni0.5-Al_2O_3SV, (D) Pd/Ni1-Al_2O_3SV

It was found that the solvothermal made catalysts (Pd/Ni0-Al_2O_3SV, Pd/Ni0.3-Al_2O_3SV, Pd/Ni0.5-Al_2O_3SV and Pd/Ni1-Al_2O_3SV) had no significantly difference in the TEM images with and without Ni modification. However, agglomeration of finger-like particles was observed for the Pd/α-Al_2O_3 (Pd/Ni0-Al_2O_3SV) whereas spherical-shape particles were found for the Pd/Ni-modified Al_2O_3 catalyst. The finger-like α-Al_2O_3 particles are normally obtained by calaination of the solvothermal-made α-Al_2O_3 powder at high temperature (Mekasuwandumrong and Pavarajarn, 2006 and Mekasuwandumrong and Silveston, 2003). Based on TEM analysis, palladium particles/clusters with average paticle size ca. 10-20 nm were found to be deposition on the catalyst supports.

5.2.1.6 NH_3 Temperature Programmed Desorption (NH_3-TPD)

Temperature programmed desorption of NH_3 (NH_3-TPD) for catalyst supports prepared by solvothermal were performed in order to obtain information about ammonia adsorption behavior on the acid site of catalyst samples. The results are shown in Figure 5.9.

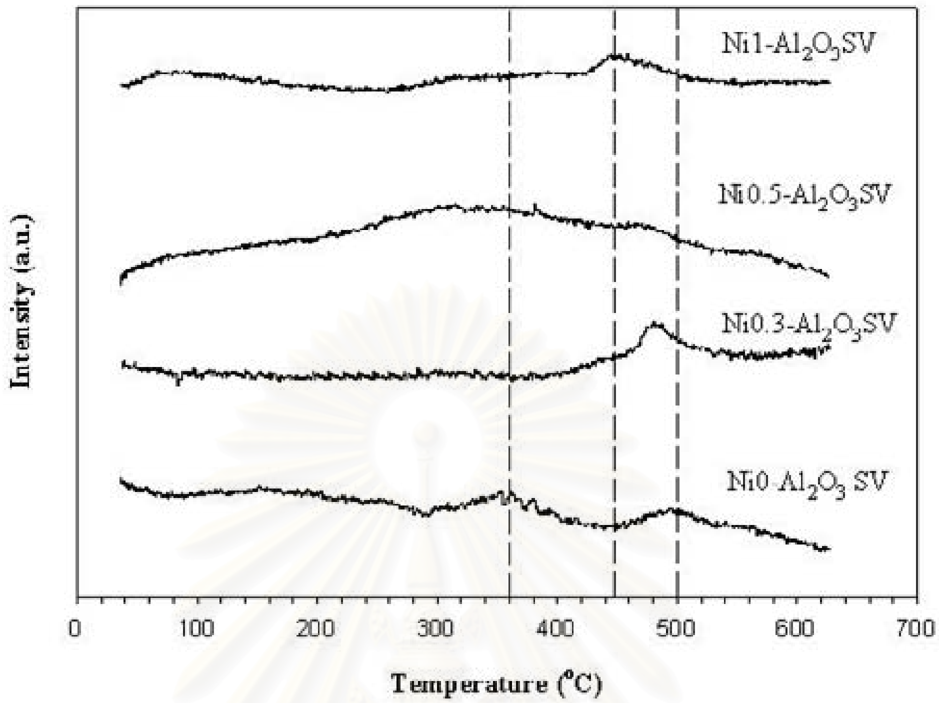
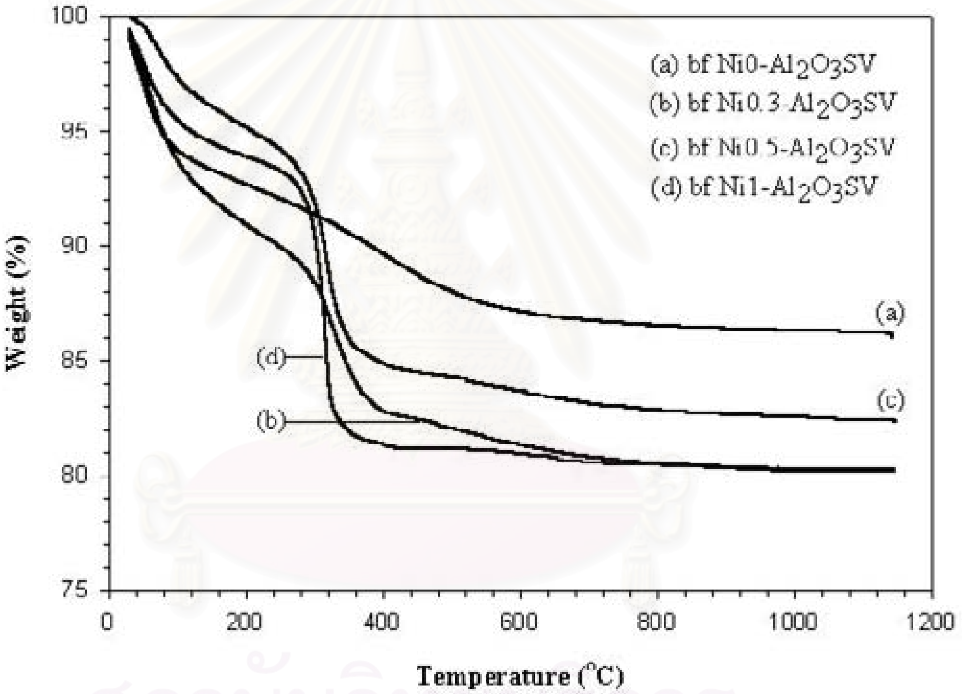


Figure 5.9 NH_3 temperature programmed desorption of Ni-modified Al_2O_3 with various molar ratios of Ni to Al by solvothermal

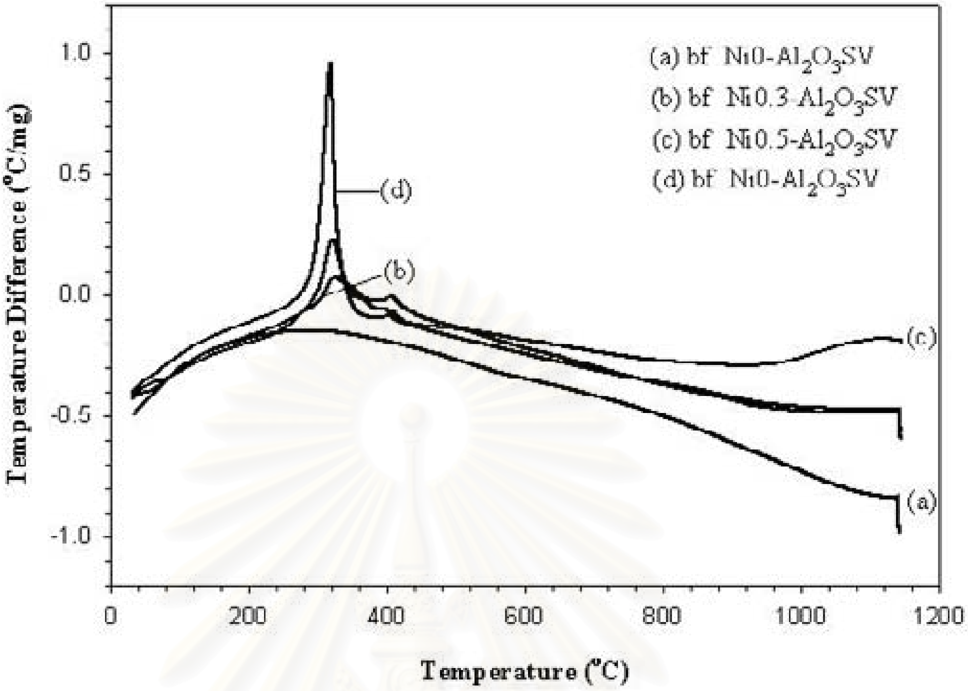
The profiles were found that the α-Al_2O_3 powder (Ni0-Al_2O_3SV) had two desorption peaks corresponding to different acid sites which were still observed at ca. 360 and 500°C. For Ni0.3-Al_2O_3SV, it formed $NiAl_2O_4$ spinel which had low surface acidity. However, very small peak was observed at ca. 480ºC and the profile became almost flat. A small broad peak for Ni0.5-Al_2O_3SV and a small peak for Ni1-Al_2O_3SV which was observed at ca. 450ºC, due probably to the formation of NiO species which some acidity may be remained.

5.1.1.7 Thermal gravimetric analysis (TGA)

The catalyst supports before calcined of Ni-modified alumina prepared by solvothermal were determined using SDT Analyzer Model Q600 from TA Instruments. The analysis was performed at a rate of 10ºC/min to a desired temperature 1150ºC and held at that temperature for 1 h. Thermal gravimetric (TG) and differential temperature analysis (DTA) of Ni-modified alumina prepared by solvothermal before calcined are shown in Figure 5.10.



(A)



(B)

Figure 5.10 Thermal gravimetric analysis (TGA) of Ni-modified alumina prepared by solvothermal before calcined: (A) in terms of Temperature (ºC) and Weight (%), (B) in terms of Temperature (ºC) and Temperature Difference (ºC/mg

The overall weight loss increased from 14 to 20% as the Ni/Al ratio increased from 0 to 1. Two weight-decrease steps were clearly detected. The first was observed below 250^{o}C and was due to the desorption of physisorbed water. The second weight decrease occurred at around 250-400^{o}C could be attributed to the combustion of organic moieties forming on catalyst surface. The exothermic DTA peaks were clearly observed at around 318^{o}C which should be assigned to the exothermic heat from combustion process. Intensities of DTA peaks and overall weight loss increased as the Ni/Al ratio increased. These results suggest that the acetylacetonate groups from Ni precursor were not decomposed completely and remained on the surface of catalyst.

5.2.2 Catalytic Performance of 0.3%Pd/Ni-modified Al_2O_3 Prepared by Solvothermal

The performance of 0.3%Pd catalysts supported on Ni-modified Al_2O_3 in acetylene hydrogenation was evaluated at the temperature 40ºC, space velocities 39435, 24433, 16901 and 9288 h^{-1}. Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.). Removal of trace amount of acetylene in ethylene feed stream is vital for the commercial production of polyethylene since acetylene acts as a poison to the polymerization catalyst.

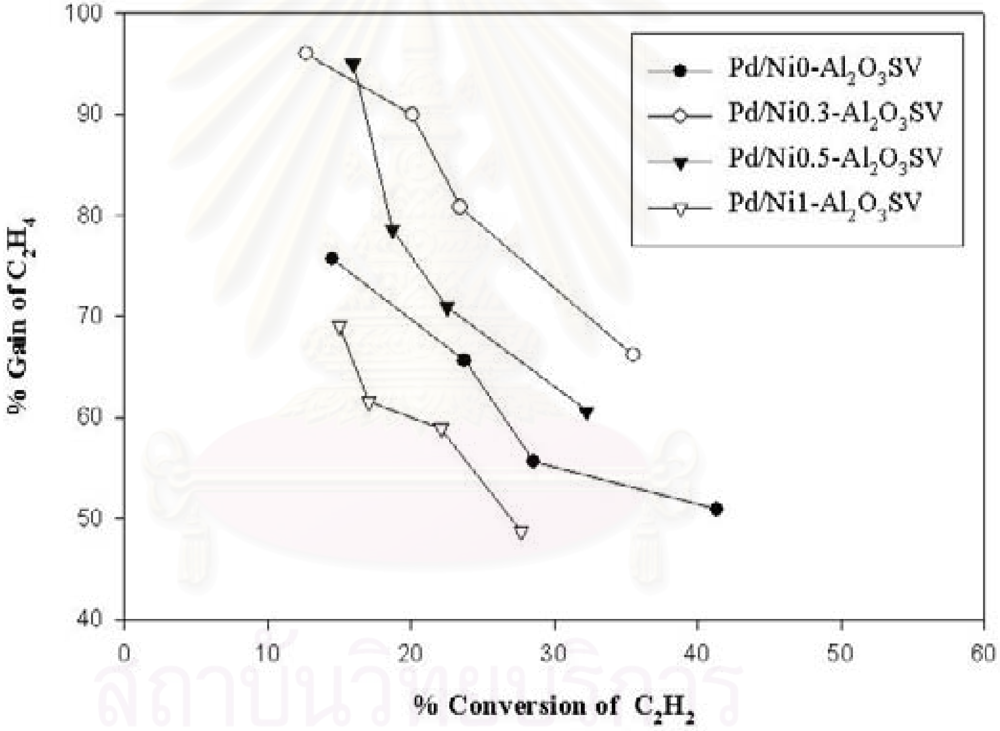


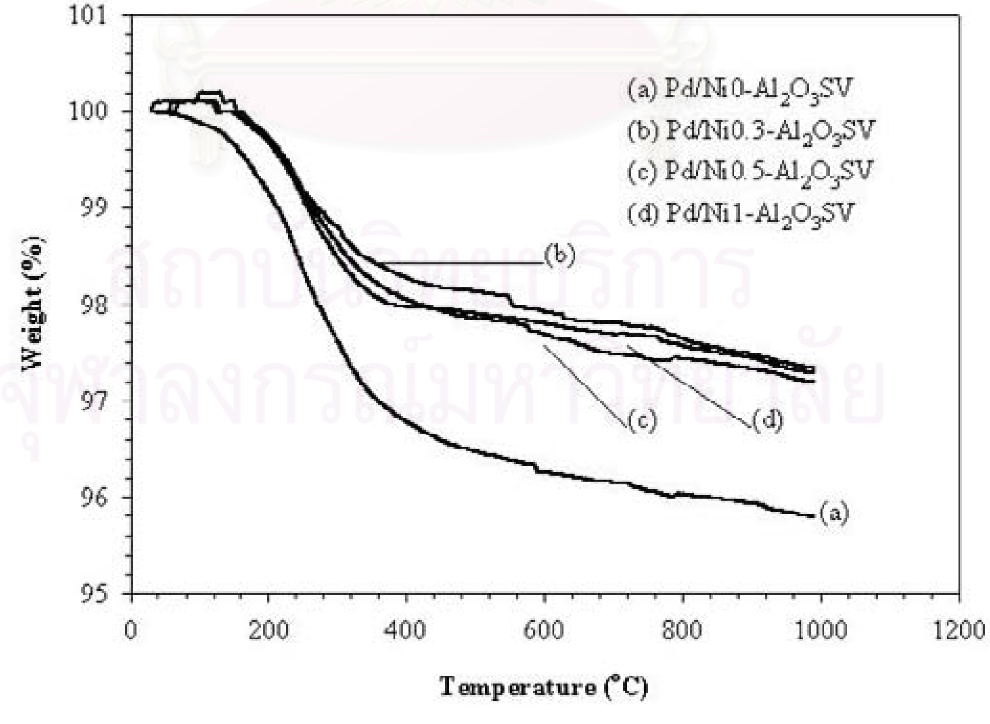
Figure 5.11 Catalytic performance of catalysts prepared by solvothermal

Figure 5.11 shows percent gain of ethylene with percent conversion of acetylene for Pd/α-Al_2O_3 (Pd/Ni0-Al_2O_3SV) and Pd/Ni-modified α-Al_2O_3 catalysts (Pd/Ni0.3-Al_2O_3SV, Pd/Ni0.5-Al_2O_3SV, and Pd/Ni1-Al_2O_3SV). It was found that Ni/Al ratio to 0.3 (Pd/Ni0.3-Al_2O_3SV) showed higher gain of ethylene than any other molar ratio. For other molar ratios, the catalytic performance was improved in the order: Pd/Ni0.5-Al_2O_3SV > Pd/Ni0-Al_2O_3SV > Pd/Ni1-Al_2O_3SV.

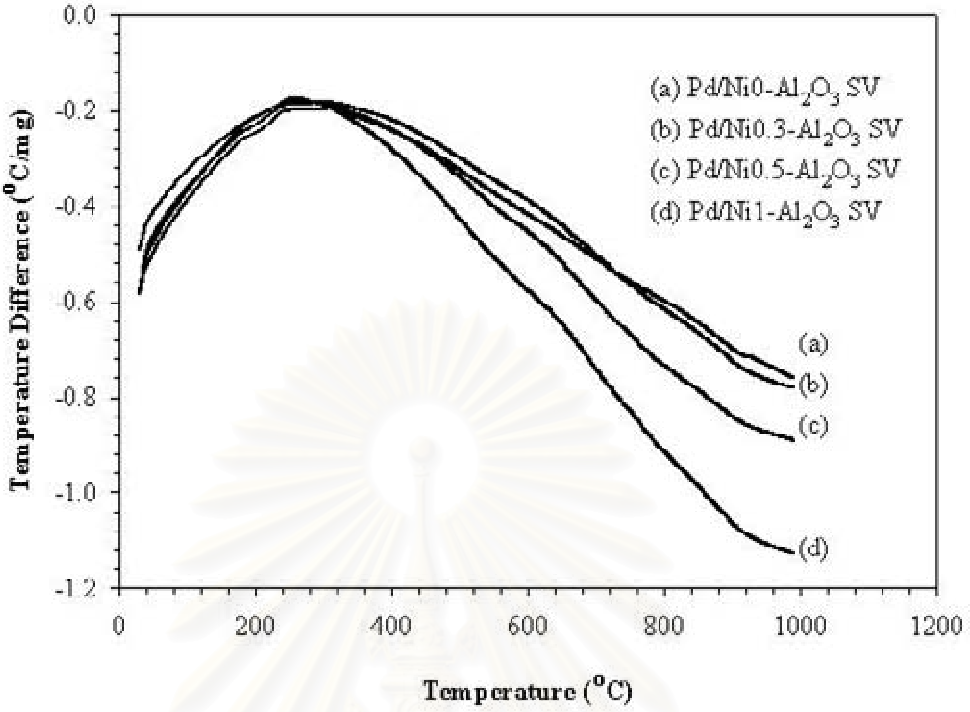
The catalytic activity and ethylene gain in the selective acetylene hydrogenation in excess ethylene over Pd-based catalysts were found to be dependent on many factors such as metal dispersion (Pd metal particle size) (Panpranot *et al.*, 2006), thermodynamic adsorption differences between acetylene and ethylene (Bond *et al.*, 1962), and carbonaceous product formation (Borodzinski *et al.*, 1962 and Borodzinski *et al.*, 2000), etc. In this case, it is likely that formation of $NiAl_2O_4$ may enhance the catalytic performance of Pd/Ni-modified Al_2O_3 catalysts (Peña *et al.*, 1995) because the best catalystic performance was found for Pd/Ni0.3-Al_2O_3SV where only $NiAl_2O_4$ was formed.

5.2.3 Catalyst Deactivation

The amount of carbonaceous deposits on the catalyst samples in selective hydrogenation of acetylene were measured by thermal gravimetric analysis. The weight losses corresponding to coke deposit on the catalyst samples are shown in Figure 5.12. The coke content of the catalysts was determined by combustion in SDT Analyzer Model Q600S thermal gravimetric analyzer (TGA). Samples were heated from room temperature to 1000ºC at 5ºC/min in a flow of 100 ml/min of O_2.



(A)



(B)

Figure 5.12 Thermogravimetric analysis (TGA) of Pd supported on Ni-modified alumina prepared by solvothermal after reaction: (A) in terms of Temperature (ºC) and Weight (%), (B) in terms of Temperature (ºC) and Temperature Difference (ºC/mg)

Figure 5.12 presents typical TGA-DTA profiles of Pd supported on α-Al_2O_3 and Ni-modified Al_2O_3 after reaction. There was one evident exothermic peak in the DTA curve, which was originated from the oxidation of coke on the surface of used catalyst. DTA curves of catalysts show one similar peak. This means type of coke species exist in the deactivated catalyst which called soft coke (Xiangjing *et al.*, 2006 and Jovanovic *et al.*, 1997). The exothermic DTA peaks of catalyst samples were clearly observed at around 300^{o}C. The weight loss of Pd supported on Ni-modified Al_2O_3 (Pd/Ni0.3-Al_2O_3SV, Pd/Ni0.5-Al_2O_3SV and Pd/Ni1-Al_2O_3SV) were around 2.6 wt.%. which were lower than that of Pd supported on α-Al_2O_3 (Pd/Ni0-Al_2O_3SV) (4.2 wt.%). Such results indicate that formation of $NiAl_2O_4$ could reduce coke deposition on the catalyst surface. The results are in good agreement with those reported by other researchers. For examples, Al-Ubaid and Wolf (Al-Ubad *et al.*, 1998) found a much greater stability for Ni supported on the nickel aluminate than on other supports. Bhattacharyya and Chang (Bhattacharyya *et al.*, 1994) have recently proposed the use of a nickel aluminate spinel catalyst in order to reduce coke formation in CH_4/CO_2 reforming. Rostrup-Nielsen (Rostrup-Nielses *et al.*, 1984) shows that carbon nucleation requires nickel ensembles of certain size, and its aggregation will be much slower and lower coking rates, can be expected if the metal is stabilized.

5.3 Commercial α-Al_2O_3 Supported Pd Catalysts

The most frequently studied support for palladium catalyst in selective acetylene hydrogenation is α-Al_2O_3, which has low acidity and high thermal stability. In this study selective hydrogenation of acetylene, commercial Al_2O_3 from Sigma-Aldrich was used as a support for Pd catalyst in selective acetylene hydrogenation for comparison purposes.

5.3.1 Characterization of the Pd Catalyst on Commercial α-Al_2O_3 Support

5.3.1.1 BET Surface Areas

The BET surface area of catalyst support measured by N_2 physisorption measurement is shown in Table 5.7.

Table 5.7 BET surface areas of commercial α-Al_2O_3

Sample	BET S.A. (m^2/g)
α- Al_2O_3 commercial	0.5

The BET surface area of commercial α-Al_2O_3 was 0.5 m^2/g which was not significantly different from the catalyst supports prepared by sol-gel and solvothermal method.

5.3.1.2 X-ray Diffraction (XRD)

Phase identification is carried out on the basis of data from X-ray diffraction analysis. The XRD pattern of Pd catalysts supported on commercial α-AL_2O_3 from Sigma-Aldrich is shown in Figure 5.13. All the XRD peaks indicate the presence of alumina only alpha phase. No XRD peaks for palladium or palladium oxide were observed due probably to the very low amount of Pd present on the catalyst (Kontapakdee, 2005).

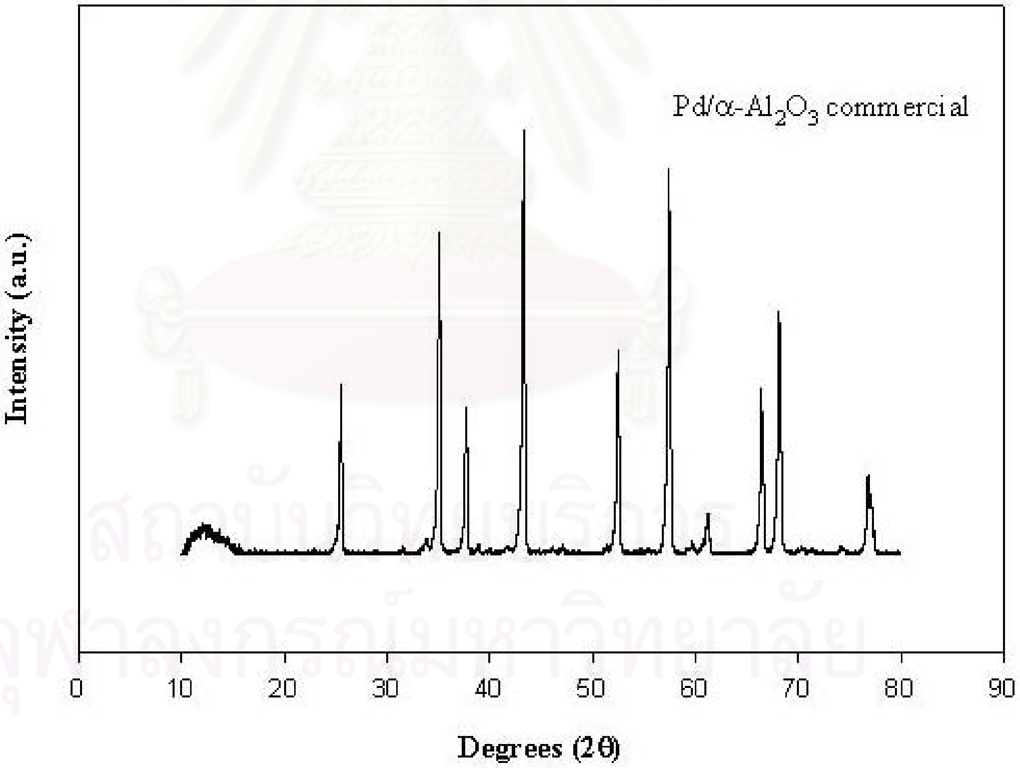


Figure 5.13 The XRD pattern of Pd catalyst supported on commercial α-Al_2O_3

5.3.1.3 Crystallite Size

The average crystallite size of each crystal phase was calculated from the Scherrer equation. The average crystallite size of Pd catalyst supported on commercial α-Al_2O_3 is shown in table 5.8. It was found that the crystallite size of α-Al_2O_3 was ca. 391.6 nm.

Table 5.8 Crytsallite size of Pd catalyst supported on commercial α-Al_2O_3

Sample	Crystallite size (nm)
Pd/α-Al_2O_3 commercial	391.6 (α-Al_2O_3)

5.3.1.4 Metal Active Sites

The amounts of CO chemisorption on the catalyst, the percentages of palladium dispersion and average Pd^0 particle size are given in Table 5.9. It was found that CO chemisorption, percentages of palladium dispersion and average Pd^0 particle size of Pd supported on commercial α-Al_2O_3 were not significantly different to all the catalysts prepared by sol-gel and solvothermal method.

Table 5.9 Results from CO chemisorption of Pd supported on commercial α-Al_2O_3

Sample	CO chemisorption $\times 10^{17}$ (molecule CO/g cat.)	Pd dispersion (%)	d_P Pd^0 (nm)
Pd/α-Al_2O_3 commercial	5.91	3.48	32

5.3.1.5 NH_3 Temperature Programmed Desorption (NH_3 TPD)

NH_3 temperature programmed desorption of commercial α-Al_2O_3 and γ-Al_2O_3 are shown in Figure 5.14. Comparing the desorption peak area of the reference γ-alumina, the desorption peak areas of the commercial α-Al_2O_3 powder was relatively low due probably to the dramatically decrease of the surface area. It is typical property of α-Al_2O_3 that possesses low acidity. Only a small broad peak at 300-500°C was observed.

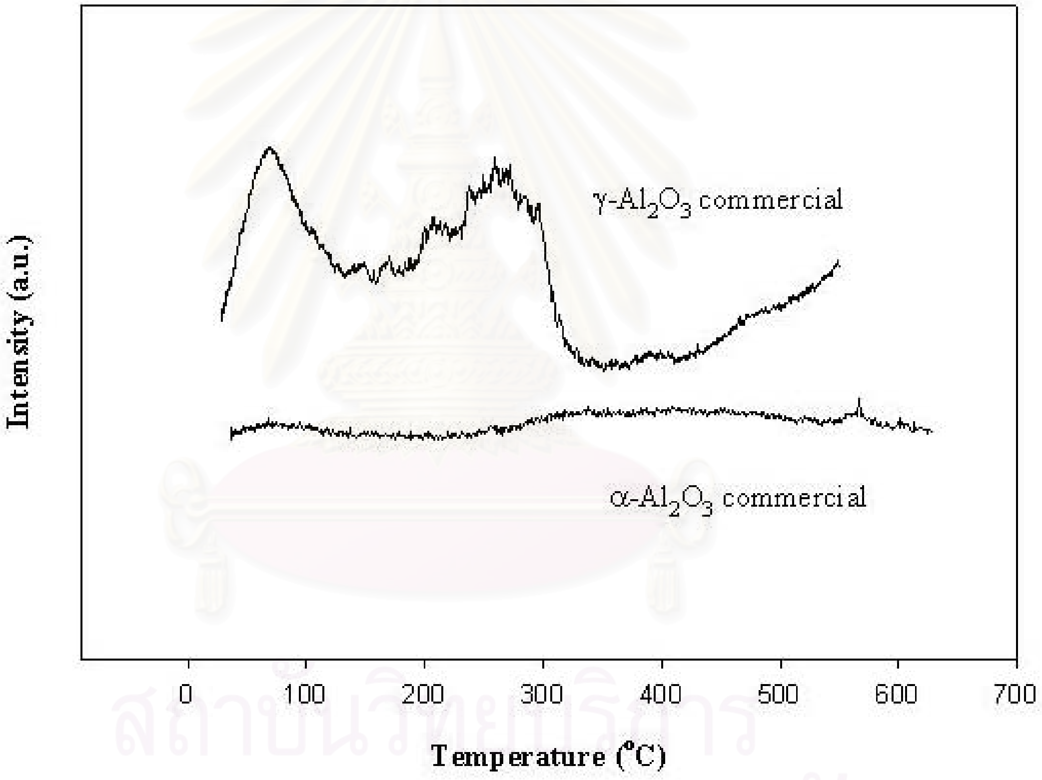


Figure 5.14 NH_3 temperature programmed desorption of commercial α-Al_2O_3

5.3.2 Catalytic Performance of Commercial Catalyst

Catalytic performance of 0.3%Pd supported on commercial α-Al_2O_3 was studied in selective hydrogenation of acetylene. The reaction was performed at the temperature 40°C. Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4

(TIG Co., Ltd.), a GHSV of 39435, 24433, 16901 and 9288 h^{-1} were used. Figure 5.15 shows catalytic performance of commercial catalyst. Compared to Pd catalyst supported on the catalyst supports prepared by sol-gel (Figure 5.5) and solvothermal method (Figure 5.11), the ones supported on commercial α-Al_2O_3 showed the worst catalytic performances in selective acetylene hydrogenation. Pd/α-Al_2O_3 exhibited much lower ethylene gain than sol-gel and solvothermal made catalysts at relatively low acetylene conversions.

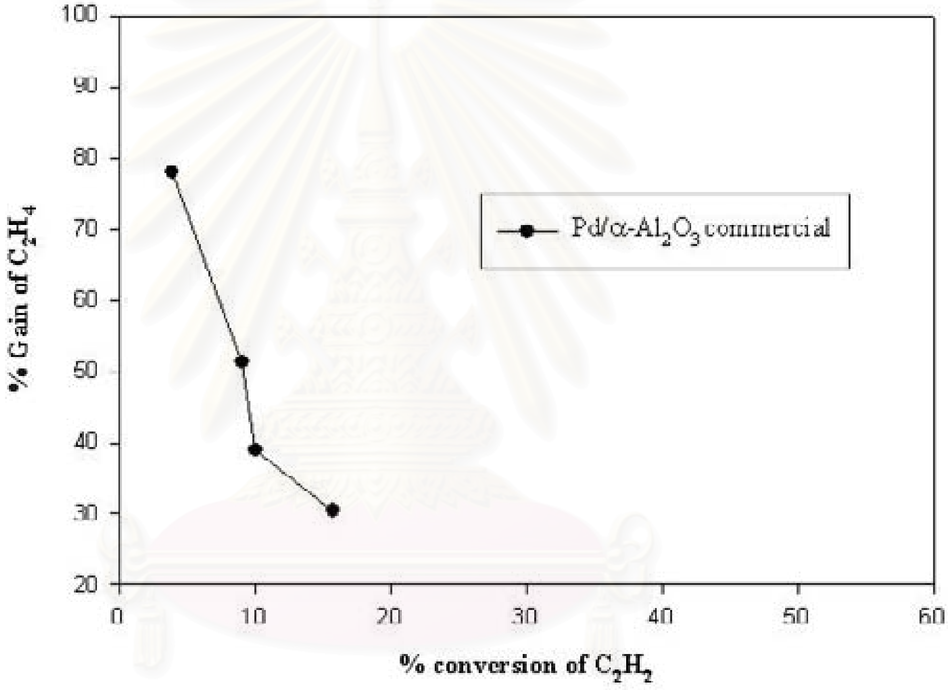
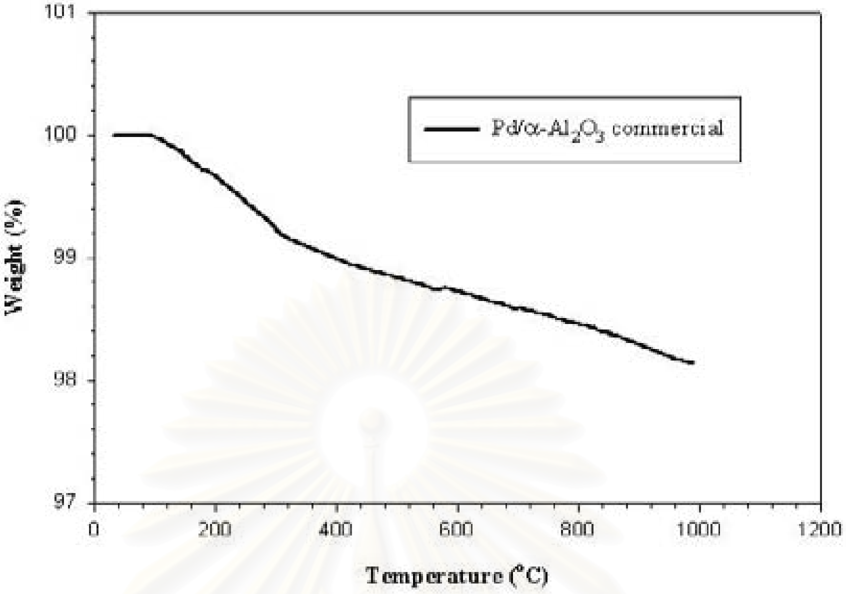


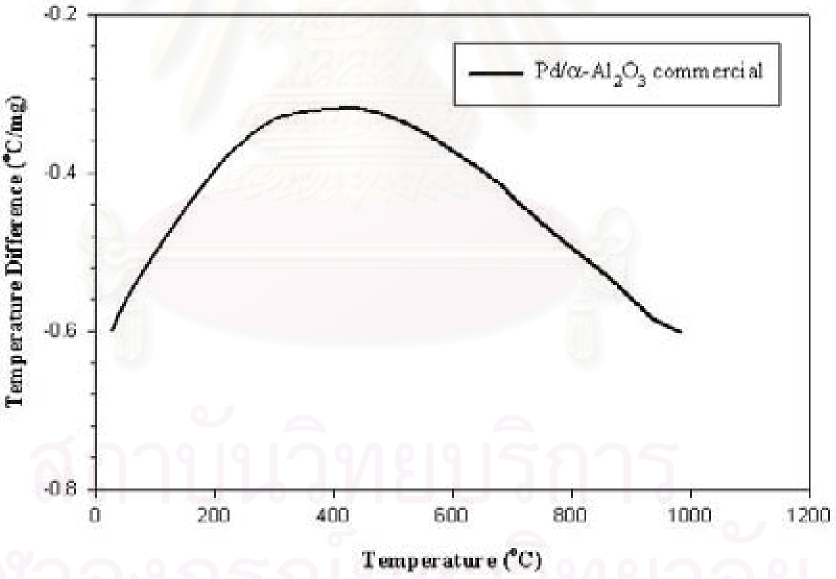
Figure 5.15 Catalytic performance of commercial catalyst

5.3.3 Catalyst Deactivation

The amount of coke on the catalyst sample in selective hydrogenation of acetylene was measured by thermal gravimetric analysis. The weight loss corresponding coke deposit on the catalyst samples is shown in Figure 5.16. From this figure, it shows that the weight loss of Pd supported on commercial α-Al_2O_3 was around 2 wt.%. The exothermic DTA peak of used catalyst was clearly observed at around 400°C.



(A)



(B)

Figure 5.16 Thermal gravimetric analysis (TGA) of Pd supported on commercial α-Al_2O_3 after reaction: (A) in terms of Temperature (ºC) and Weight (%), (B) in terms of Temperature (ºC) and Temperature Difference (ºC/mg)

5.4 Effect of Nickel Aluminate Formation on the Properties of Pd Catalysts Supported on Sol-gel and Solvothermal Derived Ni-modified α-Al_2O_3 (Ni/Al=0.5)

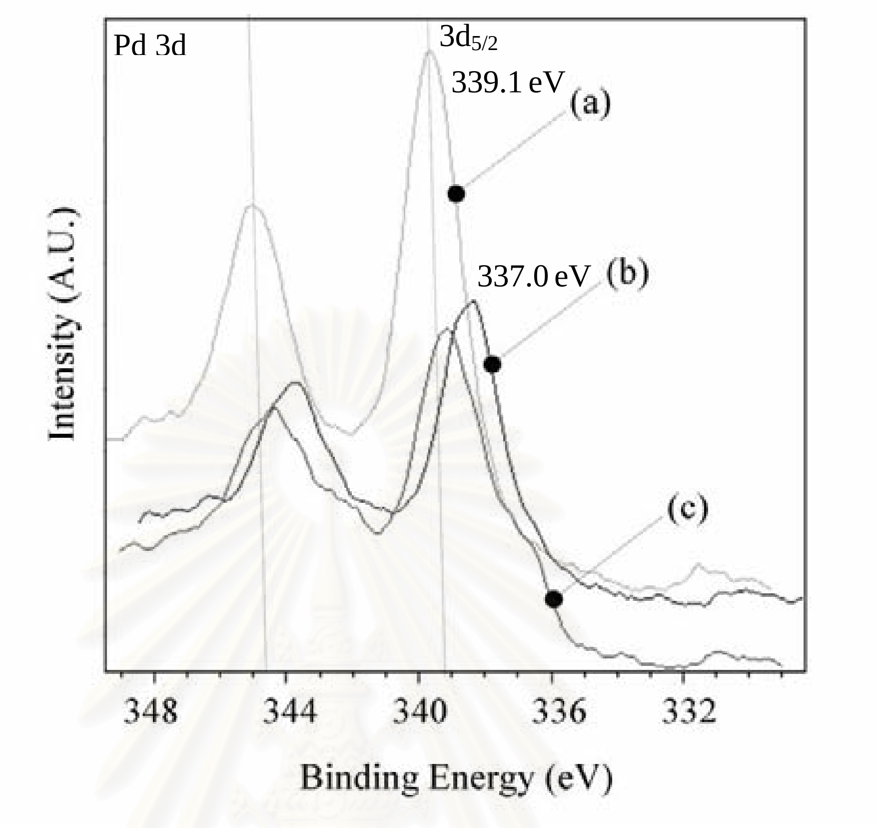
From the results shown in section 5.1-5.3, it was found that the performances of Pd catalysts supported on Ni-modified α-Al_2O_3 were improved compared to those supported on the non-modified α-Al_2O_3. Moreover, when comparing the samples prepared by different techniques, the sol-gel-made samples showed higher ethylene selectivity than those of the solvothermal-derived ones. The ethylene selectivity was improved in the order: Pd/Ni0.5Al_2O_3SG > Pd/Ni0.5-Al_2O_3SV ≈ Pd/Ni0-Al_2O_3SG > Pd/ Ni0-Al_2O_3SV >> Pd/α-Al_2O_3 commercial.

The catalytic activity and ethylene selectivity in the selective acetylene hydrogenation in excess ethylene over Pd-based catalysts were not dependent on the BET surface areas all the catalysts because there were no significantly differences and still quite low, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature. It is likely that formation of $NiAl_2O_4$ in the sol-gel made Ni-modified Al_2O_3 resulted in the improved catalytic performance of Pd/Ni-modified α-Al_2O_3 catalysts. The best catalytic performance was found for Pd/Ni0.5-Al_2O_3SG where only $NiAl_2O_4$ was formed.

From the XRD patterns, the sol-gel- and solvothermal-made Pd/α-Al_2O_3 catalysts (Pd/Ni0-Al_2O_3SG, Pd/Ni0-Al_2O_3SV) exhibited all the characteristic peaks of α-Al_2O_3 structure while the diffraction lines for Pd/Ni-modified α-Al_2O_3 catalyst (Pd/Ni0.5-Al_2O_3SG) could be assigned to a spinel-type $NiAl_2O_4$ structure; space group Fd3m (West *et al.*, 1997). Additional peaks corresponding to NiO were also presented at 43.3, 44.8 and 62.9°2θ for the product obtained from solvothermal synthesis (Pd/Ni0.5-Al_2O_3SV). The XRD characteristic peaks associated with Pd^0 or PdO phase were not observed in all the samples. This was probably due to the very low amount of Pd present and/or a very good dispersion of Pd phase on all the alumina supports. Formation of $NiAl_2O_4$ may enhance the catalytic performance of Pd/Ni-modified Al_2O_3 reducing acidity of the α-Al_2O_3 support as shown by the NH_3-TPD results.

The NH_3 temperature program desorption profiles for the sol-gel and solvothermal-made α-Al_2O_3 and the Ni-modified α-Al_2O_3 supports are shown in the previous sections. Comparing the desorption peak area of the reference γ-alumina, the desorption peak areas of the nanocrystalline α-Al_2O_3 powders obtained from both sol-gel and solvothermal syntheses were relatively low due probably to the dramatically decrease of the surface area after calcination at high temperature. However, two desorption peaks corresponding to different acid sites of α-Al_2O_3 samples were observed. For the Ni-modified α-Al_2O_3-sol-gel (Pd/Ni0.5-Al_2O_3SG), no distinctive peaks were observed and the profiles became almost flat. Such results indicate that acidity of the α-Al_2O_3 samples was drastically decreased by incorporation of Ni atoms. The results are in good agreement with those reported by other researchers. For examples, Otero Areán et al. (Otero Arean *et al.*, 2001) measured acidity of Ni-doped alumina by IR spectroscopy of CO adsorbed at liquid nitrogen temperature. A decrease in both Lewis and Brønsted acidity was observed as the Ni contents increased in the Ni-alumina solid solution. The very low Brønsted acidity also appears to be typical for many oxide spinels as well as other aluminate spinels such as $MgAl_2O_4$ and $ZnAl_2O_4$ (Otero Arean *et al.*, 1995 and Otero Arean *et al.*, 1997). A small broad peak was observed for the Ni-modified α-Al_2O_3-solvothermal (Pd/Ni0.5-Al_2O_3SV) due probably to the formation of NiO species which some acidity may be remained.

Because of its surface sensitivity, XPS is used to monitor the interaction between surface Pd and the alumina supports. The elemental scans for Pd 3d of the Pd/α-Al_2O_3 and the Pd/Ni-modified α-Al_2O_3 catalysts are shown in Figure 5.17. The binding energies of Pd $3d_{5/2}$ of Pd catalysts are found to be 339.1-337.0 eV, indicating PdO on the surface (Aungkapipattanachai, 2005). It was found that the binding energy of Pd $3d_{5/2}$ for the Pd catalyst supported Ni-modified α-Al_2O_3 prepared by sol-gel shifted to lower binding energy while for those of all the other catalysts, the binding energies for Pd 3d were at the same binding energies. It is likely that Pd catalyst supported on $NiAl_2O_4$ spinel may result in a lower interaction between Pd and the alumina support.



Figuer 5.17 XPS results of Pd 3d for (a) Pd/Ni0-Al_2O_3SG (b) Pd/Ni0.5-Al_2O_3SG (C) Pd/Ni0.5-Al_2O_3SV

Based on the reaction mechanisms for acetylene hydrogenation on Pd/Al_2O_3 catalysts in the literatures (Lamb *et al.,* 2004), there are three active sites on the Pd metal surface and one active site on the alumina support. The three sites on the palladium surface are responsible for selective hydrogenation of acetylene to ethylene, direct ethane formation from acetylene and oligomer formation whereas ethylene hydrogenation is believed to take place on the support by means of a hydrogen transfer mechanism (Lobo and Trimm, 1973, Somorjai *et al.,* 1979 and Moses *et al.,* 1984). It was claimed that the carbonaceous deposits present act as bridges for hydrogen spill over. It is well known that acidity on alumina surface promotes formation of carbonaceous deposits on catalyst surface. When Ni was incorporated in alumina lattice (i.e., in terms of $NiAl_2O_4$ formation), the acidity of alumina decreased drastically and thus reduced the formation of carbonaceous deposits and hydrogen spillover. In summary, Pd catalyst supported on Ni-modified α-Al_2O_3 can be used as an effective catalyst for producing high ethylene selectivities at relatively high acetylene conversions especially when $NiAl_2O_4$ are formed (Peña *et al.*, 1995). Promotion with other second metals such as Ag is then not necessary in order to improve the catalytic performance of these Pd-based catalysts (Ngamsom, 2002, Aungkapipattanachai, 2005 and Kontapakdee, 2005).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions obtained from the experimental results of Pd supported on Ni-modified Al_2O_3 supports with various molar ratios of Ni to Al, synthesized by different methods. Additionally, recommendations for further study are given in section 6.2.

6.1 Conclusions

1. Modification of α-Al_2O_3 support with nickel has shown to result in a better catalytic performance of Pd/α-Al_2O_3 catalysts in selective hydrogenation of acetylene in excess ethylene compared to the commercial α-Al_2O_3 supported ones. For Ni/Al = 0.5 ethylene selectivities were improved in the order: Pd/Ni-modified α-Al_2O_3-sol-gel > Pd/Ni-modified α-Al_2O_3-solvothermal ≈ Pd/α-Al_2O_3-sol–gel > Pd/α-Al_2O_3-solvothermal >> Pd/α-Al_2O_3-commercial.

2. The improvement in catalyst performance is probably due to both a decrease in surface acidity of α-Al_2O_3 and modification of Pd surface activity due to $NiAl_2O_4$ formation.

3. For Ni-modified α-Al_2O_3 prepared by sol-gel method, an appropriate amount of Ni/Al that gave the best properties when used as a support for Pd catalyst was 1 while for those obtained from solvothermal method, Ni/Al = 0.3 yielded the best catalytic performance. These were probably due to the differences in the crystallization mechanism for the formation of $NiAl_2O_4$ and NiO species during synthesis.

4. The formation of $NiAl_2O_4$ could reduce coke deposition on the catalyst surface of Pd/Ni-modified Al_2O_3.

6.2 Recommendations

1. The effect of modification of the alumina support with other metal such as Zn, Co, Fe and Ga, etc. for selective hydrogenation of acetylene over Pd supported catalysts should be investigated.

2. The effect of Ni-modified Al_2O_3 should be studied for other catalytic reactions such as liquid phase hydrogenation.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calulation of support composition (Ni-Modified Al_2O_3)

Preparation of Ni-modified Al_2O_3 with various molar ratios of Ni to Al (0.3, 0.5 and 1) 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: - Nickel nitrate-6-hydrate ($Ni(NO_3)_2 \cdot 6H_2O$)
Molecular weight = 290.69 g/mol
- Nickel (II) acetylacetonate $[CH_3COCH{=}C(O)CH_3]_2Ni$
Molecular weight = 256.69 g/mol
Calculation:

Sol-gel method

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

Aluminium nitrate nonahydrate 24.0735 g consisted of aluminium equal to:

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

For Ni/Al = 0.3, 0.0642 mole of aluminium

Nickel required $= 0.0642 \times 0.3 = 0.0193$ mol
$= 0.0193 \times 58.69 = 1.1304$ g

Nickel 1.1304 g was prepared from $Ni(NO_3)_2 \cdot 6H_2O$ and molecular weight of Ni is 58.69 mol

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

$$= (290.69/1.1304) \times 58.69 = 5.59 \text{ g}$$

- For molar ratio of Ni/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 Ni/Al = 0.5, 0.0642 mole of aluminium

Nickel required = 0.0642×0.5 = 0.0321 mol

= 0.0321×58.69 = 1.8839 g

Nickel 1.8839 g was prepared from $Ni(NO_3)_2{\cdot}6H_2O$ and molecular weight of Ni is 58.69 mol

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

= (290.69/1.8839)×58.69 = 9.33 g

- For molar ratio Ni/Al = 1 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 Ni/Al = 1, 0.0642 mole of aluminium

Nickel required = 0.0642×1 = 0.0642 mol

= 0.0642×58.69 = 3.7679 g

Nickel 3.7679 g was prepared from $Ni(NO_3)_2{\cdot}6H_2O$ and molecular weight of Ni is 58.69 mol

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

= (290.69/3.7679)×58.69 = 18.66 g

Solvothermal method

- For molar ratio Ni/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 Ni/Al = 0.3, 0.0735 mole of aluminium

Nickel required = 0.0735×0.3 = 0.0221 mol

= 0.0221×58.69 = 1.2941 g

Nickel 1.2941 g was prepared from $[CH_3COCH=C(O)CH_3]_2Ni$ and molecular weight of Ni is 58.69 mol

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

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_2Ni \times \text{nickel required}}{\text{MW of Ni}}$$

= (256.69/1.2941)×58.69 = 5.66 g

- For molar ratio Ni/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 Ni/Al = 0.5, 0.0735 mole of aluminium

Nickel required = 0.0735×0.5 = 0.0367 mol

= 0.0367×58.69 = 2.1568 g

Nickel 2.1568 g was prepared from $[CH_3COCH=C(O)CH_3]_2Ni$ and molecular weight of Ni is 58.69 mol

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

$$= \frac{\text{MW of } [CH_3COCH=C(O)CH_3]_2Ni \times \text{nickel required}}{\text{MW of Ni}}$$

= (256.69/2.1568)×58.69 = 9.43 g

- For molar ratio Ni/Al = 1 is shown as follow:

Aluminium isopropoxide 15 g consisted of aluminium equal to:

Aluminium = $(26.98\times15)/203.98$ = 1.9840 g

= $1.9840/26.98$ = 0.0735 mol

For Ni/Al = 0.5, 0.0735 mole of aluminium

Nickel required = 0.0735×1 = 0.0735 mol

= 0.0735×58.69 = 4.3137 g

Nickel 4.3137 g was prepared from $[CH_3COCH{=}C(O)CH_3]_2Ni$ and molecular weight of Ni is 58.69 mol

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

$$= \frac{\text{MW of }[CH_3COCH{=}C(O)CH_3]_2Ni\times\text{nickel required}}{\text{MW of Ni}}$$

$$= (256.69/4.3137)\times58.69 = 9.43 \text{ g}$$

Calculation of palladium loading

Preparation of 0.3%Pd/Ni-modified Al_2O_3 by the incipient wetness impregnation method are shown as follows:

Reagent: - Palladium (II) nitrate hexahydrate ($Pd(NO_3)_2 \cdot 6H_2O$)
Molecular weight = 338.42
- Support: - Ni-modified Al_2O_3 and α-Al_2O_3 (commercial)

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

Palladium = 0.3 g
Titania = 100-0.3 = 99.7 g

For 1 g of Ni-modified Al_2O_3
Palladium required = 1×(0.3/99.7) = 0.003 g

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

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

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

Since the pore volume of Ni-modified 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 titania 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:

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

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:

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

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

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 Ni-modified Al_2O_3 (Ni/Al=0.5) prepared by sol-gel method

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

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

= 0.00692 radian

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

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

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

= 0.00553 radian

β = 0.00553 radian

2θ = 37.02^o

θ = 18.51^o

λ = 1.5418 Å

The crystallite size = $\dfrac{0.9 \times 1.5418}{0.00553 \cos 18.51}$ = 264.56 Å

= 26.5 nm

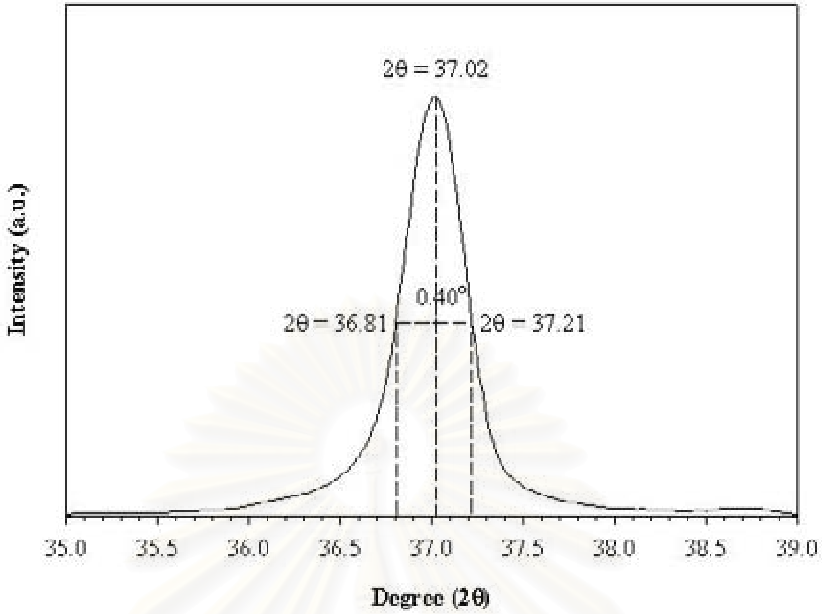

Figure B.1 The measured peak of Ni-modified Al_2O_3 (Ni/Al=0.5) prepared by sol-gel method to calculate the crystallite size.

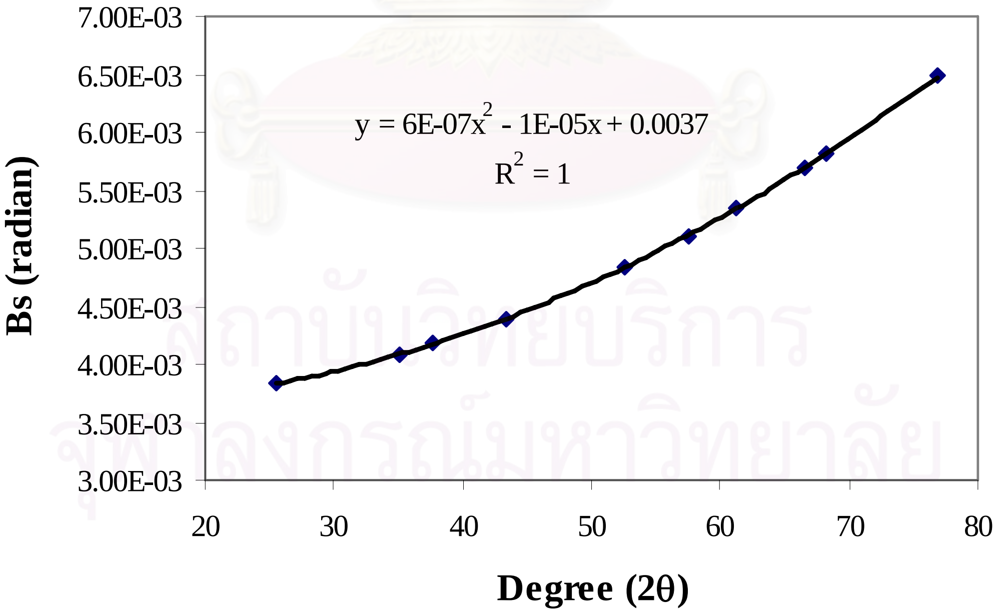

Figure B.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α-alumina as standard

APPENDIX C

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

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

Let the weight of catalyst used = W g

Integral area of CO peak after adsorption = A unit

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

Amounts of CO adsorbed on catalyst = B-A unit

Volume of CO adsorbed on catalyst = $100\times[(B-A)/B]$ 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

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

Metal active sites

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

Molecules of Pd loaded

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

Metal dispersion (%)

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

APPENDIX D

CALIBRATION CURVES

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

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

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

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

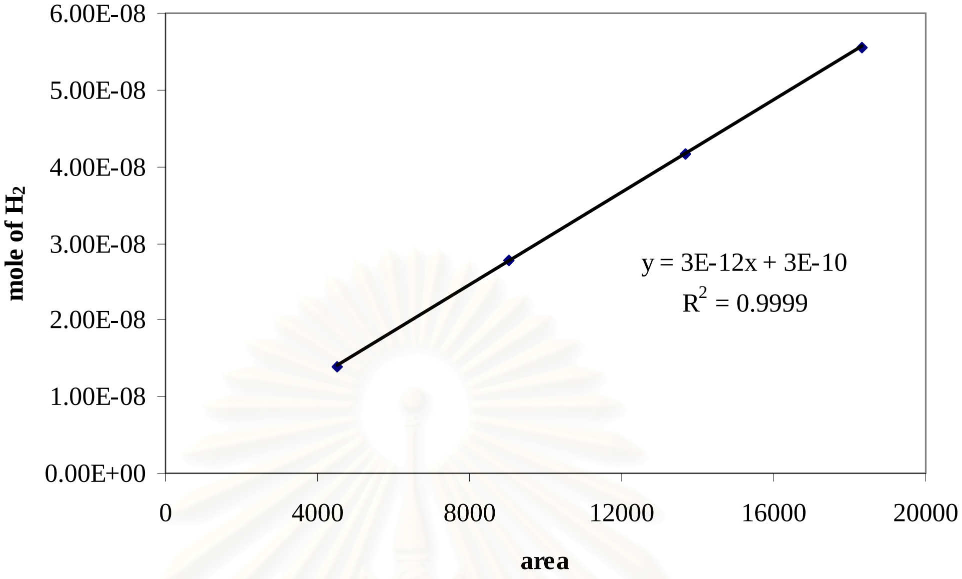

Figure D.1 The calibration curve of hydrogen from TCD of GC-8A.

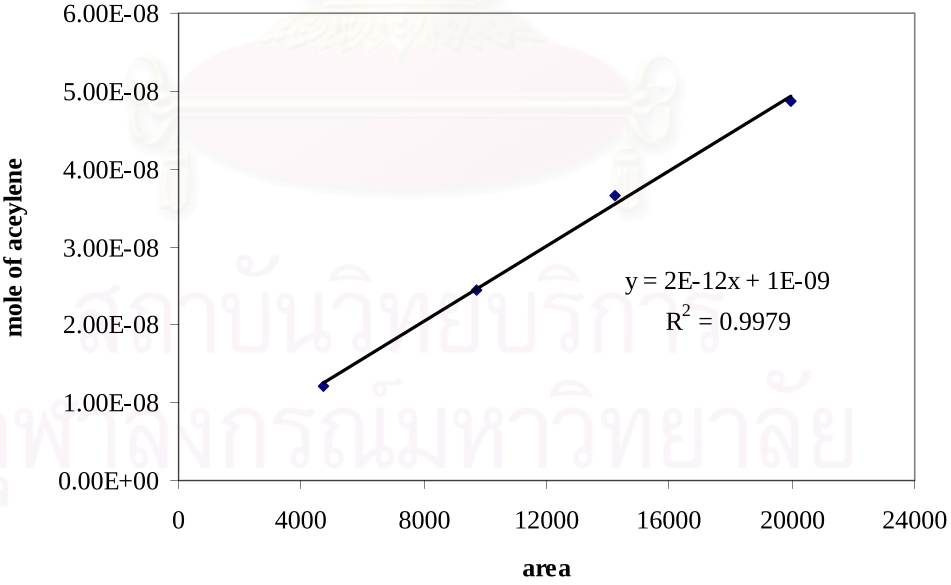

Figure D.2 The calibration curve of acetylene from FID of GC-9A.

APPENDIX E

CALCULATION OF CONVERSION AND SELECTIVITY

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

$$C_2H_2 + H_2 \xrightarrow{\hspace{2cm}} C_2H_4 \qquad (E.1)$$

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

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

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

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

mole of C_2H_2 = (area of C_2H_2 peak from integrator plot on GC-9A)×2.0×10^{-12} (ii)

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

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

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

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

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

mole of H_2 = (area of H_2 peak from integrator plot on GC-8A)×3.0×10^{-12} (vi)

APPENDIX F

LIST OF PUBLICATIONS

1. Wongwaranon, N., Mekasuwandumrong, O., Panpranot, J., and Praserthdam, P., Effect of Ni-modified Al_2O_3 on the Properties of Pd/α-Al_2O_3 Catalysts in Selective Hydrogenation of Acetylene. Proceeding of the 4th Asia Pacific Congress on Catalysis, 6-8 Dec. (2006), Singapore.

2. Mekasuwandumrong, O., Panpranot, J., Wongwaranon, N., and Praserthdam, P., Performance of Pd Catalysts Supported on Nanocrystalline α-Al_2O_3 and Ni-Modified α-Al_2O_3 in Selective Acetylene Hydrogenation. Catalysis Today (2007), submitted.

Effect of Ni-modified Al_2O_3 on the Properties of Pd/α-Al_2O_3 Catalysts in Selective Hydrogenation of Acetylene

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ABSTRACT

In this study, Ni-modified α-Al_2O_3 were prepared by sol-gel and solvothermal technique and employed as supports for Pd catalysts in selective hydrogenation of acetylene in excess ethylene. $NiAl_2O_4$ spinel was formed when 0.5%Ni was added during the preparation of α-Al_2O_3 by sol-gel method whereas the ones synthesized by solvothermal formed both nickel oxide and nickel aluminate species. Use of the Ni-modified α-Al_2O_3 prepared by sol-gel as a support for Pd catalyst resulted in a better catalytic performance in selective hydrogenation of acetylene to ethylene compared to the use of non-modified Al_2O_3 supported ones.

1. INTRODUCTION

Selective catalytic hydrogenation of acetylene to ethylene is the preferred route for acetylene removal from ethylene feedstock in polyethylene manufacturing because acetylene acts as a poison to the polymerization catalysts [1-2]. Pd/α-Al_2O_3 is the well-known catalyst employed in selective hydrogenation. However, due to poor selectivity at high acetylene conversion, oligomer formation during acetylene hydrogenation and the demand for high purity ethylene, considerable attention has been focused on the factors which improve activity and selectivity of acetylene hydrogenation catalysts. Sintering of Pd metal can increase the site for direct ethane formation thus several second metals especially the metals of group IB such as Ag, K, Si, Au, Cu, Ti, Ce, and Co have been incorporated into Pd catalysts in order to improve the catalyst performance [3]. However, modification of α-Al_2O_3 support has not been studied very often. It is the aims of this study to prepare the highly stable Ni-modified α-Al_2O_3 supported Pd catalysts that are resistant to deactivation.

2. EXPERIMENTAL

Ni-modified α-Al_2O_3 samples were prepared by sol-gel and solvothermal method using aluminium nitrate nonahydrate and aluminum isopropoxide as alumina precursor, respectively. The Ni/Al molar ratios were varied from 0-1.0 by adjusting the amount of nickel acetylacetonate added to the precursor mixture. The obtained products were heated at a rate of 10°C/min to 1150°C and held at that temperature for 1 h. Approximately 0.3 wt% of Pd was then loaded on the Ni-modified Al_2O_3 supports by incipient wetness impregnation and were calcined at 500°C for 2 h. The catalysts were characterized by N_2 physisorption, X-ray diffraction, CO pulse chemisorption, and X-ray photoelectron spectroscopy. Their catalytic performances were evaluated in the gas-phase selective hydrogenation of acetylene in a tubular down flow quartz reactor at 40-120°C and 1 atm.

3. RESULTS AND DISCUSSION

The XRD patterns of various 0.3%Pd catalysts supported on α-Al_2O_3 and Ni-modified α-Al_2O_3 with Ni/Al molar ratio 0.5 are shown in Figure 1. It was found that the Ni-modified α-Al_2O_3 prepared by sol-gel formed $NiAl_2O_4$ spinel while that prepared by solvothermal method resulted in both NiO and $NiAl_2O_4$ species. The crystallization mechanism was probably different for the two methods used resulting in different properties of the Ni-modified α-Al_2O_3 obtained. It is suggested that direct crystallization occurred for the solvothermal synthesis while sol-gel method yielded a solid precipitate at relatively low temperature and crystallization occurred during the subsequent calcination step. No XRD characteristic peaks for PdO or Pd^0 were found for all the catalysts due probably to the low amount of palladium presented. The catalytic performances of Pd/α-Al_2O_3 and Pd/Ni-modified α-Al_2O_3 in gas-phase selective hydrogenation of acetylene are shown in Figure 2. It was found that use of Ni-modified Al_2O_3 prepared by sol-gel as a support for Pd catalyst resulted in a better catalytic performance in selective hydrogenation of acetylene to ethylene compared to the use of either non-modified Al_2O_3 supported ones or that prepared by solvothermal method. It is suggested that the formation of highly stable $NiAl_2O_4$ species was responsible for an inhibition of direct ethane formation sites especially at high acetylene conversions. Modification of the active Pd surface by nickel aluminate formation is further investigated by other surface characterization technique such as X-ray photoelectron spectroscopy (XPS).

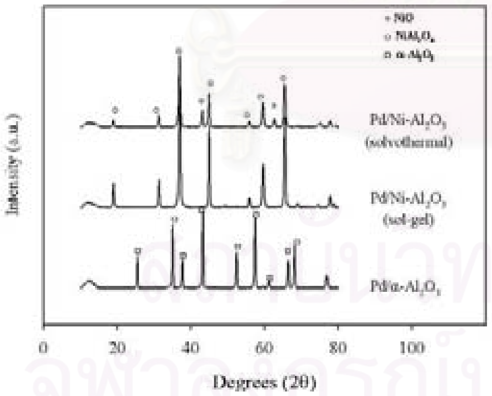

Figure 1 XRD patterns of Pd/Al_2O_3 and $Pd-Ni/Al_2O_3$ catalysts

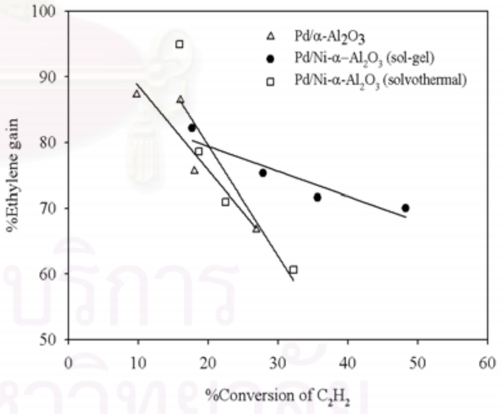

Figure 2 Performance curves of Pd/Al_2O_3 and $Pd-Ni/Al_2O_3$ catalysts

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Performance of Pd Catalysts Supported on Nanocrystalline α-Al_2O_3 and Ni-Modified α-Al_2O_3 in Selective Hydrogenation of Acetylene

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Abstract

Nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 have been prepared by sol-gel and solvothermal methods and employed as supports for Pd catalysts. Regardless of the preparation method used, $NiAl_2O_4$ spinel was formed on the Ni-modified α-Al_2O_3 after calcination at 1150°C. However, an additional of NiO peaks was also observed by X-ray diffraction for the solvothermal-made Ni-modified α-Al_2O_3 powder. Catalytic performances of the Pd catalysts supported on these nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 in selective hydrogenation of acetylene were found to be superior to those of the commercial α-Al_2O_3 supported one. Ethylene selectivities were improved in the order: Pd/Ni-modified α-Al_2O_3-sol-gel > Pd/Ni-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 NH_3 temperature program desorption studies, incorporation of Ni atoms in α-Al_2O_3 resulted in a significant decrease of acid sites on the alumina supports. Moreover, XPS revealed a shift of Pd 3d binding energy for Pd catalyst supported on Ni-modified α-Al_2O_3-sol-gel where only $NiAl_2O_4$ was formed. This modification could probably result in an inhibition of a product ethylene on the Pd surface and hence high ethylene selectivities were obtained at high acetylene conversions.

Keywords: nanocrystalline α-Al_2O_3, Ni-modified α-Al_2O_3, solvothermal, sol-gel, selective acetylene hydrogenation, nickel aluminate

1. Introduction

The selective hydrogenation of acetylene in ethylene rich stream is a crucial process in polyethylene production since acetylene poisons the polymerization catalysts [1-2]. Pd-based catalyst supported on alumina with low Pd loading (0.1-0.3 wt.%) is typically employed for this reaction due to its good activity and selectivity and the easily desorption of ethylene on the catalyst surface [3]. With respect to selectivity changes, catalysts of low Pd dispersion have been suggested to give better selectivity towards ethylene at high acetylene conversions [4-6]. Thus, alumina used as Pd catalyst support in this reaction contains mostly the alpha phase alumina since it possesses relatively low specific surface area and low acidity compared to other ‘transition’ alumina.

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. For examples, Co catalysts supported on nanocrystalline Al_2O_3 [7] and ZrO_2 [8] have been found to exhibit higher hydrogenation activities and selectivities toward long chain hydrocarbons than those of the commercial micron-sized Al_2O_3 and ZrO_2 supported ones. Physical and chemical properties of TiO_2 are modified when they are synthesized in the nanometer range resulting in an improvement of its photocatalytic activity [9].

Several techniques have been reported for preparation of nanocrystalline ‘transition’ alumina such as sol-gel method [10], hydrothermal synthesis [11], microwave synthesis [12], emulsion evaporation [13-14], precipitation from solution [15], and solvothermal synthesis [16-17]. 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 material. Desired shape and size of particles can be produced by controlling process conditions such as solute concentration, reaction temperature, reaction time, and the type of solvent [18].

In the present study, nanocrystalline α-Al_2O_3 and Ni-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 nickel is also interesting because it can form nickel aluminate spinel ($NiAl_2O_4$) which is a highly stable material that can have beneficial effect on the catalyst performance. Moreover, formation of $NiAl_2O_4$ in some Ni-based hydrogenation catalysts has shown high resistance to coke formation [19-21].

2. Experimental

2.1 Preparation of Nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3

Nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 were prepared by sol-gel and solvothermal methods. For the sol-gel method, 24 g of aluminium nitrate nonahydrate (Aldrich) was dissolved in 50 cc of ethanol. The experiment was conducted in the reflux-condenser reactor at the temperature about 70-80^oC for 18 h. Then, urea solution, which consist of 60 g of urea and 50 ml of distilled water, was added to adjust pH of sol. The mixture was rested at the same temperature for 24 h to be gelled at neutral condition. The obtained product was calcined with 2 steps heating rate to avoid overflowing of gel during calcinations, i.e. 3^oC/min from room temperature to 500^oC and continue heating at 5^oC/min to 1150^oC. Then, temperature was hold for 3 h. For the preparation of Ni-modified α-Al_2O_3, a desired amount of nickel nitrate-6-hydrate (Aldrich) was added to the precursor mixture and then followed the same procedures as that of α-Al_2O_3.

For the solvothermal method, α-Al_2O_3 and Ni-modified α-Al_2O_3 were prepared using a mixture of aluminum isopropoxide 15.0 grams and appropriate amount of nickel (II) acetylacetonate. The starting materials were suspended in 100 mL of toluene in beaker, and then set up in autoclave. In the gap between the beaker and autoclave wall, 40 mL of toluene was added. After the autoclave was completely, the suspension was heated to 300^{o}C at the rate of 2.5^{o}C/min and held at that temperature for 2 h. However, the same synthesis method is performed at various holding temperature. Autogenous pressure during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the obtained product carried out in a furnace. The product was heated at a rate of 10^{o}C/min to a desired temperature 1150^{o}C and held at that temperature for 1 h. For comparison purposes, a commercial α-Al_2O_3 (JRC-ALO2) was also employed as Pd catalyst support.

2.2 Preparation of α-Al_2O_3 supported Pd catalysts

The Pd/α-Al_2O_3 catalysts were prepared by incipient wetness impregnation of Al_2O_3 support with a desired amount of an aqueous solution of palladium (II) nitrate hydrate (Aldrich). The catalysts were dried overnight at 110°C and then calcined in N_2 flow 60 cm^3/min with a heating rate of 10°C/min until the temperature reached 500°C and then in air flow 100 cm^3/min at 500°C for 2 h. The final Pd loading of the catalysts was determined by atomic absorption spectroscopy (Varian Spectra A800) to be ca. 0.3 wt%.

2.3 Catalyst Characterization

Surface area measurements were carried out by nitrogen adsorption in a Micromeritic Chemisorb 2750 system. Each sample was degassed at 200^{o}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. X-ray diffraction patterns of the catalyst samples were obtained with a SIEMENS D5000 X-ray diffractometer using Cu K_α radiation with a Ni filter. The pattern were recorded between 20–80° (2θ) using a scanning velocity of 0.02^{o}/s. Metal active sites were measured using CO chemisorption technique at room temperature in a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software. Before chemisorption measurement, 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. Ammonia temperature program desorption (NH_3-TPD) was also 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 samples adsorbed ammonia at 40^{o}C, then heated up to 650^{o}C at a heating rate of 10^{o}C/min. The distribution of palladium on catalyst supports were observed using AJEM-200CX transmission electron microscope operated at 160 kV. Surface compositions of the catalysts were analyzed using an AMICUS photoelectron spectrometer equipped with Mg K_α X-ray as primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV.

2.4 Reaction Study

Catalytic performance of the catalysts was studied in selective hydrogenation of acetylene. The experiment was performed in a quartz tube reactor (i.d. 10.1 mm). Before starting of the reaction, the catalyst was reduced in H_2 at 150°C for 2 h. Then the reactor was purged with argon and cooled down to the reaction temperature, 40°C. Feed gas composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (TIG Co., Ltd.), a GHSV of 39435, 24433, 16901 and 9288 h^{-1} were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S2 columns, respectively). Acetylene conversion as used herein 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. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated.

3. Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of the sol-gel- and the solvothermal-made Pd/α-Al_2O_3 and the Pd/Ni-modified α-Al_2O_3 catalysts with Ni/Al atomic ratio 0.5 after calcinations at 1150^{o}C are shown in **Figure 1**. The patterns in the lower half of the figure correspond to the sol-gel-made powder while the patterns in the upper part of the figure are for those prepared by solvothermal synthesis. Both the sol-gel- and solvothermal-made Pd/α-Al_2O_3 catalysts exhibited all the characteristic peaks of α-Al_2O_3 structure. While the diffraction lines for Pd/Ni-modified α-Al_2O_3 catalyst could be assigned to a spinel-type $NiAl_2O_4$ structure; space group Fd3m [22]. Additional peaks corresponding to NiO were also presented at 43.3 and 62.9°2θ for the product obtained from solvothermal synthesis. The XRD characteristic peaks associated with Pd^0 or PdO phase were not observed in all the samples. This was probably due to the very low amount of Pd present and/or a very good dispersion of Pd phase on all the alumina supports.

TEM micrographs were taken in order to physically measure the size of the palladium oxide particles and/or palladium clusters. It can be seen that the sol-gel made catalyst (**Figure 2a and 2b**) was consisted of agglomerated particles with primarily irregular shape structure. For those prepared by solvothermal method, agglomeration of finger-like particles were observed for the Pd/α-Al_2O_3 whereas spherical-shape particles were found for the Pd/Ni-modified α-Al_2O_3 catalysts (**Figure 2c and 2d**, respectively). 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 [23-24]. Based on TEM analysis, palladium particles/clusters with average particle size ca. 5-10 nm were found to be deposited on the alumina supports.

The physical and chemical properties of Pd/α-Al_2O_3 and Pd/Ni-modified α-Al_2O_3 catalysts are summarized in **Table 1**. The average crystallite size of each crystal phase was calculated from the Scherrer equation. The average crystallite sizes of the α-Al_2O_3 prepared by sol-gel and solvothermal method were 34 and 58 nm, respectively. While, the crystallite sizes of $NiAl_2O_4$ formed in the Ni-modified α-Al_2O_3 prepared by sol-gel and solvothermal method were 23 and 27 nm, respectively. In all cases, the average crystallite sizes of $NiAl_2O_4$ were smaller than those of α-Al_2O_3. Such results suggest that crystal growth rate for $NiAl_2O_4$ was slower than that of α-Al_2O_3. The surface areas of all the catalysts were not significantly different and still quite low, due probably to high agglomeration of these nanocrystalline particles during calcinations at high temperature. The amounts of CO chemisorption on the catalysts, the Pd dispersions, and the average Pd metal particle sizes determined from CO chemisorption are also given in **Table 1**. The pulse CO chemisorption technique was based on the assumption that one carbon monoxide molecule adsorbs on one palladium site [25-29]. The amounts of CO chemisorption decreased from 7.5 to 5.4 $*10^{17}$ sites/g cat. and 8.1 to 7.4 $*10^{17}$ sites/g cat. corresponding to the decreasing in Pd metal dispersion from 4.4 to 3.2 and 4.8 to 4.3 % by modification with Ni atoms by sol-gel and solvothermal method, respectively. The percentages of Pd dispersion calculated from the CO chemisorption results were in the order Pd/α-Al_2O_3-solvothermal > Pd/α-Al_2O_3-sol–gel ≈ Pd/Ni-modified α-Al_2O_3-solvothermal > Pd/Ni-modified α-Al_2O_3-sol-gel. The average Pd^0 particle sizes for all the catalysts were calculated to be 24-35 nm.

Figure 3 shows the NH_3 temperature program desorption profiles for the sol-gel and solvothermal-made α-Al_2O_3 and the Ni-modified α-Al_2O_3 supports. Comparing the desorption peak area of the reference γ-alumina, the desorption peak areas of the nanocrystalline α-Al_2O_3 powders obtained from both sol-gel and solvothermal syntheses were relatively low due probably to the dramatically decrease of the surface area after calcination at high temperature. However, two desorption peaks corresponding to different acid sites were still observed at ca. 320 and 400-500^oC for both α-Al_2O_3 samples. For the Ni-modified α-Al_2O_3-sol-gel, no distinctive peaks were observed and the profiles became almost flat. Such results indicate that acidity of the α-Al_2O_3 samples was drastically decreased by incorporation of Ni atoms. The results are in good agreement with those reported by other researchers. For examples, Otero Areán et al. [30] measured acidity of Ni-doped alumina by IR spectroscopy of CO adsorbed at liquid nitrogen temperature. A decrease in both Lewis and Brønsted acidity was observed as the Ni contents increased in the Ni-alumina solid solution. The very low Brønsted acidity also appears to be typical for many oxide spinels as well as other aluminate spinels such as $MgAl_2O_4$ and $ZnAl_2O_4$ [31-32]. A small broad peak was observed for the Ni-modified α-Al_2O_3-solvothermal due probably to the formation of NiO species which some acidity may be remained.

Because of its surface sensitivity, XPS is used to monitor the interaction between surface Pd and the alumina supports. The elemental scans for Pd 3d of the Pd/α-Al_2O_3 and the Pd/Ni-modified α-Al_2O_3 catalysts are shown in **Figure 4**. It was found that the binding energy of Pd 3d for the Pd catalyst supported Ni-modified α-Al_2O_3 prepared by sol-gel shifted to lower binding energy while for those of all the other catalysts, the binding energies for Pd 3d were at the same binding energies. It is likely that Pd catalyst supported on $NiAl_2O_4$ spinel may result in a lower interaction between Pd and the alumina support.

3.2 Catalyst Performance in Selective Acetylene Hydrogenation

The catalyst performance in selective hydrogenation of acetylene to ethylene was studied for all the catalyst samples using a fixed bed flow reactor. Changes in ethylene selectivity with acetylene conversion for Pd/α-Al_2O_3 and Pd/Ni-modified α-Al_2O_3 catalysts are shown in **Figure 5**. In general, ethylene selectivity decreases with increasing acetylene conversion due to the fact that the ethylene is produced as an intermediate in acetylene hydrogenation reaction. Compared to Pd catalyst supported on the commercial α-Al_2O_3, the ones supported on nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 showed superior catalytic performances in selective acetylene hydrogenation with Pd/Ni-modified α-Al_2O_3 exhibited higher selectivity than Pd/α-Al_2O_3. When comparing the samples prepared by different techniques, the sol-gel-made samples showed higher ethylene selectivity than those of the solvothermal-derived ones. The ethylene selectivity was improved in the order: Pd/Ni-modified α-Al_2O_3-sol-gel > Pd/Ni-modified α-Al_2O_3-solvothermal ≈ Pd/α-Al_2O_3-sol–gel > Pd/α-Al_2O_3-solvothermal >> Pd/α-Al_2O_3-commercial.

During long-time investigation by many research groups, the catalytic activity and ethylene selectivity in the selective acetylene hydrogenation in excess ethylene over Pd-based catalysts are found to be dependent on many factors such as metal dispersion (Pd metal particle size) [33], thermodynamic adsorption differences between acetylene and ethylene [34], and carbonaceous product formation [35, 36], etc. Based on the reaction mechanisms for acetylene hydrogenation on Pd/Al_2O_3 catalysts in the literatures [37], there are three active sites on the Pd metal surface and one active site on the alumina support. The three sites on the palladium surface are responsible for selective hydrogenation of acetylene to ethylene, direct ethane formation from acetylene and oligomer formation whereas ethylene hydrogenation is believed to take place on the support by means of a hydrogen transfer mechanism. It was claimed that the carbonaceous deposits present act as bridges for hydrogen spillover [38]. It is well known that acidity on alumina surface promotes formation of carbonaceous deposits on catalyst surface. When Ni was incorporated in alumina lattice (i.e., in terms of $NiAl_2O_4$ formation), the acidity of alumina decreased drastically and thus reduced the formation of carbonaceous deposits and hydrogen spillover. In summary, Pd catalyst supported on Ni-modified α-Al_2O_3 can be used as an effective catalyst for producing high ethylene selectivities at relatively high acetylene conversions especially when $NiAl_2O_4$ are formed. Promotion with other second metals such as Ag is then not necessary in order to improve the catalytic performance of these Pd-based catalysts.

4. Conclusions

The catalytic performance of Pd catalysts supported on nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 prepared by sol-gel and solvothermal methods was studied in the selective hydrogenation of acetylene in excess ethylene. While the use of sol-gel method resulted in only $NiAl_2O_4$ formation, those prepared by solvothermal gave both $NiAl_2O_4$ and NiO species. Acidity of the nanocrystalline α-Al_2O_3 was significantly decreased by incorporation of Ni atoms in α-Al_2O_3. Ethylene selectivities were improved in the order: Pd/Ni-modified α-Al_2O_3-sol-gel > Pd/Ni-modified α-Al_2O_3-solvothermal ≈ Pd/α-Al_2O_3-sol–gel > Pd/α-Al_2O_3-solvothermal >> Pd/α-Al_2O_3-commercial. The improvement in catalyst performance is probably due to both a decrease in surface acidity of α-Al_2O_3 and modification of Pd surface activity due to $NiAl_2O_4$ formation.

Acknowledgements

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

Sample	d_{XRD}[1] (nm)	BET surface area (m^2/g)	CO chemisorption ($*10^{17}$ sites/g-cat)	% dispersion	d_P[2] Pd^0 (nm)
Sol-gel					
Pd/α-Al_2O_3	34^{α}	1.5	7.51	4.42	25
Pd/Ni-α-Al_2O_3	27^{NA}	1.9	5.37	3.16	35
Solvothermal					
Pd/α-Al_2O_3	54^{α}	4.7	8.10	4.76	24
Pd/Ni-α-Al_2O_3	23^{NA}, 26^{N}	1.4	7.35	4.32	26

[1] Average crystallite size calculated by Scherrer equation.

[2] Average Pd metal particle size calculated from CO chemisorption results. $d_P = 1.12/D$ where D = Pd dispersion [25].

$^{\alpha}$ α-Al_2O_3

^{NA} $NiAl_2O_4$

^{N} NiO

List of Figures

Figure 1 XRD patterns of the various Pd catalysts supported on nanocrystalline α-Al_2O_3 and Ni-modified α-Al_2O_3 prepared by sol-gel and solvothermal methods.

Figure 2 TEM micrographs of Pd/α-Al_2O_3 and Pd/Ni-modified α-Al_2O_3 prepared by sol-gel and solvothermal methods.

Figure 3 NH_3 temperature program desorption profiles for the sol-gel and solvothermal-made α-Al_2O_3 and the Ni-modified α-Al_2O_3 supports.

Figure 4 XPS results of Pd 3d for (a) Pd/α-Al_2O_3-sol-gel (b) Pd/Ni-modified α-Al_2O_3-sol-gel and (c) Pd/Ni-modified α-Al_2O_3-solvothermal.

Figure 5 Performance of sol-gel (circle; ○) and solvothermal (triangle; Δ) made Pd/α-Al_2O_3 (filled symbols), Pd/commercial α-Al_2O_3 (filled square; ■) and Pd/Ni-modified α-Al_2O_3 (open symbols) catalysts in selective acetylene hydrogenation.

.

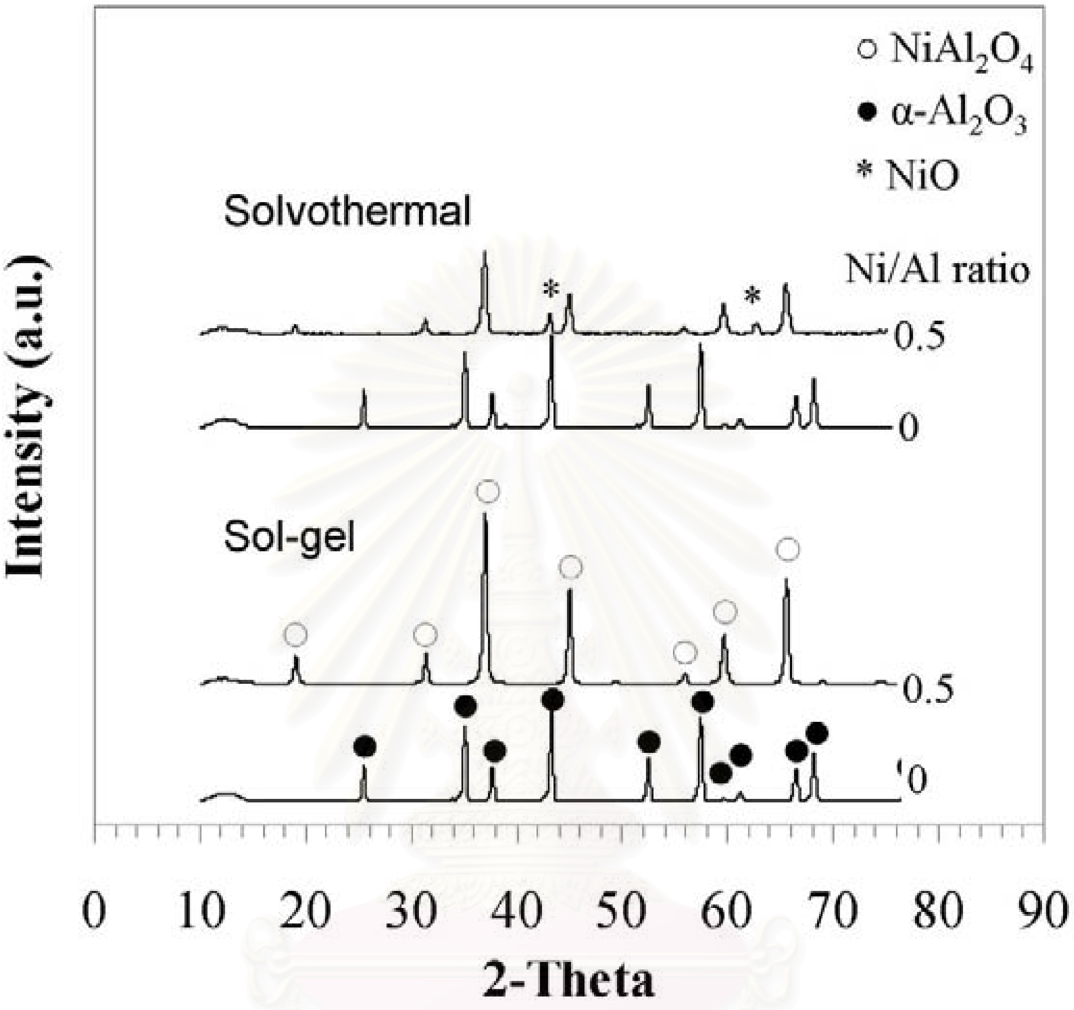
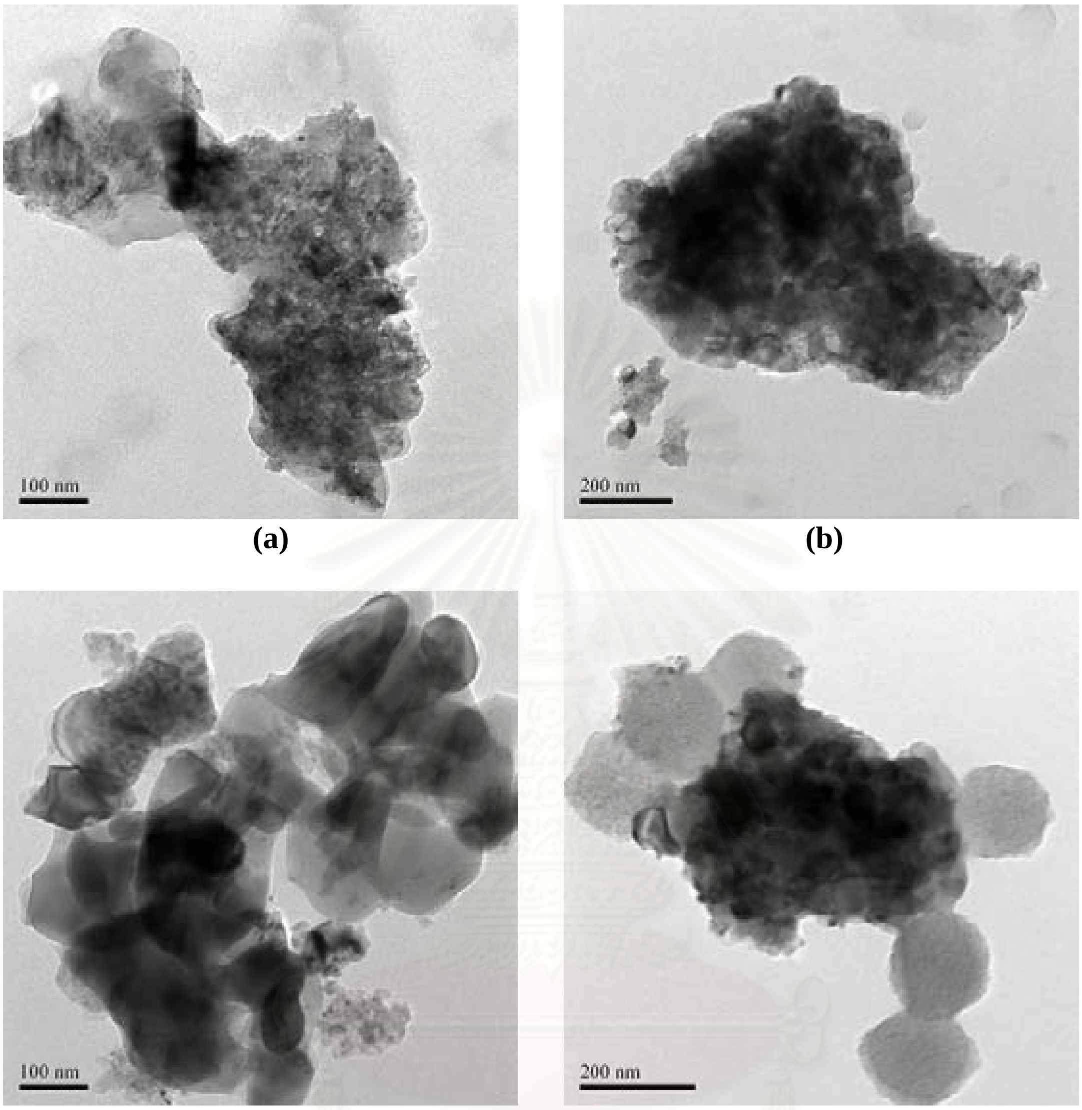

○ $NiAl_2O_4$
● α-Al_2O_3
* NiO
Solvothermal
Ni/Al ratio
0.5
0
Sol-gel
0.5
0
Intensity (a.u.)
0
10
20
30
40
50
60
70
80
90
2-Theta

Figure 1



(a) **(b)**

(c) **(d)**

Figure 2

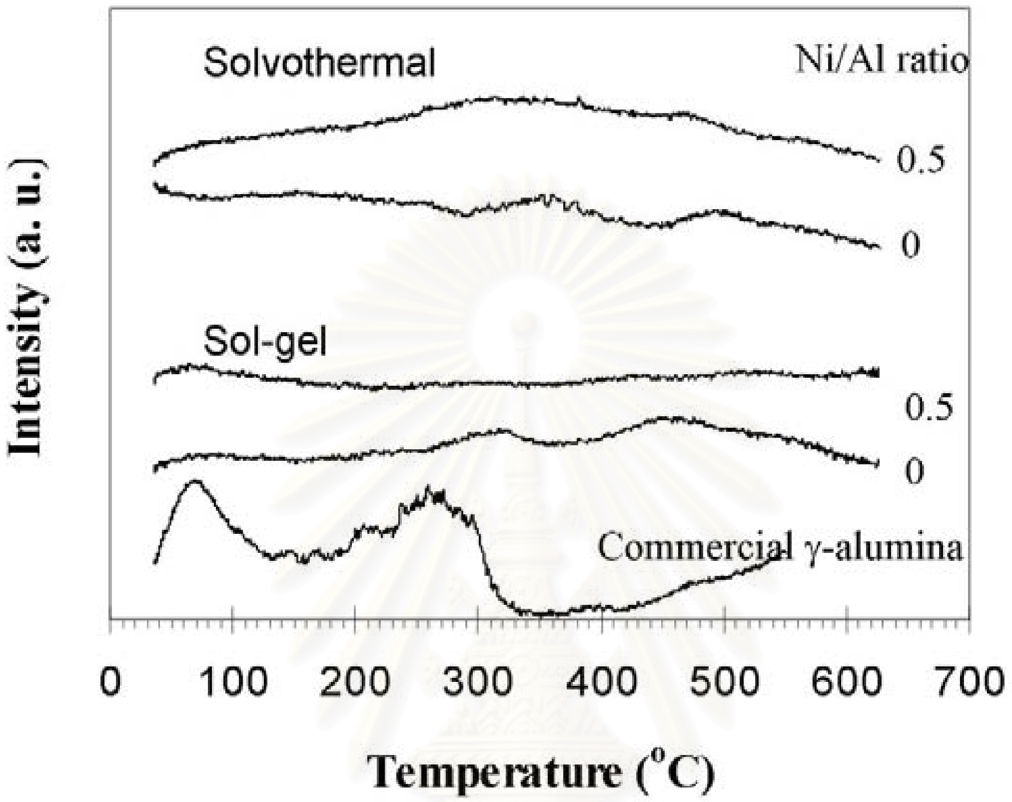

Solvothermal
Ni/Al ratio
0.5
0
Sol-gel
0.5
0
Commercial γ-alumina
Intensity (a. u.)
0
100
200
300
400
500
600
700
Temperature (°C)

Figure 3

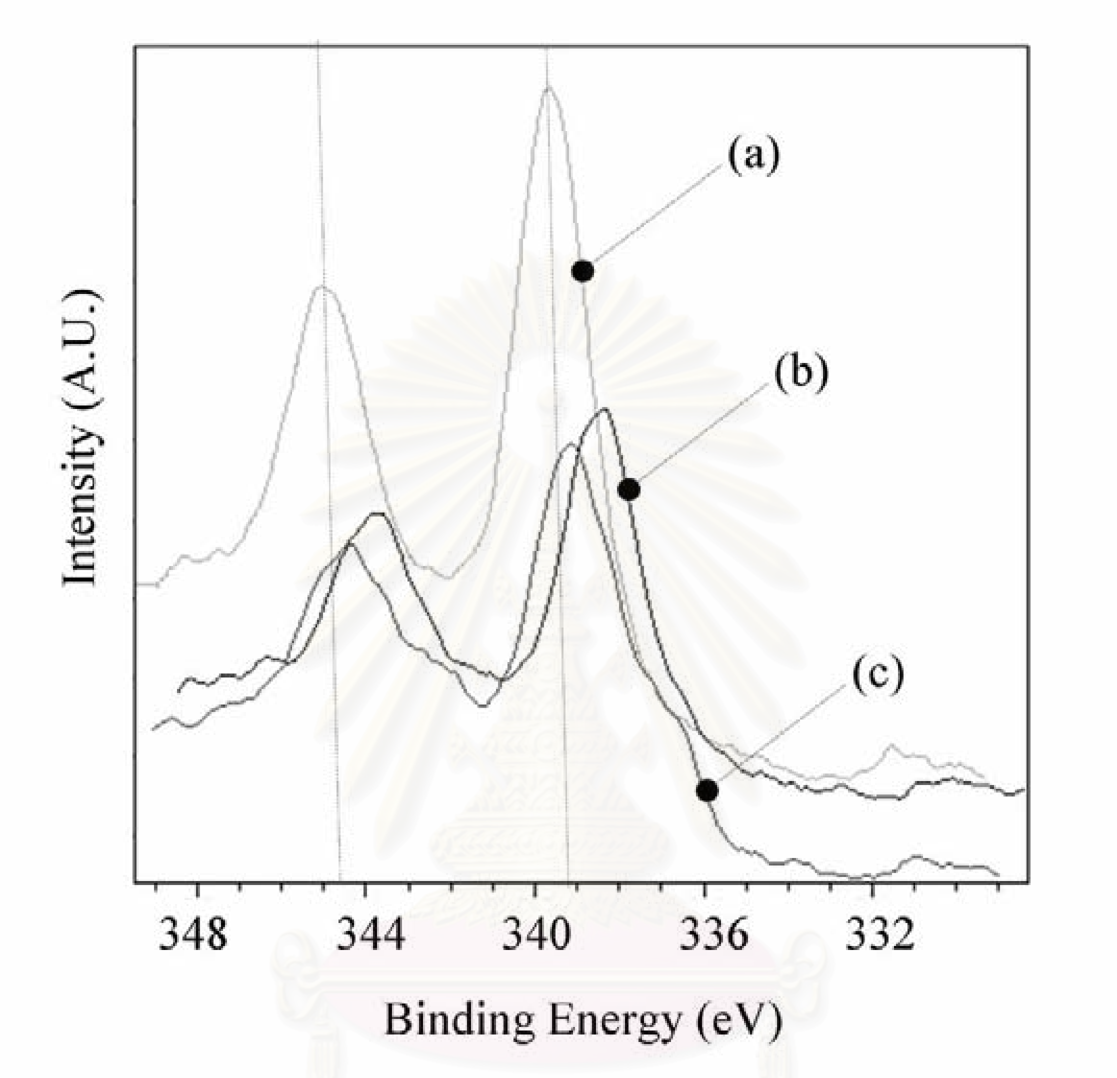


Figure 4

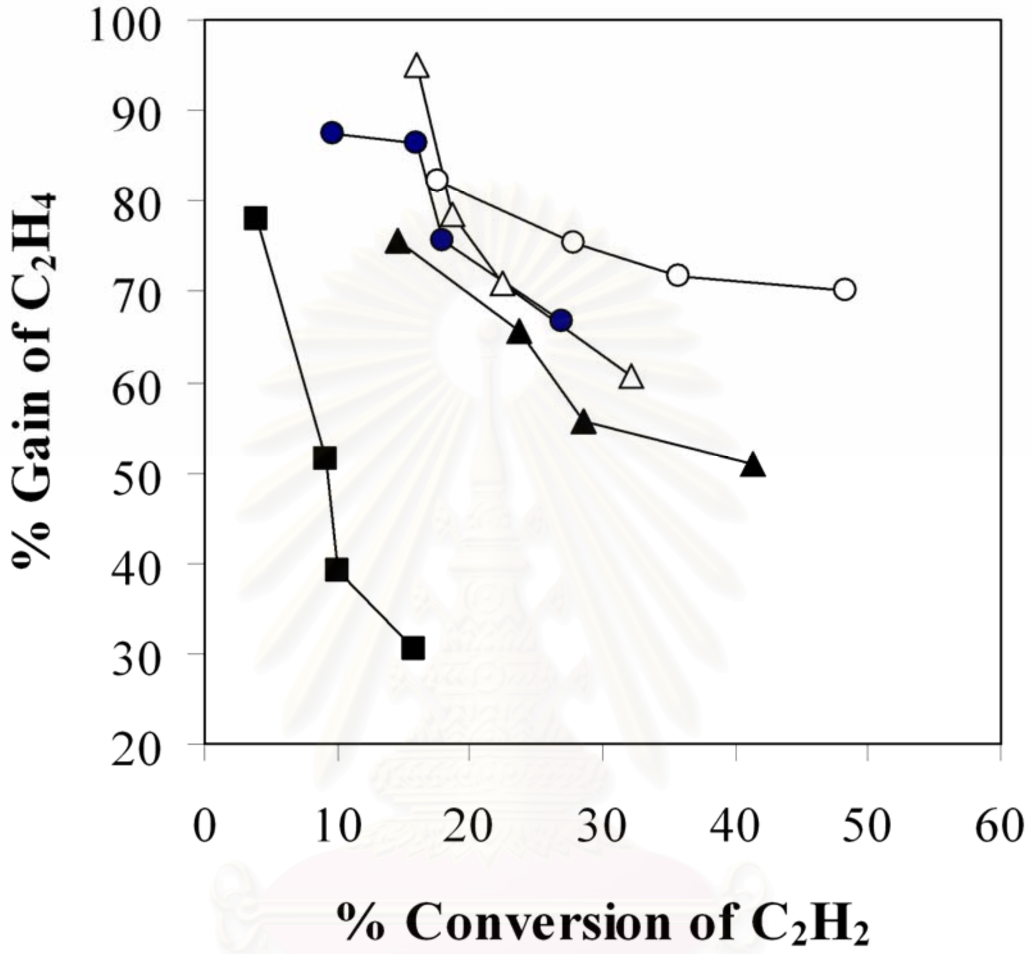

% Gain of C_2H_4
% Conversion of C_2H_2
100
90
80
70
60
50
40
30
20
0
10
20
30
40
50
60

Figure 5

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