PREPARATION AND CHARACTERIZATION OF Pd-Ni/SiO_2 CATALYSTS FROM A METAL CLUSTER

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การเตรียมและการวิเคราะห์ลักษณะตัวเร่งปฏิกิริยา Pd-Ni/SiO$_2$ จากคลัสเตอร์ของโลหะ

นางสาวจารุนันท์ วงศ์วิวัฒนา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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PREPARATION AND CHARACTERIZATION OF Pd-Ni/SiO$_2$ CATALYSTS FROM A METAL CLUSTER

Suranaree University of Technology Council has approved this thesis, submitted in partial fulfillment of the requirements for a Master's Degree.

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จารุนันท์ วงศ์วิวัฒนา : การเตรียมและการวิเคราะห์ลักษณะตัวเร่งปฏิกิริยา Pd-Ni/SiO_2 จากคลัสเตอร์ของโลหะ (PREPARATION AND CHARACTERIZATION OF Pd-Ni/SiO_2 CATALYSTS FROM A METAL CLUSTER) อาจารย์ที่ปรึกษา : ผศ. ดร. จตุพร วิทยาคุณ, 88 หน้า ISBN 974-533-171-6

งานวิจัยนี้เป็นการศึกษาการเตรียมและวิเคราะห์ลักษณะของตัวเร่งปฏิกิริยา PdNi/SiO_2 โดยเตรียมจากการจุ่มเคลือบสารละลายของสารประกอบโลหะคลัสเตอร์ $[\text{PPh}_4]_4[\text{Pd}_{13}\text{Ni}_{13}(\text{CO})_{34}]$ บนตัวรองรับซิลิกา ทั้งนี้ได้เปรียบเทียบกับตัวเร่งปฏิกิริยาที่เตรียมวิธีนี้กับตัวเร่งปฏิกิริยา PdNi/SiO_2 ที่เตรียมจากการจุ่มเคลือบสารละลายของเกลือผสมระหว่าง Pd(OAc)_2 และ Ni(OAc)_2 เทคนิคที่ใช้วิเคราะห์ลักษณะได้แก่ เทคนิคเอ็กซ์เรย์ฟลูออเรสเซนซ์ (XRF) เทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ (XRD) กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) เทคนิค BET ในการหาพื้นที่ผิว และยังได้ศึกษาปฏิกิริยารีดักชันตามอุณหภูมิ (TPR) และการดูดซับไฮโดรเจน การศึกษาเริ่มจากการเตรียมตัวเร่งปฏิกิริยาจากคลัสเตอร์ก่อนแล้วจึงหาปริมาณโลหะด้วยเทคนิค XRF เพื่อนำปริมาณโลหะดังกล่าวมาเตรียมตัวเร่งปฏิกิริยาจากสารละลายเกลือที่มีปริมาณโลหะเท่ากัน ผลของการศึกษาสมบัติของตัวเร่งปฏิกิริยาด้วย XRD พบว่าตัวเร่งปฏิกิริยาที่เตรียมจากคลัสเตอร์มีการกระจายตัวของโลหะดีกว่าและไม่เกิดการรวมตัวเป็นอนุภาคที่มีขนาดใหญ่เมื่อเทียบกับตัวเร่งปฏิกิริยาที่เตรียมจากเกลือผสมของโลหะ การศึกษาลักษณะพื้นผิวโดยใช้ SEM และการหาพื้นที่ผิวของตัวเร่งปฏิกิริยาพบว่าไม่มีความแตกต่างกันในตัวเร่งปฏิกิริยาทั้งสองแบบ ส่วนข้อมูลที่ได้จากเทคนิค TPR ชี้ให้เห็นว่าตัวเร่งปฏิกิริยา PdNi/SiO_2 ที่เตรียมจากคลัสเตอร์ถูกรีดิวซ์ได้ง่ายกว่าตัวเร่งปฏิกิริยาที่เตรียมจากเกลือ และอุณหภูมิของการเกิดรีดักชันของนิกเกิลใน PdNi/SiO_2 ลดต่ำลงเมื่อเทียบกับสาร Ni/SiO_2 เนื่องจากการเกิดโลหะผสมระหว่างนิกเกิลและแพลาเดียม ส่วนขนาดของตำแหน่งที่ทำหน้าที่เร่งปฏิกิริยานั้นจะคำนวณได้โดยวัดการดูดซับของไฮโดรเจน ซึ่งพบว่าตัวเร่งปฏิกิริยาจากคลัสเตอร์ดูดซับไฮโดรเจนได้น้อยกว่าตัวเร่งปฏิกิริยาที่เตรียมจากเกลือ

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม………………………..
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JARUNAN WONGWIWATTANA : PREPARATION AND CHARACTERIZATION OF $Pd-Ni/SiO_2$ CATALYSTS FROM A METAL CLUSTER
THESIS ADVISOR : ASST. PROF. JATUPORN WITTAYAKUN, Ph.D.
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This research included the preparation and characterization of $PdNi/SiO_2$ catalysts prepared by impregnation of the solution of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster on silica. The results were compared with $PdNi/SiO_2$ catalysts prepared from a salt mixture between $Pd(OAc)_2$ and $Ni(OAc)_2$. The characterization techniques included X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmette-Teller (BET) surface analysis, temperature-programmed reduction (TPR), and hydrogen adsorption. The procedure began from the $PdNi/SiO_2$ catalyst preparation from cluster and the metal loading was determined by XRF. Similar loading was prepared from metal salt precursor. XRD results indicated that $PdNi/SiO_2$ from cluster had better metal dispersion and did not sintered as much as those prepared from salt. The surface of catalysts from both precursors by SEM investigation exhibited similar morphology. Comparison of reduction temperature from TPR indicated that, nickel oxide in $PdNi/SiO_2$ catalysts from cluster was reduced more easily than Ni/SiO_2 reference and those from salt. This was an evidence of the alloy formation between Pd and Ni. However, the hydrogen adsorption capability which directly related to number of active sites of $PdNi/SiO_2$ catalysts from cluster was lower than those from salt.

School of Chemistry	Student………………………………………..
Academic year 2002	Advisor……………………………………….
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Jarunan Wongwiwattana

CONTENTS

Page

CONTENTS (CONTINUED)

Page

CONTENTS (CONTINUED)

Page

APPENDICES

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

Figure **Page**

LIST OF FIGURES (CONTINUED)

LIST OF TABLES

CHAPTER I
INTRODUCTION

Catalysis is one of popular fields of applied science that has got a lot of attention because results from research can easily be applied to industry. Research in catalysis has been conducted by researchers who have diverse educational background as chemistry, physics, material science, chemical engineering, etc. The popularity of catalysis can be reflected by the large number of research publications from the past to present in research journals around the world. Many researchers are interested in developing new catalysts that give higher activity with better selectivity.

Group 10 elements including nickel, palladium, and platinum are three of the most important metals used as heterogeneous catalysts. These metals are utilized to assist in the formation of numerous products both in the field of bulk and fine chemicals.

Bimetallic particles have received increasing attention in the past 20 years especially as catalysts since the addition of the second metal provides a method of controlling the activity, selectivity, and stability of the catalysts for certain reactions. In the bimetallic catalysts supported on high-surface-area refractories, i.e., the fine particles dispersed on inorganic oxide supports such as Al_2O_3, SiO_2, TiO_2, and MgO, the shape, size, and composition of metal particles as well as the interactions with supports have been studied to explore the properties of metal nanoclusters. Several factors may affect the compositions and structure of bimetallic particles, including the bulk immiscibility of each component in a phase diagram.

This thesis work focuses on development new catalytic material from organometallic cluster precursor. The work involves preparation and characterization of bimetallic Pd-Ni/SiO_2 prepared by impregnation of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ solution on silica support. This bimetallic Pd/Ni cluster was interested because it consists of precise number of metal atoms and can be prepared by a simple method in high yield. To our knowledge, there is no report on bimetallic Pd/Ni catalysts from organometallic cluster due to the cluster availability.

The latter parts of this thesis include related literature review, experimental procedures, results and discussion that will lead to conclusions. The details of preparation of bimetallic Pd-Ni/SiO_2 by impregnation as well as characterization techniques by various instrumental techniques will be given in Chapter 3. Research was mostly performed at the Center for Scientific and Technological Equipment, at Suranaree University of Technology including catalyst preparation and analyses by powder X-rays diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF), infrared spectroscopy (IR), Braunauer-Emmett-Teller (BET) surface area analysis, and thermal methods. Hydrogen adsorption and ICP analyses of some catalysts were completed at the Chemical Resources Laboratory, Tokyo Institute of Technology, Japan by courtesy of Professor Yutaka Morikawa. All results of catalysts prepared from cluster will be compared with those of catalysts prepared by conventional method from a mixture of palladium and nickel salt solution.

1.1 Research Objectives

1. To prepare PdNi/SiO_2 catalysts by deposition of $[[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ and a mixture of palladium and nickel salts on silica support by impregnation technique.
2. To study the effect of calcination temperature on catalyst properties.
3. To characterize and compare properties of catalysts from both precursors by techniques including powder X-ray diffraction (XRD), scanning electron microscopy (SEM), BET Surface Area Analysis (BET), X-ray fluorescence (XRF), thermogravimetric analysis (TGA), temperature-programmed reduction (TPR) and ICP.

1.2 Scope and Limitations of Study

The research was focus on preparation of Pd-Ni/SiO_2 catalysts from a high-nuclearity metal cluster, $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ and a mixture of palladium-nickel salt supported on silica by impregnation technique. The metal loading of the catalysts prepared from the cluster was first determined and catalysts with similar loading were prepared by use of a mixture of metal salts. The influence of calcination temperature and time on catalyst properties will be investigated.

The catalysts were further characterized by a variety of techniques including XRD, SEM, BET surface area, TPR, and H_2-TPD. The properties of interest were the amount and type of active site, active metal dispersion, metallic particle size, and interaction between two metals. In addition, the metal loading was determined or confirmed by XRF, and partially by ICP. Both chemical and physical properties of catalysts obtained from each class of starting materials will be closely examined and compared.

1.3 Expected Results

It was expected that catalysts prepared from Pd-Ni cluster precursor showed better catalyst properties than those prepared from metal salts as follows:

1. Pd-Ni catalysts from clusters were expected to have narrower particle size distribution and better metal dispersion than that of salt precursor.
2. TPR results could confirm whether Pd and Ni were intact in the alloy.
3. The reduction temperature of Ni in Pd-Ni/SiO_2 catalysts from the cluster was expected to be lower in the presence of Pd .
4. Milder preparation and activation conditions for Pd-Ni catalysts from cluster precursor were also expected.

CHAPTER II
LITERATURE REVIEW

2.1 Background of Heterogeneous Catalysis

A catalyst is a substance that increases the rate of a chemical reaction without itself being consumed or undergoing a chemical change. Catalyst can lower the activation energy of the reaction without changing the thermodynamics of overall reaction. There are two types of catalyst according to the phase of the catalyst and reagents involved in reaction of interest. If the phase of catalysts is similar to starting material and product, it is called homogeneous catalyst. In contrast, if the phase is different, it is called heterogeneous catalyst.

Catalysts that are interested in this study are heterogeneous catalysts that are in solid phase and can be used for gas or liquid starting materials. The simplest method to prepare heterogeneous catalysts is by using inorganic metal salts such as palladium chloride adsorbed on supporting materials such as silica (SiO_2), alumina (Al_2O_3), zeolites, or resins (impregnation technique), followed by oxidation at high temperatures (calcination). Supports are materials that are chemically inactive, usually porous resulting in high surface area, and can tolerate high temperature and pressure in catalytic processes. By deposition of active species on solid support, the amount of active species is minimized while the active surface area increases for small particles of active species. The resulting metal oxide crystals are then reduced into metal particles by a reductant such as hydrogen gas.

However, catalysts prepared by conventional method do not provide good control of particle size distribution and metal composition. High temperature in calcination and reduction steps usually cause metal sintering in which small metal particle aggregation occurs and lower the catalyst surface area and catalytic performance. It is important to find new catalyst preparation method that allow good control of particle size and distribution on the support as well as does not require high temperature for catalyst activation. Metal cluster is an alternative catalyst precursor.

2.2 Cluster in Catalysis

Metal clusters are complexes containing at least three metal-metal bonds that form triangular or larger metal-core structures (Shriver, 1994). This definition excludes linear metal chains and cage compounds in which metal atoms are held together by bridging ligands without the presence of direct metal-metal bonds. Non-ligated metal clusters denoted as "naked clusters", for example, main-group elements such as Sn_9^{3-}, As_{11}^{3-}, and Sn_7^{3-} may exist as salts per se or in inert media or matrices (King, 1994).

The most common type of metal cluster consists of transition metal atoms stabilized by main-group ligands. There are marked differences in the nature of bonding between the early and late transition metals. Clusters of early transition metals (*i.e.*, metal atoms with fewer valence electrons than half-filled subshells) commonly have metals in oxidation states of 2+ and 3+ and are usually associated with both σ- and π-donor ligands such as O^{2-}, S^{2-}, Cl^-, Br^-, I^- and OR^-. These ligands can bond with the metal framework as terminal, edge-bridging, or face-bridging. The geometries of these clusters possess high symmetry such as face-capping $\{M_6Y_8\}^{n+}$ and edge-bridging $\{M_6Y_{12}\}^{n+}$ octahedra which may have an additional six ligands terminally bound on each metal center, thereby corresponding to $\{M_6Y_8X_6\}^{n+6z}$ and $\{M_6Y_{12}X_6\}^{n+6z}$ formulas, respectively. These clusters have been well studied because they are readily accessible via solution chemistry (Prokopuk and Shriver**,** 1994; Cotton and Wilkinson, 1988).

On the other hand, clusters of late transition metals normally possess ligands that can withdraw via π backbonding metal-core electron density that otherwise would reside in metal-metal antibonding orbitals (Cotton and Wilkinson, 1988). Such clusters normally have metal atoms in low oxidation states; the most common class is composed of homometallic and heterometallic carbonyl clusters. Carbon monoxide is a flexible ligand because it can coordinate to metal atoms as a terminal, edge-bridging, or face-bridging ligand. In general, carbonyl ligands donate σ electron density to a metal center and accept π electron density from the metal back into antibonding MOs. Hydride ligands are also often found in clusters containing late transition metals (Horwitz and Shriver, 1984). Comprehensive reviews of metal cluster chemistry can be found in several books (Schmid, 1994; Gzalez-Moraga, 1993; Shriver, Kaesz, and Adams, 1990; de Jongh, 1994).

Metal clusters are of particular interest in catalytic reactions as models for metal surfaces; they may also be considered as intermediates between molecular compounds and solid-state materials. Large clusters such as $[Rh_{13}(CO)_{24}H_3]^{2-}$, $[Pt_{26}(CO)_{32}]^{2-}$, $[Pt_{38}(CO)_{44}]^{2-}$, and $[Os_{20}(CO)_{40}]^{2-}$ have metal-core geometries that resemble close-packed metal atoms in small naked metal crystallites (Albano et. al, 1975; Ceriotti et al 1980; Amoroso, 1991). The metal-core atoms of each of these large metal carbonyl clusters can be thought of as a metal aggregate that is stabilized by CO ligands on its metal surface. Such clusters can be used as precursors for preparing heterogeneous catalysts (Ichikawa, 1992; Süss-Fink and Meister, 1993). In general, heterogeneous catalysts are usually obtained by using inorganic metal salts such as palladium chloride adsorbed on supporting materials such as SiO_2, Al_2O_3, zeolites, or resins (impregnation technique), followed by oxidation at high temperatures (calcination). The resulting metal oxide crystals are then reduced into metal particles by reductants such as hydrogen. However, catalysts prepared by this general method do not provide good control of particle size distribution and metal composition. Metal clusters which have been used instead of metal salts to impregnate a support in order to prepare heterogeneous catalysts and such clusters possess attractive features such as solubility in organic solvents. Milder conditions can be used to activate the catalysts prepared from metal clusters. In addition, transition metal clusters have been used directly as homogeneous catalysts because they are soluble in organic solvents. Small clusters containing carbonyl ligands, either homonuclear or mixed-metal, have been reported to catalyze reactions such as carbonylation, hydrogenation, syn-gas reactions, and polymerization (Adams and Barnard, 1998; Chatani et al, 1998; Gladfelter and Roesselet, 1990).

Clusters with at least 12 metal atoms have been arbitrarily designated as high-nuclearity clusters. These clusters are particularly interesting with regard to the bonding and packing of metal atoms. In principle, the properties of the metal cores should approach those of the bulk metal as the cluster size increases. It is often observed that high-nuclearity transition metal carbonyl clusters have darker colors than those exhibited by low-nuclearity metal clusters. The dark color indicates that such high-nuclearity clusters have many closely spaced energy levels. With increasing metal nuclearity, the separation between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) decreases and approaches band structure of extended solid (Thimmappa, 1995).

Transition metal clusters can be prepared by various methods including photolysis, thermal condensation (pyrolysis), redox condensation, electrochemical activation, and reactions involving either ligand elimination or ligand substitution. Extensive reviews can be found in the literature.

Many researchers are interested to synthesize, isolate, characterize, and investigate chemical/physical properties of high nuclearity carbonyl and carbonyl/phosphine clusters of late transition metals. Recent studies include the discoveries of homometallic/heterometallic palladium carbonyl trimethylphosphine clusters isolated from reactions of a Pd-Ni cluster precursor and trimethylphosphine either in the presence or the absence of acetic acid (Tran et al, 1998); syntheses and characterizations of bimetallic palladium/gold (Tran et al, 1999) or nickel/copper (Mlynek, 1997), and trimetallic palladium/nickel/gold carbonyl clusters (Tran et al, 1999) obtained from reductive condensations of appropriate metal complexes with $[NMe_4]_2[Ni_6(CO)_{12}]$; and a bimetallic palladium/platinum carbonyl phosphine hydride cluster generated from a reduction of a mixture of palladium and platinum complexes with$[NMe_4]_2[Ni_6(CO)_{12}]$ (Bemis and Dahl, 1997).

The most crucial method used to determine the structures of clusters is single-crystal X-ray crystallographic analysis. Both the composition as well as non-hydrogen atomic positions of a cluster can be obtained if a single crystal can be grown and if there is no crystal-disorder or crystal-turning. Nuclear magnetic resonance (NMR), infrared spectroscopy (IR), cyclic voltammetry (CV), and elemental analysis are also widely used to characterize metal clusters. Multinuclear NMR is especially useful for metal carbonyl clusters containing phosphine and/or hydride ligands, because the nature of chemical shifts and splitting patterns can be used to identify the presence of these ligands as well as to characterize ligands with different bonding and chemical environments. An IR spectrum of a cluster is particularly useful for determining the presence and nature of coordination mode of carbonyl groups, which have the frequencies in the range of 1600 to 2200 cm^{-1}. In metal carbonyl clusters the ν(C-O) frequencies of terminal, edge-bridging and face-bridging carbonyl ligands are generally in the range of 1950-2150 cm^{-1}, 1750-1900 cm^{-1}, and 1700-1800 cm^{-1}, respectively (Gzalez-Moraga, 1993).

In general, the structures of low-nuclearity ligated transition metal clusters are based on triangles, tetrahedra, octahedra, and prisms. High-nuclearity metal clusters are likely to form regular or semi-regular polyhedral structures and usually contain one or more interstitial atoms or require main group atoms as part of the cage.[1] Giant metal carbonyl clusters can be considered as condensed clusters that share vertices, edges, and faces in which the degrees of connectivities of metal atoms increase and often lead to close-packed arrangements. Late transition metal atoms such as palladium form 16- and 14-electron complexes as well as 18-electron complexes. Since clusters with similar numbers of metal atoms are more likely to have the same number of cluster valence electrons, it is valuable to relate the total number of cluster valence electrons to the metal polyhedral topology.

Metal clusters are complexes containing at least three metal-metal bonds that form triangular or larger metal-core structure (Shriver, 1994). Metal clusters are of particular interest in catalytic reactions as models for metal surfaces. They may also be considered as intermediates between molecular compounds and solid-state materials. Large clusters such as $[Rh_{13}(CO)_{24}H_3]^{2-}$, $[Pt_{26}(CO)_{32}]^{2-}$, $[Pt_{38}(CO)_{34}]^{2-}$, and $[Os_{20}(CO)_{40}]^{2-}$ have metal-core geometries that resemble close-packed metal atoms in small naked metal crystallites (Adams, 1990; Braunstein, 1999; Raithby,1998). The metal-core atoms of each of these large metal carbonyl clusters can be thought of as a metal aggregate stabilized by CO ligands on its metal surface. Such clusters can be used as precursors for the preparation of heterogeneous catalysts.

Metal clusters have been used instead of metal salts to impregnate a support in order to prepare heterogeneous catalysts and such clusters possess attractive features such as solubility in organic solvents (Gates, 1992, and 2000). Milder conditions can be used to activate the catalysts prepared from metal clusters. Because metal atoms in the clusters are in low oxidation states, they can be reduced more easily than conventional metal salt precursors.

In addition, transition metal clusters have been used directly as homogeneous catalysts because they are soluble in organic solvents. Small clusters containing carbonyl ligands, either homonuclear or mixed-metal, have been reported to catalyze reactions such as carbonylation, hydrogenation, syn-gas reactions, and polymerization. Clusters of Pt, Rh, Ir, Ru can be synthesized in the cavity of zeolites by a procedure called "ship-in-bottle" which includes carbonylation of ion-exchanged metal. (Ichikawa, 2000). The formation of carbonyl clusters can be confirmed by infrared spectroscopy. After decarbonylation by heat, the metal atoms are still intact and active catalysts.

In the past decade, more interest has been given to supported bimetallic catalysts because of the activity improvement. There are several reports that bimetallic catalysts show better catalytic performance than monometallic catalysts of the same metals. Bimetallic catalysts can be prepared by coimpregnation of two metal salts on inorganic support. However, it is difficult to keep two metals intact. To solve this problem, many researchers have considered bimetallic clusters as catalytic precursors. In many cases, heterometallic clusters containing either palladium or platinum have been employed because both of their oxides are easy to reduce. Note that reduction is an important step in catalyst activation to change a catalyst into action form. For examples, bimetallic Pt-Pd/SiO_2-Al_2O_3 catalysts exhibit much higher activities in aromatic hydrogenation of distillates than monometallic Pt/SiO_2-Al_2O_3 and Pd/SiO_2-Al_2O_3 catalysts (Fujikawa, 1999). The Pd species dispersed on Pt particles are responsible for the high activity of the bimetallic catalysts. $Mo_2Pd_2Cp_2(CO)_6(PPh_3)_2/\gamma$-$Al_2O_3$ catalyst give rise to higher selectivity in phenylisocyanate than conventional catalysts prepared by mixing the individual components (Adams, 1998). When Pd is combined with gold which is a relatively inert metal, the resulting catalyst is more active for hydrogenation of 1,3-cyclooctadiene than Pd and Au alone (Toshima, 1992).

The main advantages expected from the use of mixed-metal cluster compounds as precursors to heterogeneous catalysts (Adams, 1998) are listed.

(1) Efficient clustering of the metals on the surface because metal-metal bonds are present in the molecular precursor.

(2) Low initial oxidation states of the metals that make them relatively easy to activate by heating at low temperature to remove CO ligands. This will prevent sintering of metal particle.

(3) Aavoidance of surface poisoning by contaminating anions from metal salts such as Cl^-, which usually affect catalytic properties.

(4) At least partial retention of the unique geometries or stereochemical features of the molecular precursor in the mixed-metal catalysts.

(5) Preparation of catalysts having well-dispersed and uniform mixed-metal phases, which would be difficult to obtain by coimpregnation of mixed metal salt.

(6) Possibility of systematic variation in particle stoichiometry by changing precursor complexes of different compositions, stoichiometries, and structures.

Supported bimetallic catalysts derived from mixed-metal carbonyl clusters are new classes of catalytic materials and there are increasing number of catalytic reactions on these catalysts. Since new heterometallic couples and supports are found to allow fine tuning of the properties of highly dispersed catalysts, the importance of this approach will continue to grow. The heterogeneous catalysts derived from molecular mixed-metal clusters are listed in table 2.1.

From table 2.1, many catalysts contain Pd or Ni because both are active metals. However, there have been only a few reports of bimetallic Pd-Ni catalysts. Polymer-supported PVP-$PdCl_2$-$4NiCl_2$-PPh_3 bimetallic catalyst [PVP=poly(*N*-vinyl-2-pyrrolidone)] is an efficient catalyst for the hydroesterification of styrene (Wan, 1998). The high activity and selectivity of the catalyst are achieved by the synergic effect of Pd-Ni bimetallic system and the effect of polymer protection(Toshima, 1992). Bimetallic $PdNi_x$ in zeolites NaY was prepared by simultaneous exchange of the two metal ions and washed with either dilute HNO_3 acid (pH = 6) to give loading 10.3Pd + 8.6Ni or with dilute NaOH (pH = 10.5) to give loading 10.0Pd + 9.2Ni. The evidence from Temperature-Programmed Reduction (TPR) and Temperature-Programmed Desorption (TPD) techniques indicated that Pd and Ni in the same zeolite enhance each other's reducibility and form bi-metallic particles (Feeley, 1991). It was found in Pd-Ni/NaY that the reduction temperature of Pd decreased by 40 ^{0}C and that of Ni decreased by 150 ^{0}C. The bimetallic alloy catalysts were reported to have significantly higher selectivity for methane formation from CO hydrogenation (Feeley, 1992).

Table 2.1 Utilization of Molecular Mixed-Metal Clusters in Heterogeneous Catalysis (Adams, 1998).

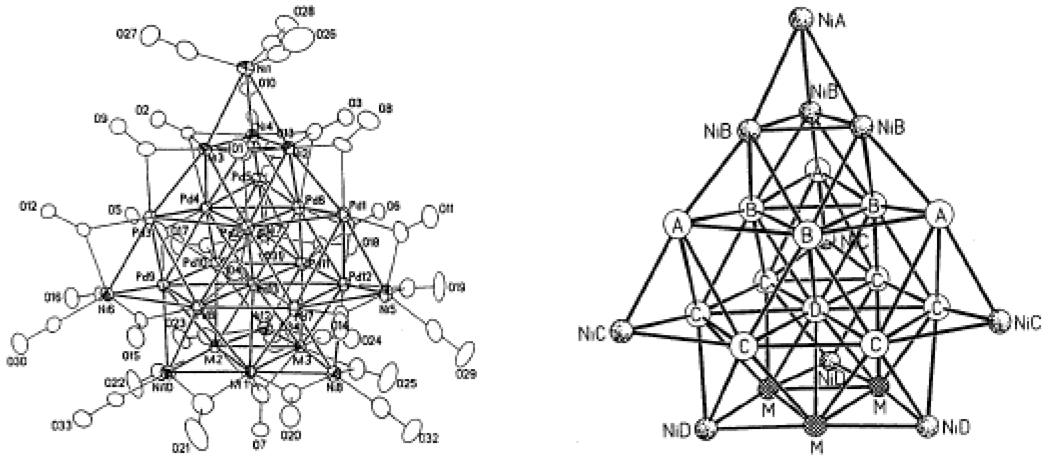
Bimetallic Couple	Precursor Cluster	Support	Catalyzed Reactions
Cr-Pd	$Cr_2Pd_3Cp_2(CO)_6(PMe_3)_2$	γ-Al_2O_3	Hydrocarbon Rearrangements
Mo-Ni	$Mo_2Ni_2S_4Cp_2(CO)_2$	γ-Al_2O_3	CO Hydrogenation
Mo-Pd	$Mo_2Pd_2Cp_2(CO)_6(PPh_3)_2$	γ-Al_2O_3	$ArNO_2$ Carbonylation
Fe-Ru	$Fe_2Ru(CO)_{12}$	SiO_2	CO Hydrogenation
Fe-Rh	$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$	SiO_2	CO Hydrogenation Olefin Hydroformylation
Fe-Pd	$[TMBA]_2[Fe_4Pd(CO)_{16}]$	SiO_2	CO Hydrogenation
Ru-Ni	$[Et_4N]_2[Ru_3Ni_3C(CO)_{13}]$	SiO_2	CO Hydrogenation
Os-Ni	$Os_3Ni_3Cp_3(CO)_9$	γ-Al_2O_3	CO and CO_2 Hydrogenation

TMBA: Trimethyl (benzyl) ammonium

There is no report on Pd-Ni catalyst prepared from bimetallic cluster due to the rare existence of cluster precursor.

Recently, $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ as PPh_4 salts was successfully separated in high yield (more than 90%) from reduction of $Pd(OAc)_2$, where OAc = CH_3COO^-, by $[Ni_6(CO)_{12}]^{2-}$ in DMF (Tran, 2000). The cluster metal core consists of 26 metal polyhedron with close-packed arrangement as shown in Figure 1.1. Because the metal-metal bonds already exist, cluster $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ will be a good candidate as a precursor for Pd-Ni/SiO_2 catalysts. The removal of carbonyl ligands in $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ (decarbonylation) can be accomplished by heat.

Because high yield of cluster $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ can be obtained by simple synthesis, it is an excellent candidate for bimetallic Pd-Ni catalyst precursor. This thesis proposal includes preparation and characterization of supported bimetallic Pd-Ni/SiO_2 catalysts from a high-nuclearity cluster precursor, $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ compared with a mixture of Pd and Ni salts by impregnation technique. The characterization of catalysts from both precursors may lead to a new way to prepare Pd-Ni catalysts with desired properties.



(a) **(b)**

Figure 1.1 (a) Structure of $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ and (b) $Ni_{13}Pd_{13}$ metal core (Tran, 2000). Atoms M are Pd/Ni with disorder.

2.3 Catalyst Preparation

There are many techniques to prepare heterogeneous catalysts such as impregnation, ion exchange, precipitation, and sol-gel method. In this work impregnation technique was employed because it is the simplest method and does not require complicate tools. When liquid is slowly added to a porous solid powder, the liquid is first absorbed in the pores and the powder will flow as if it is dry. When the pores have been filled the outside of the grains rather suddenly become wet, the grains will tend to stick together and the powder will form lumps instead of flowing freely. The situation when the pores have been filled but the outside of the grains is dry is callled "incipient wetness" and can easily be detected by shaking or stirring the powder. Before impregnation the moisture and volatile compounds can be removed from the support pores by heat or vacuum.

Impregnation offers a number of advantages: (a) the support is already in pellet form (b) The filtering and the wash of the catalyst are eliminated (c) small metal loadings are easily prepared (d) impregnation offers some control over the distribution of the metal in pellets. However, impregnation has some disadvantages such as high metal loadings are not possible and a good impregnation solution may be impossible to find. However, in this work low metal loading was used and solvents to prepare the metal solution were not difficult to find.

2.4 Catalyst Support

In general, a catalyst support should allow for a high degree of metal dispersion. The choice of support is largely determined by the nature of the reaction system. A support should be stable under reaction and regeneration conditions, and not adversely interact with solvent, reactants or reaction products. Common powdered supports include activated carbon (AC), alumina (Al_2O_3) , silica (SiO_2), silica-alumina, carbon black (C), titania (TiO_2), zirconia (ZrO_2), calcium carbonate ($CaCO_3$), and barium sulphate ($BaSO_4$).

The majority of precious metal catalysts are supported on either silica or alumina. A support can affect catalyst activity, selectivity, recycling, refining, material handling, and reproducibility. Critical properties of a support include surface area, pore volume, pore size distribution, particle size, attrition resistance, acidity, basicity, impurity levels, and the ability to promote metal-support interactions. Metal dispersion increases with support surface area.

Support porosity affects metal dispersion and distribution, metal sintering resistance, and intraparticle diffusion of reactants, products and poisons. Smaller support particle size increases catalytic activity but decreases filterability. A support should have desirable mechanical properties, attrition resistance, and hardness. An attrition resistant support allows for multiple catalyst recycling and rapid filtration. Support impurities may deactivate the metal and enhance catalyst selectivity.

The concentration of precious metal deposited on a support is typically between 1 and 10 weight percent. Relative catalyst activity will generally increase with decreasing metal concentration at constant metal loading.

In this research silica was chosen as a catalyst support because it has good thermal stability, high surface area, and relatively inert. In addition, silica is widely used as a support for many precious metals in heterogeneous catalysis.

2.5 Catalyst Characterization Techniques

In this study various characterization techniques were used to investigate the properties of Pd-Ni/SiO_2 catalysts including X-ray fluorescence, infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and temperature program reduction. In the following section, a brief overview of each technique will be described.

2.5.1 Infrared Spectroscopy (IR)

The region of the infrared spectrum which is of greatest interest to organic chemists is the wavelength range 2.5 to 15 μm. In practice, units proportional to frequency, (wave number in units of cm^{-1}) rather than wavelength, are commonly used and the region 2.5 to 15 μm corresponds to approximately 4000 to 600 cm^{-1}.

The atoms in a molecule are constantly oscillating around average positions. Bond lengths and bond angles are continuously changing due to this vibration. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule produces an oscillating electric field with the same frequency as the frequency of incident IR radiation. Every molecule will have its own characteristic spectrum. The bands that appear depend on the types of bonds and the structure of the molecule (http://www.organicworldwide.net/infrared.html).

Fourier transform infrared (FT-IR) spectroscopy measures dominantly vibrations of functional groups and highly polar bonds. Thus these chemical fingerprints are made up of the vibrational features of all the samples components. FT-IR spectrometers record the interaction of IR radiation with experimental samples, measuring the frequencies at which the sample absorbs the radiation and the intensities of the absorptions. Determining these frequencies allows identification of the sample's chemical makeup, since chemical functional groups are known to absorb light at specific frequencies. FT-IR experiments generally can be classified into the following two categories: qualitative analysis - where the aim is to identify the sample and quantitative analysis - where the intensity of an absorption (or more commonly absorptions) is related to the concentration of the component (http://gepasi.dbs.aber.ac.uk/roy/ftir/ftirhome.htm).

In this study FTIR was used to characterize $[PPh_4]_4[Ni_{13}Pd_{13}(CO)_{34}]$ cluster which was one of precursors for $PdNi/SiO_2$ catalysts. Because the cluster contains carbonyl ligands, the position of carbonyl bands can confirm the formation of cluster. In metal clusters, the characterization normally done in solution phase such as acetonitrile and the bands are generally characteristic of the clusters. Examples of IR bands of clusters are listed in Table 2.1. Note that acetonitrile contains no carbonyl functional group, thus, its bands does not overlap with those of the carbonyl clusters.

Table 2.2 IR bands of some high nuclearity clusters in acetonitrile solution. (s = strong, vs = very strong, m = medium, w = weak, sh = shoulder).

Cluster	IR bands, cm^{-1}	Reference
$[NBu_4]_4[Ni_{16}Pd_{16}(CO)_{40}]$	2016(s), 1883(m), and 1820(m)	Femoni, 2000
$[NBu_4]_6[Ni_{26}Pd_{20}(CO)_{54}]\bullet xC_6H_{14}$	2015(s), 1863(ms), and 1800(w)	Femoni, 2000
$[PPh_4]_4[Ni_{13}Pd_{13}(CO)_{34}]$	2027(vs), 2001(sh), 1911 (sh), 1887(s), and 1859 (s)	Tran, 2000
$[PPh_4]_6[Ni_{32}Au_6(CO)_{44}]$	2013(s), 1990(m), 1880 (vs), and 1857(wsh)	Tran, 2000
$[PPh_4]_6[Ni_{20}Pd_6(Pd_{6-x}Ni_x)Au_6(CO)_{44}]$	2013(s), 1990(m), and 1884(vs)	Tran, 2000

The characterization by FTIR using solid material was also investigated in this work. The solution of cluster was impregnated on silica. After drying under nitrogen flow, the impregnated material was studied by IR as solid material. Powders are generally prepared by grinding with potassium bromide (KBr) powder and then pressed into a disk. The method of preparation of a powder sample is generally determined by the information required or the chemical/physical stability of the sample. KBr does not contain bands in the mid-IR region of the spectrum, and therefore preparation as halide disks potentially loses less information. Samples dispersed in halide powder must be homogenously dispersed, with a particle size small enough not to cause scatter (theorectically < 2 microns). The strength of an IR absorption spectrum is dependant on the number of molecules in the beam. With a KBr disk the strength will be dependant on the amount and homogeneity of the sample dispersed in the KBr powder. The amounts stated below are for guidance only, the bulk density of the sample or other diluents may require these to be varied. They will also have to be varied according to the diameter of the disk required. The weights quoted are for a 16 mm diameter disk. Approximately half should be used for the 13 mm diameter disks.

2.5.2 Powder X-ray Diffraction (XRD)

X-rays are electromagnetic radiation of wavelength about 1 Å (10^{-10} m), which is about the same size as atomic distances in solid. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science (http://materials.binghamton.edu/labs/xray/xray.html).

In heterogeneous catalysis, powder X-ray diffraction is used mainly to determine the phase and particle size of active metal species. Metal in catalysis occur in either metal or oxide form and the broadening of the diffraction peaks is a result from a good dispersion of small metal particles on the catalytic support (Niemantsverdriet, 2000). An important equation for X-ray diffraction is Bragg’s equation which shows a relationship between X-ray wavelength (λ) with lattice point distance (d) and the incident diffraction angle (θ).

$$n\lambda = 2d\sin\theta \qquad \text{…..(2.1)}$$

In this study, the sample was rotated within desired angle and the diffraction intensity and the diffraction angle were measured. Copper metal was used as X-ray source with wavelength of 1.315Å.

2.5.3 X-ray Fluorescence (XRF)

XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. Depending on the application, XRF can be produced by using not only X-rays but also other primary excitation sources like alpha particles, protons, or high energy electron beams.

When a primary X-ray excitation source from an X-ray tube or a radioactive source strikes a sample, the X-ray can either be absorbed by the atom or scattered through the material. The process in which an X-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the photoelectric effect. During this process, if the primary X-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic X-ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The process of emissions of characteristic X-rays is called "X-ray Fluorescence," or XRF. Analysis using X-ray fluorescence is called "X-ray Fluorescence Spectroscopy." In most cases the innermost K and L shells are involved in XRF detection. A typical X-ray spectrum from an irradiated sample will display multiple peaks of different intensities http://www.amptek.com/ xrf.html).

The characteristic X-rays are labeled as K, L, M or N to denote the shells they originated from. Another designation alpha (α), beta (β) or gamma (γ) is made to mark the X-rays that originated from the transitions of electrons from higher shells. Hence, a K_α X-ray is produced from a transition of an electron from the L to the K shell, and a K_β X-ray is produced from a transition of an electron from the M to a K shell, etc. Since within the shells there are multiple orbits of higher and lower binding energy electrons, a further designation is made as $\alpha 1$, $\alpha 2$ or $\beta 1$, $\beta 2$, etc. to denote transitions of electrons from these orbits into the same lower shell.

2.5.4 Scanning Electron Microscopy (SEM)

SEM is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEM instruments only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today (http://mse.iastate.edu/ microscopy/home.html).

The scanning electron microscope creates the magnified images by using electrons instead of light waves. The SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope. The images created without light waves are rendered black and white. Samples have to be prepared carefully to withstand the vacuum inside the microscope. The samples must be conductive material in order to be able to interact with electron, SEM samples are coated with a very thin layer of gold by a machine called a sputter coater. The sample is placed inside the microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun [at the top] emits a beam of high energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons and back scattered electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample (http://www.mos.org /sln/SEM/works.html).

In this work SEM was used to investigate the surface of catalysts with magnification of 20,000. It is possible to see the micropores of silica support and large metal particles by SEM. In addition, elemental analysis can be done using energy-dispersive X-ray spectrometry (EDX) method. EDX is different from X-ray fluorescence in that X-rays emitted from elements in the sample are observed by a solid-state detector and pulse-height analyzer without using a crystal analyzer and collimators.

2.5.5 Brunauer-Emette-Teller (BET) Surface Area Analysis

Nitrogen adsorption at 77 K is a commonly applied technique to determine various characteristics of porous materials. The amount of adsorbed nitrogen is measured as a function of the applied vapor pressure, which comprises the adsorption isotherm. The most widely used procedure for the determination of the surface area of porous materials is the BET method. Nitrogen adsorption at 77 K is generally considered to be the most suitable adsorptive for surface area determination. The BET surface area is calculated by constructing the BET plot using the relative pressure range up to 0.3. In this part of the isotherm a single layer of nitrogen molecules is formed on the surface (monolayer). Surface areas down to 1 m^2/g can be measured with the available instrument. Pore size distribution and nitrogen adsorption isotherms can be measured at relative pressures as low as 10^{-7}. This allows for the calculation of micropore size distributions between 0.4 and 2 nm. Furthermore, mesopore size distributions up to 50 nm are derived using the Kelvin equation. The amount of sample mass that is needed for the experiment typically lies between 0.1 and 1.0 gram.

In this work, only surface areas of catalysts prepared from cluster and from salts were concerned in order to compare the effect of loading and temperature that could change the surface area.

2.5.6 Temperature Programmed Reduction (TPR)

Reduction is an important step in preparation of metallic catalysts. The reduction of metal oxide (MO_n) by hydrogen is described by equation 2-1.

$$MO_n + H_2 \longrightarrow nM + H_2O \qquad \text{…..(2.2)}$$

One can predict the feasibility of the reduction from Gibbs free energy, ΔG which depends on partial pressure of water and hydrogen. The reduction is favorable thermodynamically if ΔG has negative value.

$$\Delta G = \Delta G^\circ + nRT\ln(PH_2O/PH_2) \qquad \text{…..(2.3)}$$

where ΔG = the change in Gibbs free energy for the reduction

ΔG° = the change in Gibbs free energy for the reduction at the standard conditions

n = the stoichiometric of the reaction coefficient

R = the gas constant

T = the temperature

P = the partial pressure

For many metal oxides such as noble metal, ΔG° is already negative and the reduction is thermodynamically feasible. To ensure that ΔG is negative, one can control the ratio of partial pressure of water and hydrogen. If the reduction is done under flowing nitrogen, the reduction product water is removed effectively and the second term in equation (2.3) negative.

The ratio PH_2O/PH_2 can indicate how easy the reduction can take place. Stable metal oxide has very small ratio indicating that water has to be completely removed in order to complete the reduction. For example, TiO_2 has the PH_2O/PH_2 ratio of 4×10^{-16} and it is generally found in oxide form. On the other hand, oxides of noble metal has high PH_2O/PH_2 ratio indicating that the reduction can easily occur no matter water is removed from the system or not. In this study palladium and nickel were interested and their reduction were investigated. The ratio PH_2O/PH_2 for PdO and NiO are 10^{14} and 500, respectively (Niemantsverdriet, 2000). As a result, it is certain that palladium oxide is reduced more easily than nickel oxide.

CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURES

There were 3 steps involved in the experimental procedure. The first step was synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ which was one of catalyst precursors. The second step was preparation of Pd-Ni/SiO_2 catalysts from $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster and from a mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ salts as well as the preparation of Pd/SiO_2 and Ni/SiO_2 as catalyst references, all by incipient wetness impregnation technique. The last step was catalyst characterization by several instrumental techniques including Fourier Transform Infrared Spectrometer (FT-IR), X-Ray Fluorescence (XRF), Powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmette-Teller (BET) Surface Area Analysis , Thermogravimetric Analysis (TGA).

3.1 Synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster

3.1.1 Chemicals and Materials

$[NMe_4]_2[Ni_6(CO)_{12}]$ was previously synthesized by Assist. Prof. Dr. Jatuporn Wittayakun at the University of Wisconsin-Madison, USA with courtesy of Professor Lawrence F. Dahl. It was tightly stored under nitrogen and occasionally checked by FTIR for possible decomposition. Palladium (II) acetate ($Pd(OAc)_2$) 98% and tetraphenylphosphonium bromide (PPh_4Br) 99% were purchased from Strem Chemical, Inc. USA. N,N-dimethyformamide (DMF), methanol (CH_3OH), acetone (CH_3COCH_3), acetronitrile (CH_3CN), nitrogen gas purity 99.99%, were purchased from Riedel-de Hain AG Germany, Lab-Scan Ltd. Ireland, Mallinckrodt Baker, Inc. USA, Gas and Casting Co., Ltd.Thailand, respectively. Distilled water and ice were also used for precipitation purpose. All chemicals were used as purchased without further purification.

3.1.2 Apparatus and Instruments

Apparatus for cluster preparation included glassware, septum magnetic stirrers, magnetic bars, stainless steel canulas, syringe needles, filter paper, and IR solution cell, hydraulic press device. Fourier transform infrared spectrometer (FT-IR) (Spectrum, GX Perkin-Elmer) was employed to confirm cluster formation by observing the carbonyl energy range, 2200-1600 cm^{-1}.

3.1.3 Synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ Cluster

All of the preparation steps were done under nitrogen atmosphere. All solvents and distilled water were purged with nitrogen prior to use. Apparatus set up for the synthesis is shown in Figure 3.1. The round bottle charged with starting materials was purged with nitrogen flow and the septum was used to prevent the air from entering. Stirred solutions were transferred by nitrogen pressure via a stainless steel canula. The synthesis procedure of cluster $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ which was modified from that described in reference (Tran, 2000) are summarized as follow.

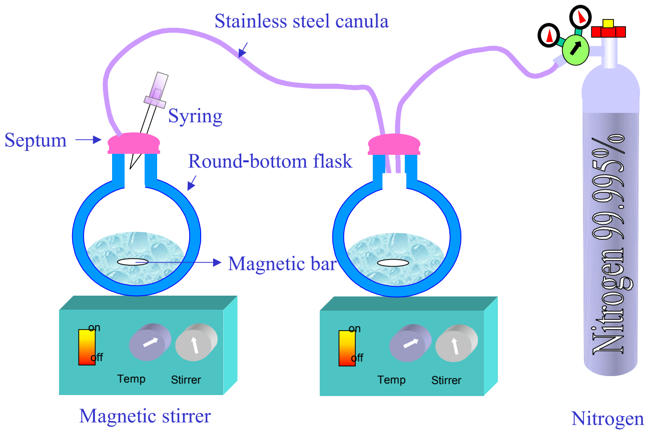
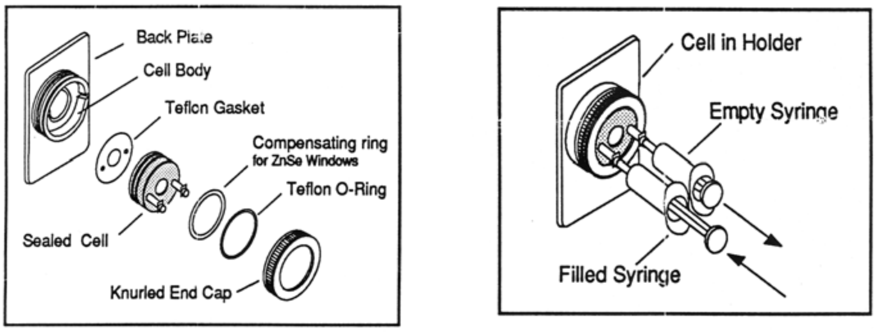


Figure 3.1 Apparatus set up for the synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$

1. $Pd(OAc)_2$ 0.28 g was dissolved in 15 ml DMF in a 250 ml round-bottom flask giving a light yellow solution.
2. $[NMe_4]_2[Ni_6(CO)_{12}]$ 0.50 g was dissolved in 15 ml DMF in another 250 ml round-bottom flask giving a cherry red solution.

3. The solution of $[NMe_4]_2[Ni_6(CO)_{12}]$ was added dropwise into the stirred $Pd(OAc)_2$ solution via a stainless steel canula within 20-25 minutes. The solution color changed from cherry red to dark brown in a few seconds.
4. The solution mixture was stirred by a magnetic stirrer at room temperature for 6 hours.
5. A solution of PPh_4Br 4.5 g in 15 ml methanol was added quickly into the solution mixture via a canula.
6. The mixture was cooled down to 0°C by an ice bath before a slow addition of 150 ml distilled water to precipitate the dark-brown $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster.
7. The precipitate was separated from the clear solution by filtration and washed with CH_3OH 50 ml four times to remove the excess PPh_4Br and other undesired reagents. The dark brown precipitate was dissolved in acetonitrile and characterized by Fourier transform infrared spectrometer (FT-IR) and the spectrum was compared with that reported in reference (Tran, 2000). Figure 3.2 demonstrates the IR solution cell assemble and how to fill the solution into it. The IR transparent windows are made of BaF_2.



(a) (b)

Figure 3.2 Liquid sample cell for FTIR measurement. (a) Assemble of IR solution cell (b) Filling solution into the cell

8. After being dried by nitrogen flow the dark-brown precipitate was dissolved with approximately 15 ml of acetonitrile and used as the extracted solution for further impregnation on silica.

3.2 Preparation of Pd-Ni/SiO_2 Catalysts from $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ Cluster and Silica by Impregnation

In this section $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ was dissolved in acetronitrile and impregnated on the dry SiO_2 support. After drying the sample was heated at 50°C or 80°C to remove carbonyl ligands (decarbonylation) on the cluster precursors. The success of decarbonylation was inspected by FTIR at various time (5, 10, 15, 20 minutes). After decarbonylation the samples were calcined at various temperature to remove $[PPh_4]^+$ cation as well as other volatile compounds and characterized by XRF, XRD, SEM, BET and TPR.

3.2.1 Chemicals and Materials

$[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster was obtained from 3.1. It was tightly stored under nitrogen and occasionally checked by FTIR for possible decomposition. Acetone, nitrogen gas, purity 99.99%, hydrogen gas, purity 99.99%, and silica (SiO_2) were purchased from Mallinckrodt Baker, Inc. USA, Gas and Casting Co., Ltd.Thailand, Japan Reference Catalyst respectively.

3.2.2 Apparatus and Instruments

Apparatus for preparation of Pd-Ni/SiO_2 catalysts from $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster by impregnation technique included glassware, septum, magnetic stirrers, magnetic bars, stainless steel, canulas, syringe needle and digital scale, oven, and furnace. The catalyst characterization included powder X-ray diffraction (D 5005 Bruker) for catalyst phase determination. X-Ray fluorescence (XRF) spectrometer, (Analyst 100 Perkin-Elmer) for the determination of catalyst metal loading. Scanning electron microscope (SEM), (JSM 6400 JEOL) for the investigation of catalyst surface morphology. Thermogravimetric analyzer (TGA), (TGA Shimudzu TGA-50) for investigation of the effect of calcination and reduction temperature on catalysts. Brunauer-Emmette-Teller (BET) surface area analyzer, (ASAP 2010 Micromeritics) for determination of catalyst surface area. Fourier transform infrared spectrometer (FT-IR, Spectrum GX Perkin-Elmer) for characterization of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$.

3.2.3 Preparation of Pd-Ni/SiO$_2$ Catalyst from $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ Cluster by Impregnation

1. Silica support was ground by morta and pestle, sieved to the size between 30 and 50 mesh (600 to 300 µm) and heated in the oven at 110°C for 3 hours to remove moisture. The picture sieved silica taken by digital camera and SEM are displayed in Figure 3.3.

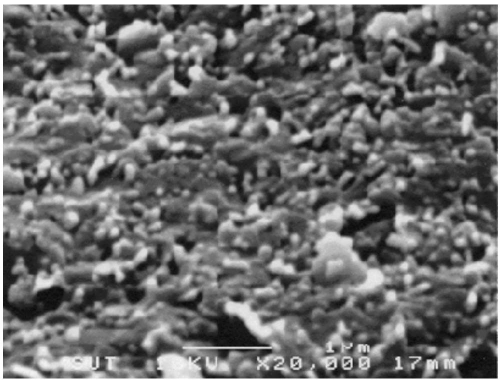


Figure 3.3 SEM picture of silica surfaced with magnification of 10 kV x 20,000

2. Before an impregnation, the incipient wetness of the silica support which is the sufficient amount of solution to fill the support pores was determined by adding water slowly to the constantly-shaked support until the support was sufficiently wet, without water spilling down to the container. That was the amount of the solution need to fill the support pores.
3. Different amounts of support were repeated for incipient wetness for the accuracy. The incipient wetness for this JRC silica was 1.8 ml/g.
4. The apparatus for impregnation is exhibitted in Figure 3.4. The amount of acetronitrile from 3 was used to dissolve $[PPh_4]_4$ $[Pd_{13}Ni_{13}(CO)_{34}]$ and the solution was dropped slowly onto the oven-dried silica support under nitrogen atmosphere.

5. The sample was dried under nitrogen flow at room temperature for 30 minutes and heated at 50 and 80 under waterbath for 5, 10, 15, and 20 minutes.
6. To characterize by IR approximately 2 mg of impregnated SiO_2 was ground well and mixed with approximate 100 mg anhydrous KBr powder packed in an evacuable die and pressed, with pressure of 15,000 lb/in^2 into a thin translucent pellet by a hydraulic device.

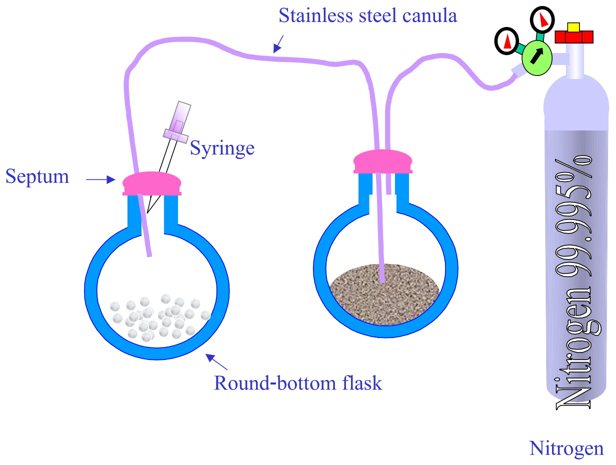


Figure 3.4 Apparatus for preparation of Pd-Ni/SiO_2 catalyst by impregnation

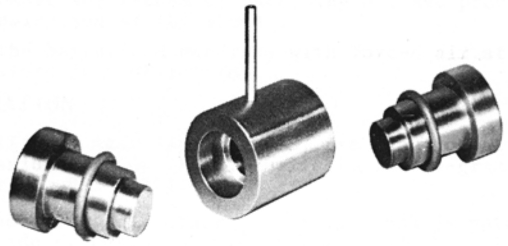


Figure 3.5 13 mm evacuable die (uni-die), Wilks model 36 for solid pellet for IR measurement.

7. The sample in closed container was calcined by heating at different temperatures (300, 400, and 500°C) for 1, 2 and 3 hours in a Honey well (Wilt industries Inc.,USA)to remove $[PPh_4]^+$ cation and other volaltile compounds.
8. The metal phase, morphology, and surface area of all catalysts were evaluated by XRD, SEM, and BET, respectively.
9. Metal loading in each catalyst was confirmed by XRF. In addition metal loading of selected samples were determined by ICP.

3.3 Preparation of Pd-Ni/SiO_2 Catalysts from a Mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ Salts by Impregnation

3.3.1 Chemicals and Materials

Palladium (II) acetate ($Pd(OAc)_2$), 98%, nickel (II) acetate tetrahydrate ($Ni(OAc)_2 \bullet 4H_2O$) , 98%, methanol (CH_3OH), acetone (CH_3COCH_3), acetronitrile, silica (SiO_2) were purchased from Strem Chemical, USA, Strem Chemical, USA, Ireland, Mallinckrodt Baker, Inc., USA, Mallinckrodt Baker, Inc., USA, Japan Reference Catalyst (JRC), respectively.

3.3.2 Apparatus and Instruments

Apparatus for preparation of Pd-Ni/SiO_2 catalysts from a Mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ salts by impregnation technique are in the same apparatus for preparation of Pd-Ni/SiO_2 catalysts from $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster by impregnation technique

3.3.3 Preparation of Pd-Ni/SiO_2 Catalysts from a Mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ Salts by Impregnation

Pd-Ni/SiO_2 catalysts were prepared from a mixed solution of $Pd(OAc)_2$ and Ni $(OAc)_2 \bullet 4H_2O$ with the Pd:Ni mole ratio of 1:1 and with the percent metal loading similar to the catalysts in 2.2 and characterized similarly.

1. An acetone the solution of $Pd(OAc)_2$ was mixed with a methanol solution of $Ni(OAc)_2 \cdot 4H_2O$. The solution mixture was stirred well by a magnetic stirrer at room temperature for 10 minutes and dropped slowly onto oven-dried silica support for impregnation.
2. The mixture was dried in air at 110°C for 1 hour and calcined in air by heating at different temperatures (300, 400, and 500°C) for 1, 2, and 3 hours to remove volatile materials including water, acetone, molecules formed from acetate decomposition and to convert Pd^{2+} and Ni^{2+} to metal oxide.
3. The metal phase, morphology, and surface area of all catalysts were evaluated by XRD, SEM, and BET, respectively.
4. The metal loading was confirmed by XRF. In addition metal loading of selected samples were determined by ICP.

3.4 Preparation of Pd/SiO_2 and Ni/SiO_2 Reference from $Pd(OAc)_2$ and $Ni(OAc)_2$

Pd/SiO_2 and Ni/SiO_2 were prepared from $Pd(OAc)_2$ and $Ni(OAc)_2 \cdot 4H_2O$, respectively, to be used as reference catalysts. The preparation procedure was similar to that of $Pd\text{-}Ni/SiO_2$ from mixed metal salt. The catalysts were characterized by XRD, SEM, TPR, BET, and XRF.

3.4.1 Chemicals and Materials

Chemicals and materials are the same in preparation of $Pd\text{-}Ni/SiO_2$ catalyst from a mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ salts by impregnation technique

3.4.2 Apparatus and Instruments

Apparatus and instruments are the same in preparation of $Pd\text{-}Ni/SiO_2$ Catalyst from a mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ salts by impregnation

3.4.3 Preparation of Pd/SiO_2 by Impregnation

1. The acetone solution of $Pd(OAc)_2$ was dropped slowly onto the silica support until the incipient wetness was reached.

2. The sample was dried in air at 110°C for 1 hour, calcined in air by heating at different temperatures (300, 400, and 500°C) for 1, 2 and 3 hours to remove volatile matters.

3. The metal phase, morphology, and surface area of all catalysts were studied by XRD, SEM, and BET, respectively.

4. The metal loading was confirmed by XRF.

3.4.4 Preparation of Ni/SiO_2 by Impregnation

1. $Ni(OAc)_2 \bullet 4H_2O$ was dissolved in CH_3OH was dropped slowly onto the silica support.
2. The sample was dried in air at 110°C for 1 hour, calcined in air by heating at different temperatures (300, 400, and 500°C) for 1, 2 and 3 hours to remove volaltile matters.
3. The metal phase, morphology, and surface area of all catalysts were studied by XRD, SEM, and BET, respectively.
4. The metal loading was confirmed by XRF.

3.5 Catalyst Characterization

3.5.1 Fourier transform infrared spectrometer (FT-IR)

Fourier transform infrared spectrometer (FT-IR) (Spectrum, GX Perkin-Elmer) for characterization of $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$. A Perkin-Elmer spectrum GX FTIR Spectrophotometer are used to take the mid IR spectra of samples. The range of measurement for CO band in $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$ cluster was between 2200 cm^{-1} and 1600 cm^{-1}. The number of scans was 12 at the resolution of 4.0 cm^{-1}.

3.5.2 Brunauer-Emmette-Teller (BET) surface area analyzer

Brunauer-Emmette-Teller (BET) surface area analyzer, (ASAP 2010 Micromeritics) was used for the determination of catalyst surface area. Before the BET experiment, each catalyst was pretreated by heat at 110°C in a hot-air oven to remove moisture and store in a dessicator. Apparatus is shown in figure 2.10. There are two part in these technique. The first part is degassing for remove moisture and impurity on the catalysts. Approximately 25 mg of catalyst was filled into a glass sample tube, weighted, and connected to degas port with seal fit. The sample was degassed at 300°C and 277 psi, and weighted again for exact weight. The sample tube was connected to the BET analyze port and the nitrogen adsorption was proceeded at –78°C from P/P_0 value of 0.01 to 0.3.

3.5.3 Powder X-ray diffractometer (XRD)

A D5005 Bruker Powder X-ray diffractometer with Ni-filtered Cu K_α radiation was used for to analyze the phase and form of metal on the silica support. Sample was neatly ground to homogeneous power, and filled in a sample pan, and pressed by a glass plate in order to get smooth surface before installing into the sample holder of the diffractometer. The K_α X-ray was generated from a Cu target with a current of 25 mA and a potential of 40 kV at 0.01° step size and 1s step time. The scan was performed over a range of 2θ angle from 5 to 60°. The intensity of the diffracted X rays is measured as a function of the diffraction angle 2θ.

3.5.4 X-Ray fluorescence (XRF) spectrometer

The composition of each catalyst especially palladium, nickel, and phosphorus was determined to confirm the prepared loading value. Prior to the analysis, a standard curve of palladium and nickel on silica was prepared by deposition of varied amount of the metals on silica. A plot between intensity and concentration was obtained for metal loading determination. However, the calibration curve for phosphorus was not made because the amount of phosporus remained in the catalysts after calcination was not expected to be very low. The catalyst sample was filled in a plastic vessel with one end closed by a thin transparent film, capped, and installed into the sample port for analysis. This nondestructive elemental analysis was operated on an Oxford ED 2000 spectrometer.

3.5.5 Scanning electron microscope (SEM)

Surface morphology of catalysts was investigated by using a scanning electron microscope, SEM, JEOL (JSM-6400) with an accelerating voltage of 15-40 kV. Before the analysis, samples were dried at 110°C in hot-air oven for one hour and cooled down in a desicator. In sample preparation, the catalyst was sprinkled over two-sided tape on a brass bar. The excess amount was blown away by air spray and the sample was heat transferred to a sputtering device to coat with goal to improve conductivity. The sample was evacuated twice before coating with a thin layer of gold sputtering. The sample was then inserted into SEM chamber where it was evacuated once more before transferring into the path of electron beam. The images from SEM was taken on polaroid films and scanned for this thesis.

In addition to the investigation of surface morphology, elemental analysis was performed by EDX method. Electron with accelerating voltage of 25 kV was directed into surface of PdNi/SiO_2 catalysts prepared from cluster and fluorescence peaks were detected. The analyzed areas included the position that seemed to be metal particle, visually smooth area, as well as areas between the cracked surface. The intensity versus energy of fluorescence was plotted.

3.5.6 Temperature-Programmed Reduction (TPR)

Thermogravimetry (TG) is a technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. The schematic diagram of the apparatus is demonstrated in Figure 3.6. TGA instrument was connected to H_2, He with controlled the gas flow. In order to enhance the steps in the thermogravimetric curve, the derivative thermogravimetric (DTG) trace is frequently drawn. This is the plot of the rate of mass change, with time, dm/dt. Several users and manufacturers call this technique Thermogravimetric Analysis (TGA) to avoid confusion with the glass temperature, T_g. The apparatus is called a thermobalance and has four major parts:

1. the electrobalance and its controller
2. the furnace and temperature sensors
3. the programmer or computer
4. the recorder, plotter or data acquisition device.

The sensitive electrobalance is placed in a temperature controlled oven so that changes in the mass of a material can be followed as a function of temperature, or of time under isothermal conditions. The sample is heated in a controlled atmosphere, or under vacuum, at a rate of 0.5-25°C/min over the temperature range of 25°C to 1200° C. (Special equipment may operate at subzero temperature)

Thermogravimetric analyzer (TGA, Shimudzu TGA-50) was a major instrument for investigation of the effect of calcination and reduction temperature on catalysts. Before the TPR experiment, the catalysts was pretreated by heat at 110°C in an oven to remove moisture and stored in a dessicator. The TPR was investigated in a TGA equipped with hydrogen and nitrogen cylinder. Each TPR experimental procedure are as follow.

1. The catalyst approximately 20 mg was charged on a sample pan and suspended in the TGA furnace.
2. The sample was heated to 450°C under nitrogen (flow rate 20 ml/min) to further remove chemisorbed volatile material compounds in the pores until constant weight was obtained.
3. The sample was cooled down to room temperature and the purge gas was switched to hydrogen (flow rate 20 ml/min) and the temperature was raised to 500°C with the rate of 2 ^{0}C/min.
4. The weight change as well as its derivative was recorded in order to see reduction temperature and amount of hydrogen consumed.
5. The temperature was lowered to room temperature.

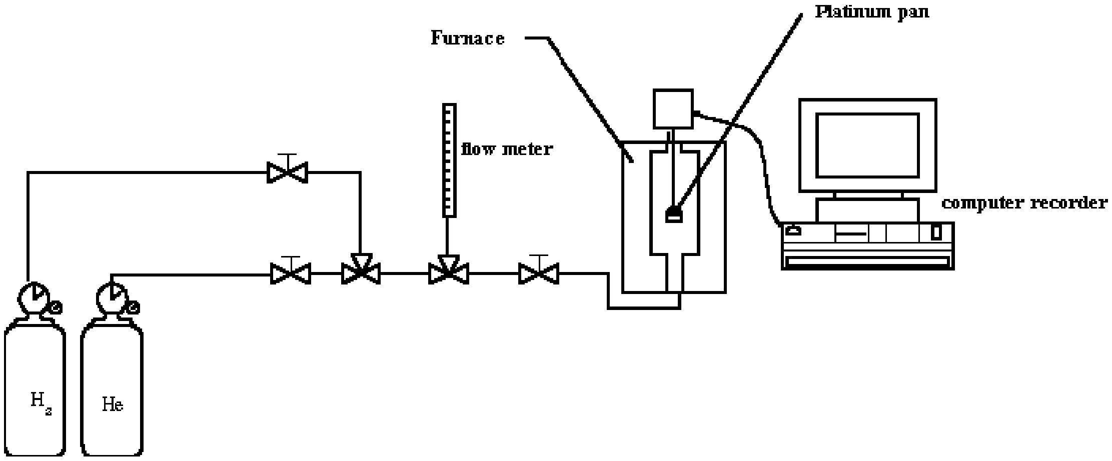


Figure 3.6 Apparatus for temperature-programmed analysis. TGA was connected with hydrogen and helium

3.5.7 Hydrogen adsorption experiment

Hydrogen adsorption was determined by a "home-made" reactor system at the Chemical Resources Laboratory, Tokyo Institute of Technology, Japan by collaboration with Professor Yutaka Morikawa. A known amount of Pd-Ni/SiO_2 catalyst was place in a U-tube reactor connected to a thermal conductivity detector (TCD) and gases. The temperature program sequence is shown in figure 3.7. Catalyst was heated from room temperature to 450°C at a 5°C/min rate under hydrogen atmosphere and held for one hour in order to complete catalyst reduction. Then the temperature was lowered to 400°C, held for 30 minutes and cooled down to room temperature and hydrogen injection was tested on the thermal conductivity detector (TCD). The catalysts was then cooled down to room temperature in nitrogen.

Results from all characterization techniques for PdNi/SiO_2 catalysts prepared from cluster and metal salts as well as standard materials are discussed in chapter IV.

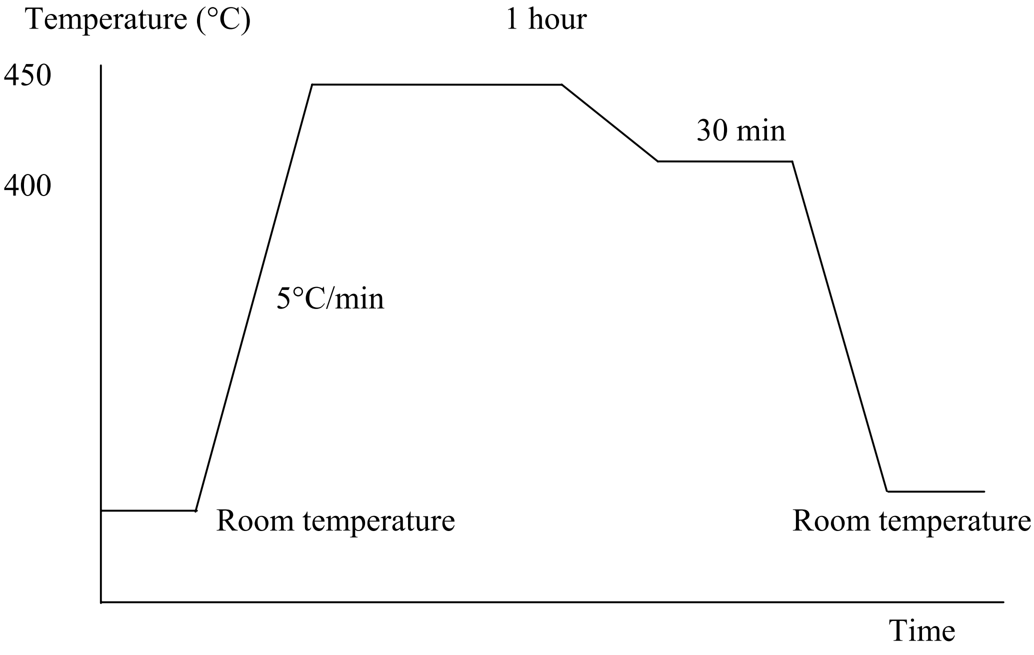


Figure 3.7 Temperature program sequence of the hydrogen adsorption experiment

CHAPTER IV
RESULTS AND DISCUSSION

This chapter begins with results characterization of $[NMe_4]_2[Ni_6(CO)_{12}]$ by IR. This nickel cluster was a starting material for the synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ which was also characterized by IR. After the $Pd_{13}Ni_{13}$ cluster was impregnated over silica, the material was characterized by IR. After drying and calcination, the resulting $PdNi/SiO_2$ catalysts were characterized by XRD, SEM, and TPR, results from those techniques are given in this chapter. In addition the number of active sites was determined by hydrogen adsorption. The properties of $PdNi/SiO_2$ prepared from cluster were discussed and compared with those from salts. The comparison indicated whether the $PdNi/SiO_2$ prepared from salt had preferable properties suitable for catalysis.

4.1 Characterization of $[NMe_4]_2[Ni_6(CO)_{12}]$ by FTIR

Starting materials for the synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ was $[NMe_4]_2$ $[Ni_6(CO)_{12}]$ and palladium acetate. The cluster $[NMe_4]_2[Ni_6(CO)_{12}]$ was dark red solid and air-sensitive. It was previously prepared, re-crystallized, and characterized by Assist. Prof. Dr. Jatuporn Wittayakun with courtesy of his former advisor, Professor Lawrence F. Dahl at University of Wisconsin-Madison, USA. Since it was prepared and kept in a closed bottle for a long time before this research started, it might decompose or change into other form. As a result, it was important to be re-characterized.

An important characterization technique for carbonyl clusters is infrared spectroscopy which can readily identify the type of carbonyl ligands from their vibrational frequencies. Carbonyl can associate with metal clusters as terminal, edge-bridging, or face-bridging ligands. Those ligation modes show IR absorption frequencies in the range of 1950-2150 cm^{-1}, 1750-1900 cm^{-1}, and 1700-1800 cm^{-1}, respectively.

The cluster $[NMe_4]_2[Ni_6(CO)_{12}]$ was dissolved in acetonitrile (CH_3CN) with was the most appropriate solvent for this purpose because it did not contain C=O bond to interfere with CO ligands. The solution color was cherry red and clear. The IR characterization was done under nitrogen because the cluster solution decomposed quickly when exposed to air. The absorption spectrum of the solution is displayed in Figure 4.1. There were three peaks at 1975(s), 1810(m), and 1780(ms) cm^{-1} corresponding to terminal and edge-bridging carbonyl ligands similar to the value reported in literature. This result confirms that the starting material maintains its structure be for the synthesis.

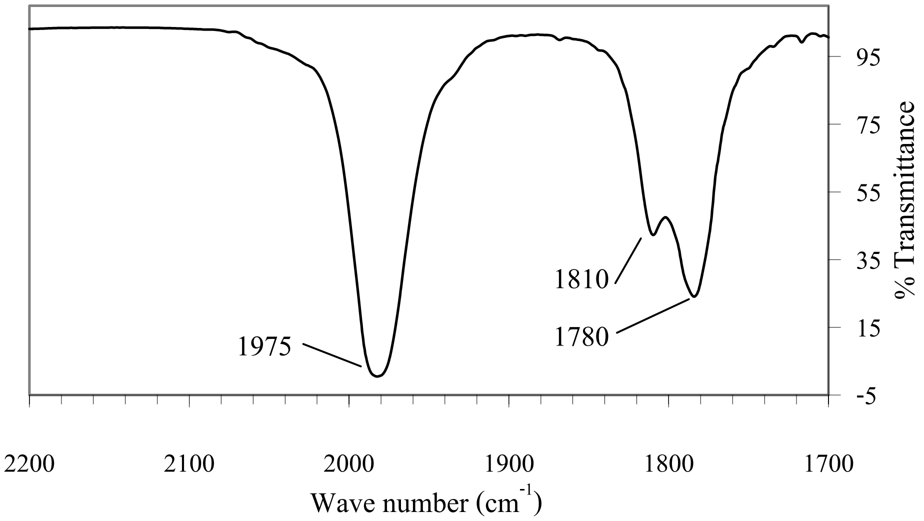


Figure 4.1 Infrared spectrum of $[NMe_4]_2[Ni_6(CO)_{12}]$ in acetonitrile

4.2 Characterization of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ by FTIR

The synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster was conducted under nitrogen atmosphere by slight modification from the procedures described in literature (Tran, 2000). The product was a dark-brown powder which readily decomposed in air into solid black powder presumably oxides of palladium and nickel. The cluster was soluble in polar solvent such as acetonitrile, acetone, DMSO, and DMF. Because of the lack in air-sensitive apparatus for cluster synthesis, the procedure was simplified to suit our laboratory. Thus, it was necessary to characterize the product from the synthesis to ensure the cluster formation. As reported by Tran and coworkers, the cluster $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ contained nine Ni-attached terminal COs, 18 doubly bridging COs, and 7 face-bridging COs.

The IR spectrum from of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster from this work (shown in Figure 4-2) was similar to that reported by Tran et al (2000). The cluster exhibited absorption maxima at 2027(vs) and 2001(sh) cm^{-1} for terminal carbonyls and at 1911(sh), 1887(s), and 1859(s) cm^{-1} for bridging carbonyls. This confirmed our success for the synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster.

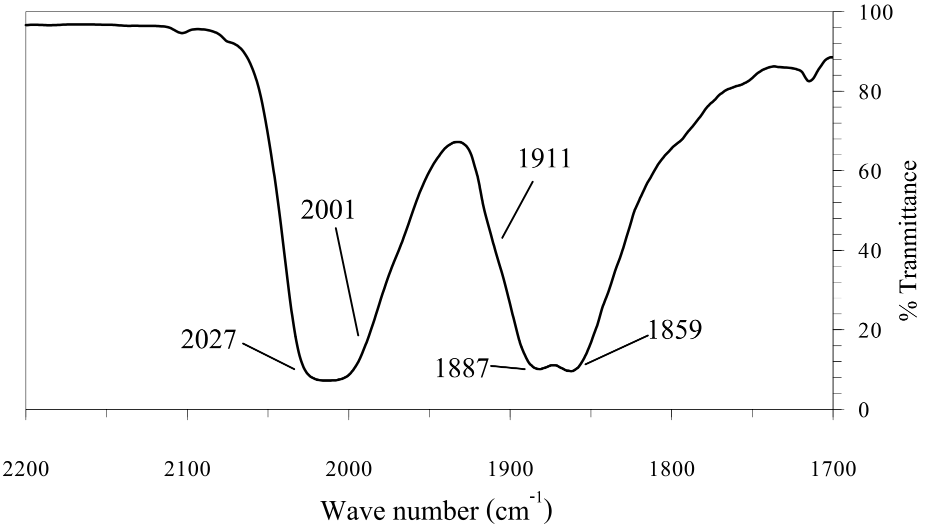


Figure 4.2 Infrared spectrum of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster in acetonitrile

4.3 Characterization of $[(PPh_4)_4][Pd_{13}Ni_{13}(CO)_{34}]$ Cluster Impregnated on Silica by FTIR

After the synthesis of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$, cluster was dissolved in acetonitrile and deposited onto silica support by impregnation under nitrogen atmosphere. The impregnated silica was dried under nitrogen flow at room temperature for 30 minutes. After drying the samples were kept under nitrogen at room temperature for 5, 10, 15 and 20 min then characterized by IR spectroscopy to determine the change of the cluster after impregnation. The sample was ground to fine powder, mixed with KBr powder, pressed into pellet by hydraulic press device, and inserted into IR path in the spectrophotometer. The spectrum was recorded in carbonyl range (1600-2200 cm^{-1}) as before. Figure 3.3 shows the FTIR spectra of silica support and $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster on silica kept under nitrogen for 5 min. The spectra were scaled for comparison. From the IR spectra, the carbonyl peaks were not observed on cluster/silica sample and the spectra was not much different for that of silica. The CO peaks were not observed might due to the amount of solid sample which was too small to detect by IR. Other possibility was that the carbonyl ligands already departed from the cluster during drying process.

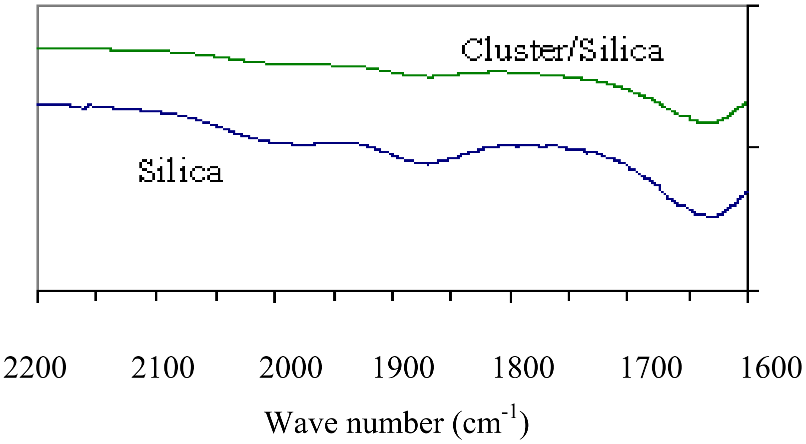


Figure 4.3 IR spectra of silica and cluster impregnated on silica

To test the adhesion between the cluster and silica after impregnation, acetronitrile was used to extract the cluster out from the silica support. In this experiment, acetonitrile was added to cluster-impregnated silica and the mixture was stirred for 5 minutes. However, the color of acetonitrile solution did not show any color of the red cluster, suggesting strong adhesion between cluster and the silica support.

The thermal effect on the carbonyl removal (decarbonylation) was also explored. The impregnated samples was dried under nitrogen at room temperature for 30 min and heated in water bath under nitrogen at 50°C and 80°C for 5, 10, 15 and 20 min. The samples were then ground and mixed with KBr to form IR pellet. The spectrum of samples heated at 50°C and 80°C are shown in Figure 4.4 and 4.5, respectively. Nevertheless, no distinguishable effect was observed by FTIR. All samples showed similar IR spectrum to silica support. This observation was an evidence that low heat could remove carbonyl ligands effectively.

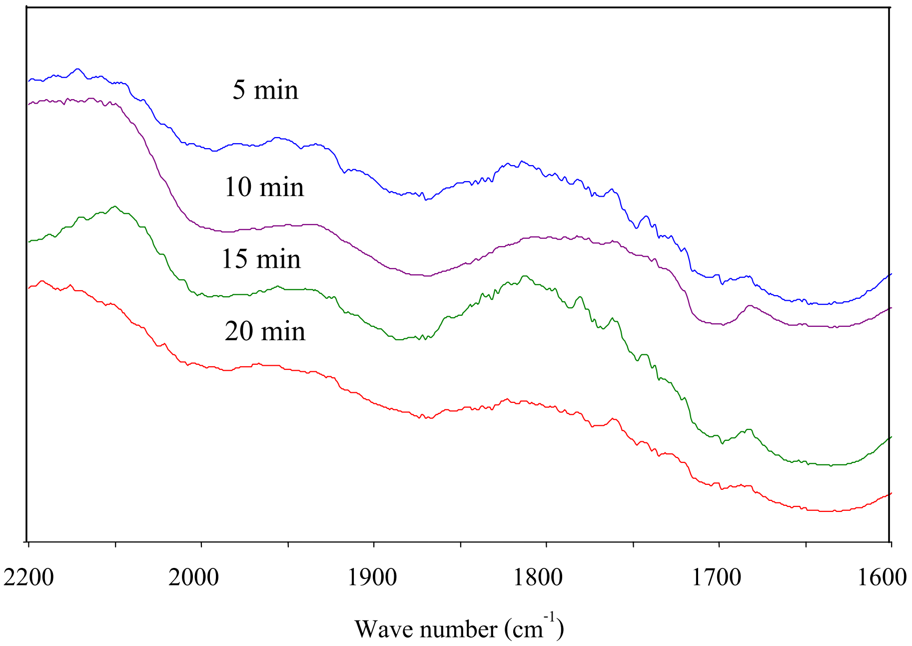


Figure 4.4 IR spectra of silica impregnated with cluster, dried at room temperature, and heat at 50°C for (from bottom to top) 5, 10, 15, 20 minutes.

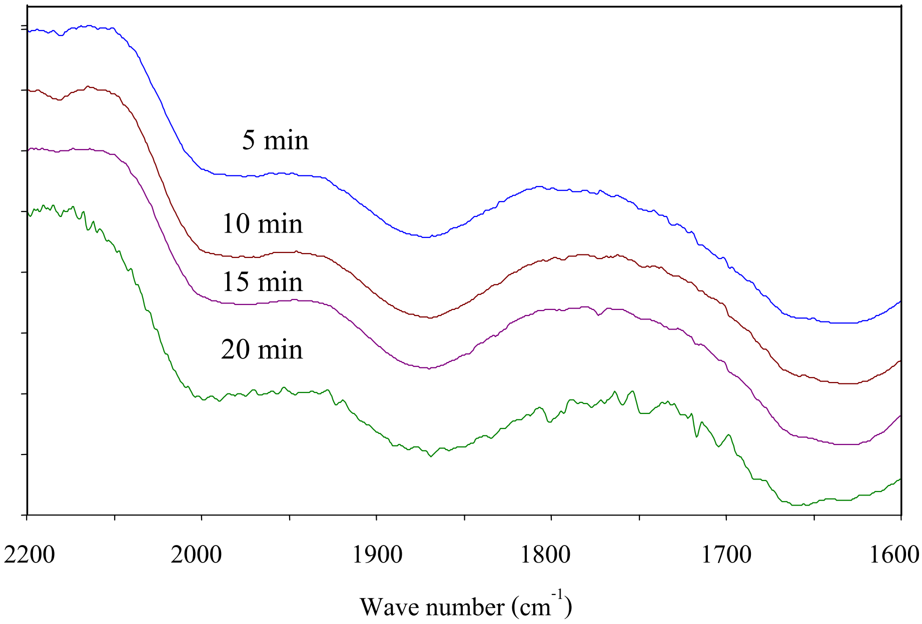


Figure 4.5 IR spectra of silica impregnated with cluster, dried at room temperature, and heat at 80°C for (from bottom to top) 5, 10, 15, 20 minutes.

4.4 Effect of Calcination on PdNi/SiO_2 from Cluster

Generally $[PPh_4]^+$ can be removed from the $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ cluster by calcination at higher than 365°C. To find the effect of calcination on the $[PPh_4]_4$ $[Pd_{13}Ni_{13}(CO)_{34}]$ cluster impregnated on silica samples, we chose the calcination conditions to be at 300, 400, and 500°C for 1, 2, 3 hours, in air. After the calcination process, the samples were characterized by XRF to find the removal temperature of $[PPh_4]^+$ cations. Table 4.1 shows the result from the XRF measurement.

Table 4.1 Concentration of palladium, nickel and phosphorus in PdNi/SiO_2 catalysts analyzed by XRF. The catalysts were calcined at 300, 400, and 500°C for 1, 2, and 3 hours.

Calcination Temperature	Time (hour)	Concentration (% weight)			
		SiO_2	Pd	Ni	P
300°C	1	87.83	6.178	5.99	Trace
	2	87.62	6.74	5.64	Trace
	3	84.76	9.24	5.97	0.02
400°C	1	82.92	10.94	6.13	-
	2	83.77	10.50	5.71	-
	3	86.16	8.37	5.45	-
500°C	1	83.47	10.80	5.72	-
	2	82.65	11.51	5.83	-
	3	81.13	13.13	5.72	-

Apparently, the XRF results show the presence of Pd and Ni from the cluster on SiO_2. From the measurement, some phosphorus can be detected by XRF at the calcination temperature of 300°C, therefore the temperature of 400°C was chosen as calcination temperature for the rest of the catalyst preparation.

4.5 Catalyst Characterization by XRD

The catalyst analysis by powder XRD was to determine the type of metal phase on silica support because metal could be in the metallic or oxide forms or both. The positions of XRD peaks are characteristic of the element. The broadening of XRD peaks is related to the metal particle size. As the particle size becomes smaller, the peaks are broader. In addition, when metal particles disperse well on the support, they have small particle size and their XRD peaks emerge with the baseline. Thus, XRD analysis is very convenient in catalysis to roughly conclude about metal phase, metal dispersion, and particle size.

Figure 4.6 shows the XRD spectrum of standard materials including silica, NiO/SiO_2, and PdO/SiO_2. Silica support for this study was obviously amorphous showing a broad 2θ peaks at 22 degree. NiO/SiO_2 catalyst gave only one peak at 34 degree while PdO/SiO2 had two peaks at 38 and 44 degrees.

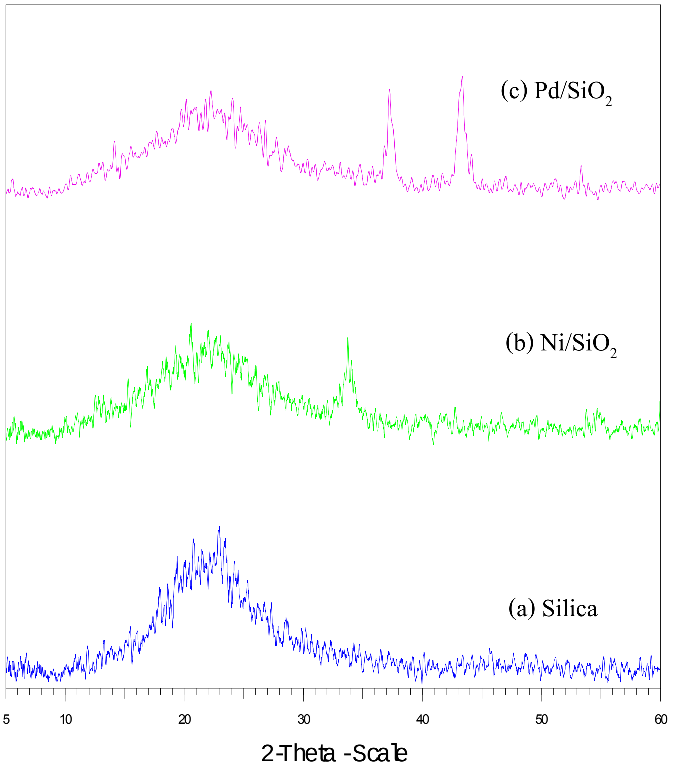


Figure 4.6 XRD pattern of silica compare with Pd/SiO_2 and Ni/SiO_2 reference

The effect of calcination time was studied by XRD on Pd-Ni/SiO_2 catalysts prepared from cluster (Figure 4.7 a) and catalysts prepared from a mixture of palladium and nickel salt (Figure 4.7 b). The catalysts were calcined at 400°C for 1, 2, and 3 hours. It was found that catalysts from both precursors displayed stronger peaks as the temperature increased. This indicated that long calcination time caused metal particles to aggregate to form larger particle on the surface. In the case of catalysts from cluster, It was difficult to see the metals peaks after calcination for one hour. This might due to good metal dispersion on he support and the metal particles have small particle size. When left longer, the peaks near 34 degree were observable more clearly indicating metal sintering. However, the PdO peaks were clearly seen in catalysts prepared from metal salts in all calcination time indicating the larger metal particle than the case of catalysts from cluster. For the catalysts from salt, the particle size also increased with calcination time. The migration of metal particle to form larger aggregate on the surface can tell the strength of metal-support interaction. If the metal particle migrates easily, it means the metal-support interaction is not very strong.

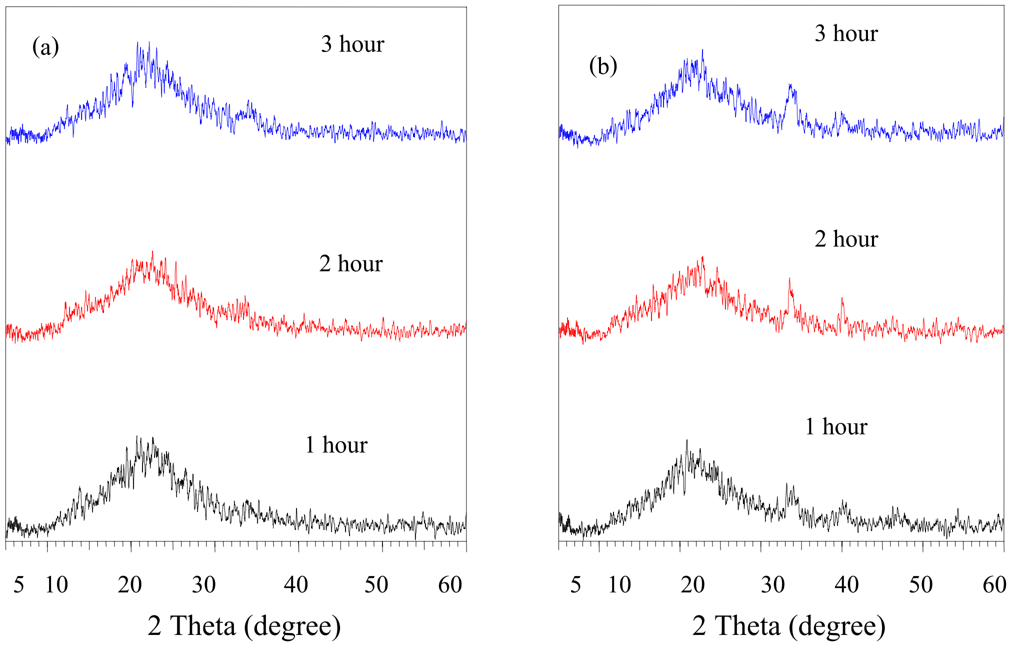


Figure 4.7 XRD pattern of Pd-Ni supported on Silica calcined at 400°C for 1, 2, and 3 hour (a) Pd-Ni cluster/SiO_2 (b) Pd-Ni salt/SiO_2

For catalysts calcined at 500°C, the peaks of catalysts from salt were also larger and sharper than that of catalysts from cluster for all calcination time. This result confirmed again that better metal dispersion of metal on support could be obtained when a cluster precursor was used. However, the degree of sintering for this calcination temperature was not so obvious. As shown in Figure 4.8, the XRD peaks for catalysts calcined at 500°C were not much different for the calcination time of 1, 2, and 3 hours. It might be concluded that the metal sintering was fast at this temperature and the higher temperature assisted the metal to anchor on the support more strongly. After strong metal-support interaction was formed, the rate of sintering was slow.

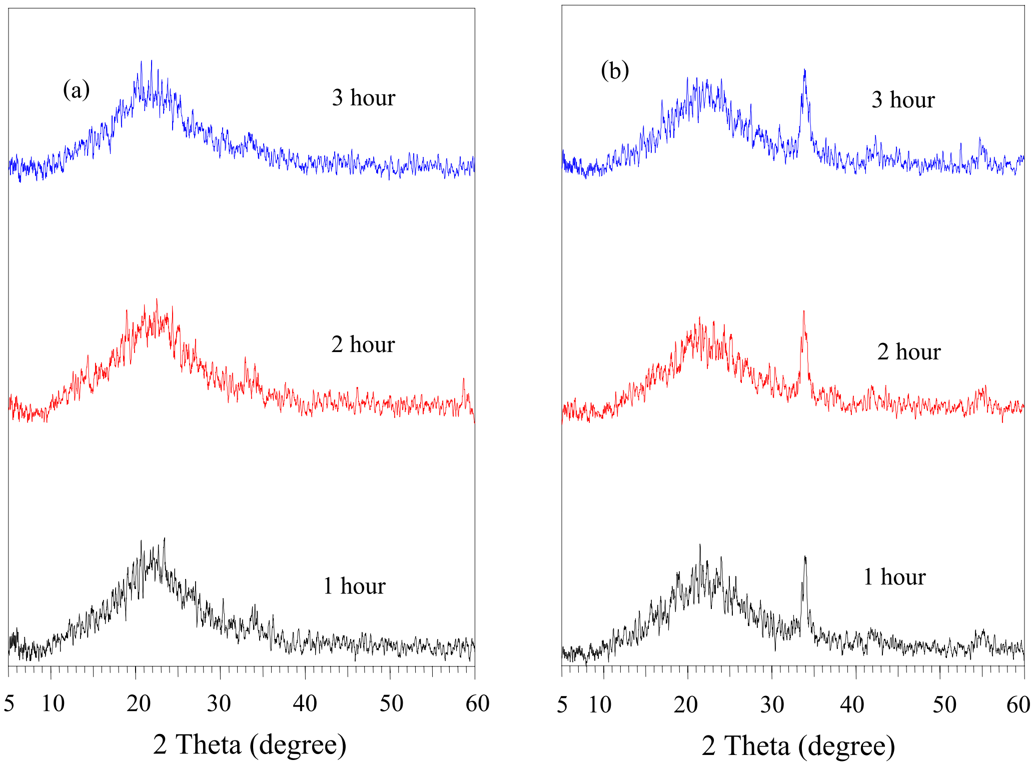


Figure 4.8 XRD pattern of Pd-Ni supported on Silica calcined at 500°C for 1, 2, 3 hour (a) Pd-Ni cluster/SiO2 (b) Pd-Ni salt/SiO_2

To investigate the effect of calcination temperature on catalysts prepared from cluster, the catalysts from the same loading was calcined at 300, 400, 500, 600°C for one hour and analyzed with XRD. The spectra were shown in Figure 4.9. It was found that spectrum from the calcination temperature of 300, 400, 500°C were similar. However, the metal peak started to show at 600°C due to sintering. Thus, for the catalysts prepared from cluster, calcination temperature should be lower than 600°C to avoid sintering. Because sintering were easily observed at 500°C (Figure 4.8) and 600°C (Figure 4.9), only calcination temperature at 400°C was selected though out the remaining of the study.

In general, the catalytic activity depends on the amount of active species but metal particle size of supported catalyst increases with metal loading. Thus, it was interesting to explore the change in metal dispersion with metal loading. For this purpose, different metal loading was prepared from both cluster and metal salt, namely, 2.39, 7.03, and 10.69 % by weight. After impregnation and dry, all loadings were calcined at 400°C for one hour. The XRD spectra of catalysts prepared from cluster were shown in Figure 4.10 a. All metal loading displayed very broad peaks and almost indistinguishable from the baseline. On the other hand, the metal peaks of catalysts prepared from metal salts were larger as the loading increased. This was a normal behavior that was expected for catalysts prepared by conventional method.

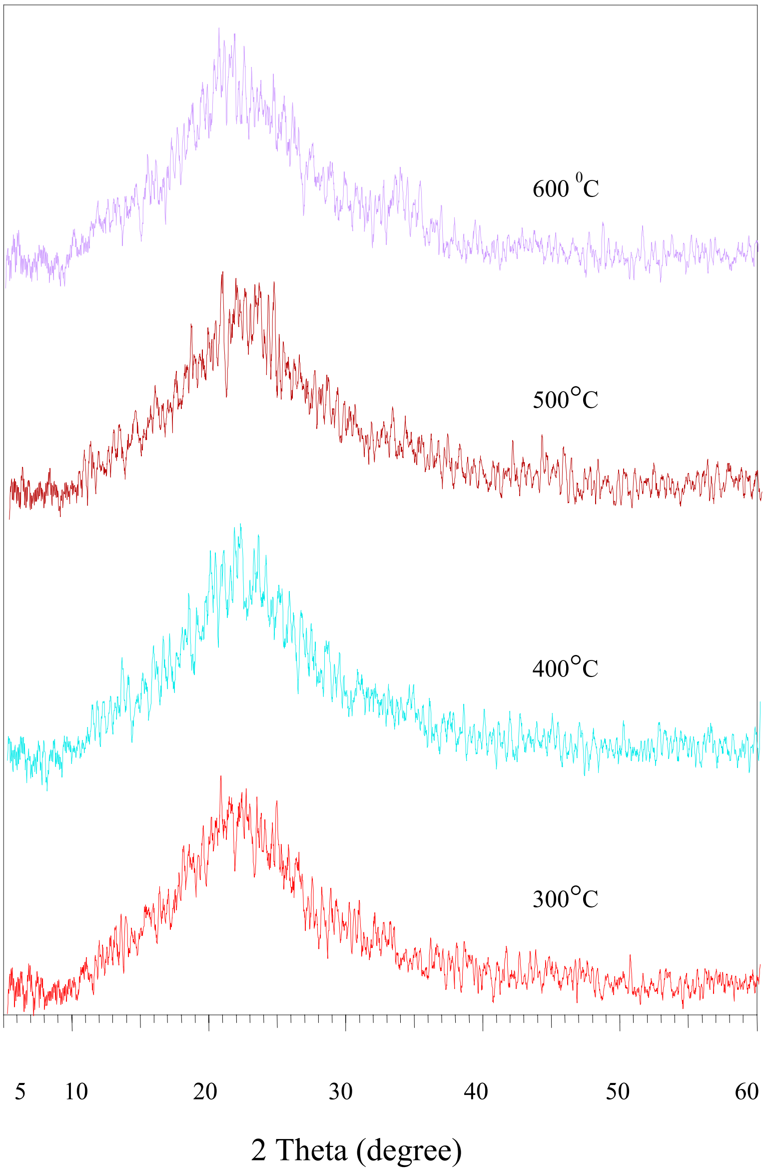


Figure 4.9 XRD pattern of cluster supported on silica calcined at different temperature.

Good metal dispersion is required in catalysis because it means the metal particles have small size. In the other words, the surface area per metal particle is higher and the catalytic activity is usually higher. When similar metal loading from cluster and salt precursors was compare, the catalysts prepared from metal cluster always gave better metal dispersion.

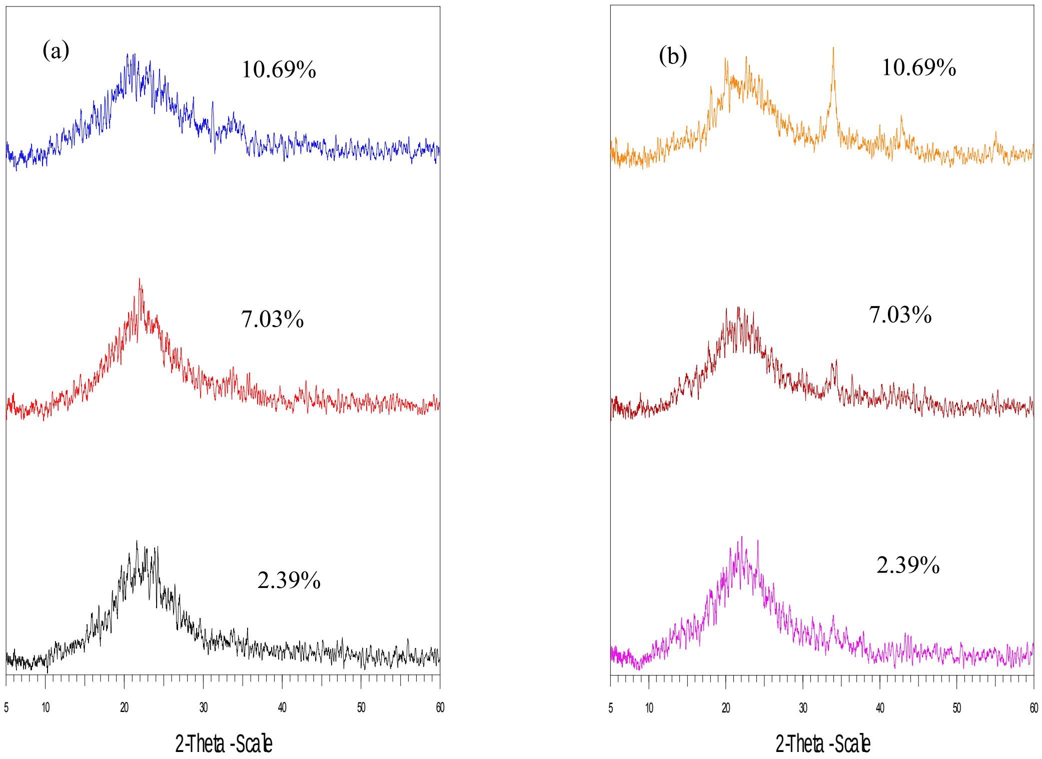
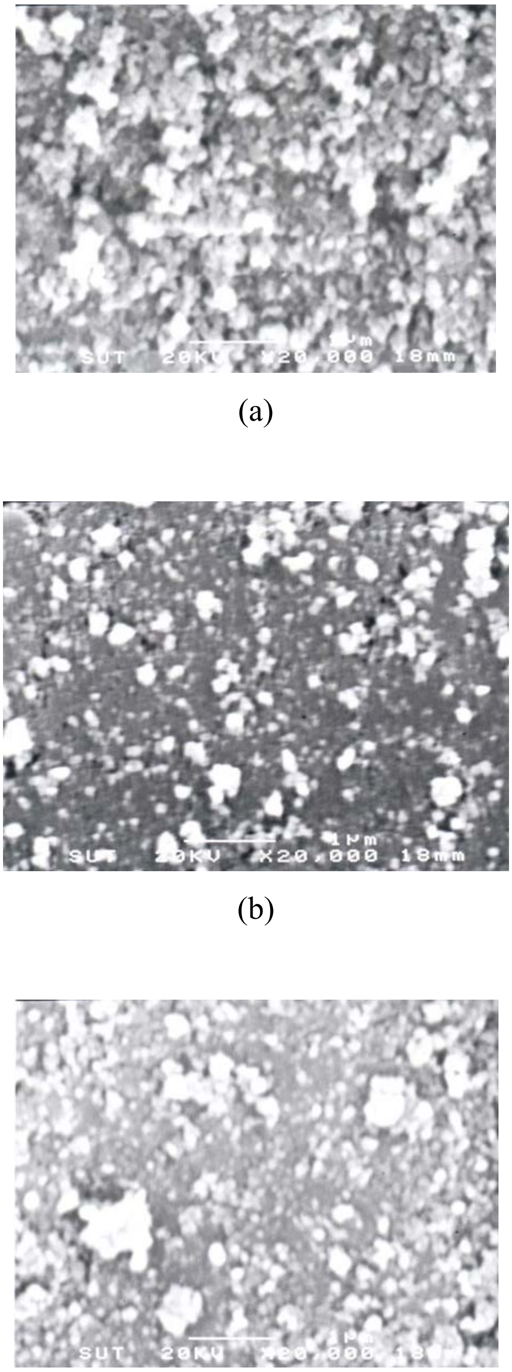


Figure 4.10 XRD pattern of Pd-Ni/SiO_2 salt different loading calcined at 400°C for 1 hour (a) Pd-Ni cluster/SiO_2 (b) Pd-Ni salt/SiO_2

4.6 Catalyst Characterization by SEM

Morphology of all catalysts was studied by SEM to investigate the nature of surface. All images were taken with the 20 kV electron beam at 20,000 magnification. Figure 4.11 (a) shows the surface of Pd/SiO_2 while Figure 4.11 (b) shows the surface of Ni/SiO_2. At the beginning it was suspected that the white spherical shapes on the surface were metal particles. However, when compare Figure 4.11 with the image of silica support, no difference was observed. Thus, the white particles were the part of silica surface.

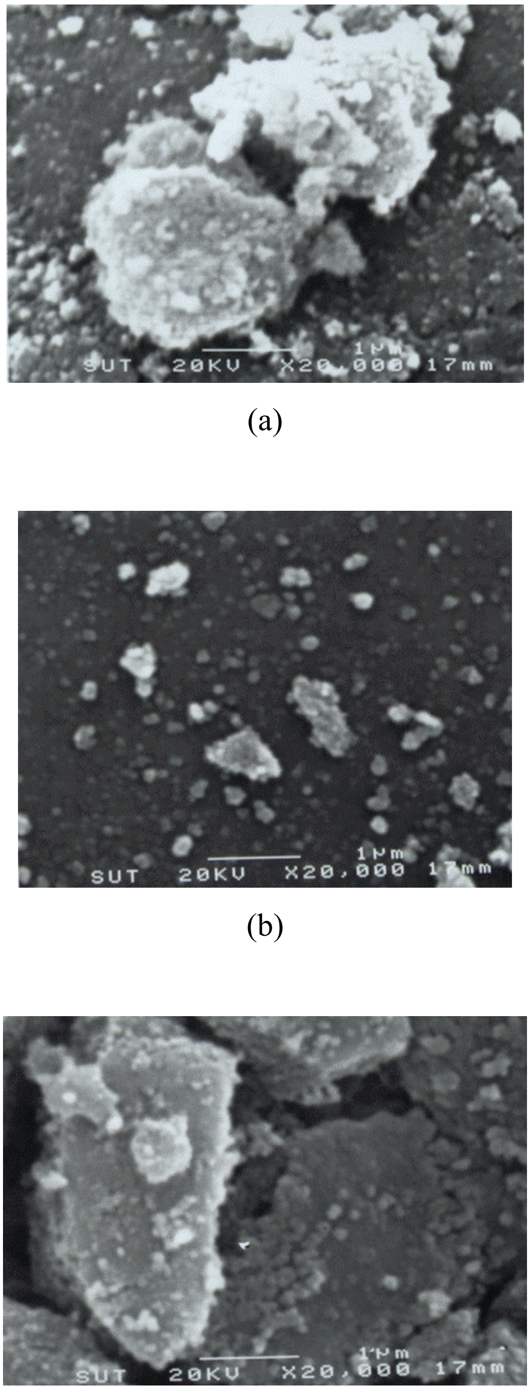


(a)

(b)

(c)

Figure 4.11 SEM micrograph taken with 20 kV with 20,000 magnification. (a) SiO_2 (b) Pd/SiO_2 dry in air at 400°C 1 hour (c) Ni/SiO_2 dry in air at 400°C for 1 hour



(a)

(b)

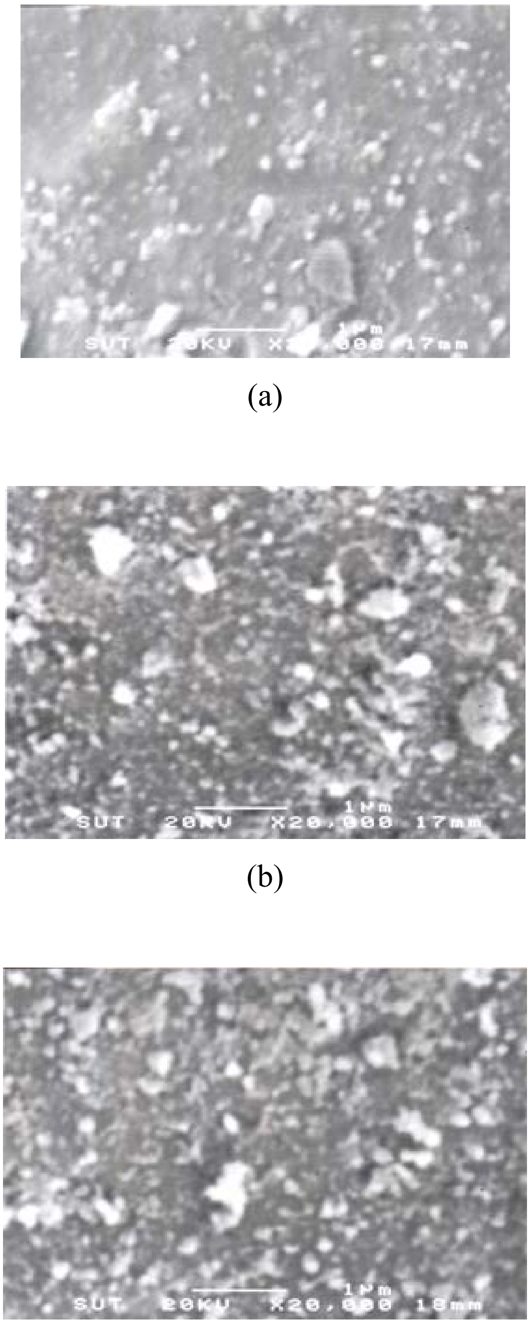
(c)

Figure 4.12 SEM images of Pd-Ni/SiO_2 catalysts prepared from metal salts with various loading calcined at 400°C for 1 hour taken by 20kV with magnification of 20,000. (a) 2.3992% (b) 7.0291% (c) 10.6991%

Figure 4.12 displays images of PdNi/SiO_2 catalysts prepared from metal salts with various loading, i.e., 2.3992, 7.0291, and 10.6991%, and calcined at 400°C for 1 hour. In Figure 4.12 (a) and (c), the image of rough area was presented while Figure 4.12 (b) was the image of a more smooth area. By comparing to the silica surface, the surface of these catalysts seemed to be covered with metal particles, especially in catalysts with higher loading. However, it is not practical in terms of economics to prepare catalysts with the high loading. It was done in this study for comparison purpose.

The effect of calcination time was interested in this study. From XRD analysis, it was found that calcination at 400°C was suitable for this study. Thus, the catalysts prepared from metal salts were calcine at this temperature for 1, 2 and 3 hours. Even though there was a slight difference in XRD spectrum, the SEM images of these catalysts were similar. As shown in Figure 4.12 the white sphere on the surface could be either part of silica support or metal particles.

Pd-Ni/SiO_2 catalysts prepared from clusters with different loading (namely, (a) 2.3992%, (b) 7.0291%, and (c) 10.6991%) were also studied by SEM. In Figure 4.13 there was no distinction among catalysts prepared from clusters. It was hard to conclude the existence of metal particle. Because the surface of these catalysts was also similar to the surface of silica support, it was concluded that the metal species dispersed well on the support. To investigate the dispersion of metal, it was necessary to do elemental analysis (EDX method) on various position of the surface. For this purpose, the electron energy was increased to 25 kV and the beam was zoomed randomly to the surface of the catalysts. From the EDX measurements in all areas, i.e. either at what seemed to be metal particles or smooth areas, both Pd and Ni were detected with similar ratio. Figure 4.14 is an example of EDX analysis on smooth surface of the catalyst. An additional peak not marked in the figure was gold from sample preparation by coating. However, in Figure 4.15, the EDX was done on the crack of the surface and gold peak was not detected. The difference between Figure 4.14 and 4.15 indicate that the electron beam for EDX analysis was small and the EDX results were reliable. From EDX analysis, it was concluded that Pd-Ni/SiO_2 prepared by impregnation of cluster on silica support contain contained good metal dispersion.

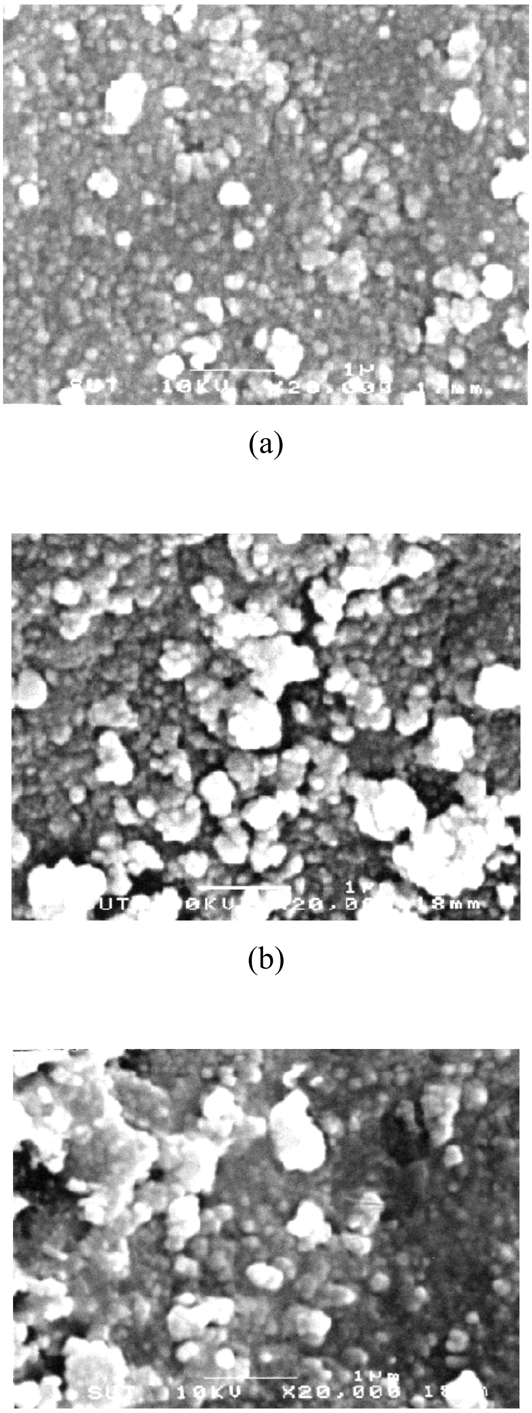


(a)

(b)

(c)

Figure 4.13 SEM images of 10.6991%Pd-Ni/SiO$_2$ catalysts prepared from metal salts and calcined at 400°C for (a) 1 hour (b) 2 hours (c) 3 hours



(a)

(b)

(c)

Figure 4.14 SEM images of Pd-Ni/SiO_2 catalysts prepared from cluster with various loading calcined at 400°C for 1 hour taken by 20kV with magnification of 20,000 (a) 2.3992% (b) 7.0291% (c) 10.6991%

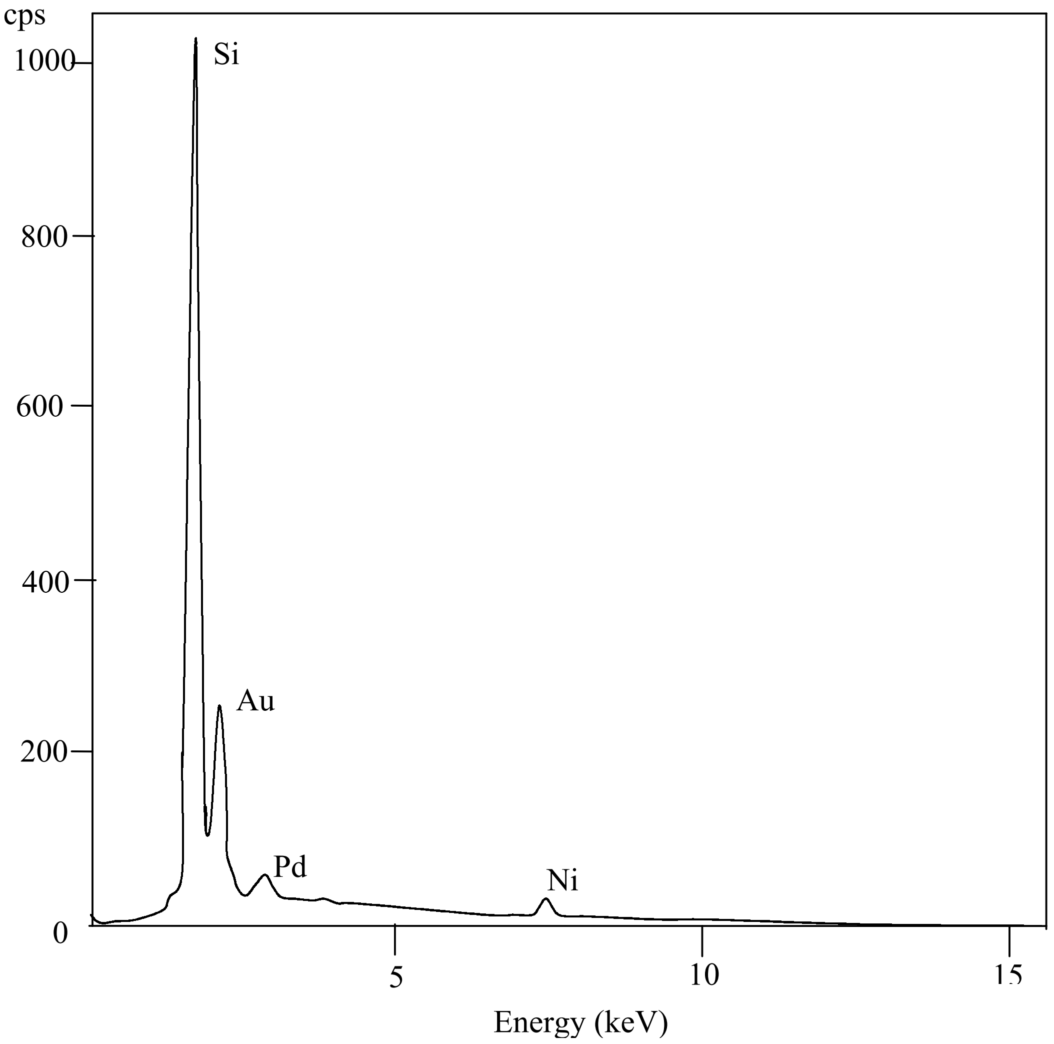


Figure 4.15 Elemental analysis by EDX method on Pd-Ni/SiO$_2$. The peaks of silicon, palladium, nickel were shown as marked. The additional peak is from gold coating

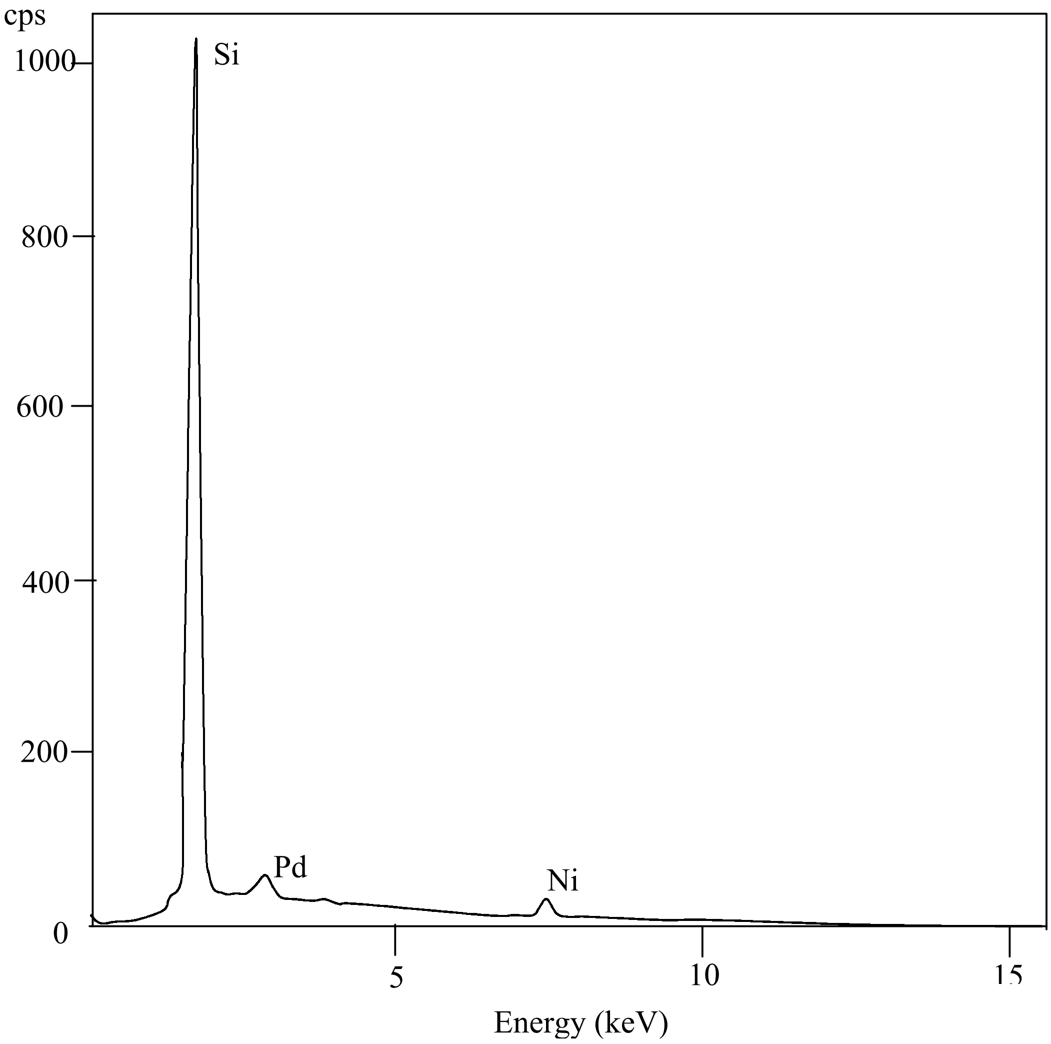


Figure 4.16 Elemental analysis by EDX method on Pd-Ni/SiO_2 at the crack of the surface. The peaks of silicon, palladium, nickel were shown as marked. The gold peak disappeared because the inside of the crack was not coated

4.7 Characterization of Pd-Ni/SiO_2 Catalyst by TPR

TPR experiment was done to study the reduction nature of Pd-Ni/SiO_2 catalysts prepared from cluster and metal salt. The studies of silica, Pd/SiO_2, and Ni/SiO_2 were also done as reference test. Before the TPR experiment, the catalysts was pretreated by heat at 110°C in an oven to remove moisture and stored in a dessicator. The TPR was investigated in a TGA equipped with 5% hydrogen in helium balance. The catalyst approximately 20 mg was charged on a sample pan and suspended in the TGA furnace. The sample was heated to 450°C under nitrogen (flow rate 20 ml/min) to remove moisture in the pores until constant weight was obtained. The sample was cooled down to room temperature and the purge gas was switched to 5% hydrogen in helium balance (flow rate 20 ml/min) and the temperature was raised to 500°C with the rate of 2°C/min. The weight change with time and temperature recorded. The weight loss was due to reduction. In order to see reduction temperature clearly as well as the amount of hydrogen consumed, the derivative of weight loss with time was plotted. After reduction was complete and the sample weight became constant, the temperature was cooled back down to room temperature.

The weight loss of silica with the reduction conditions was not significant. The TPR profile of silica is shown in Figure 4.17 and use as reference to compare with silica supported catalysts. The weight loss of silica support was observed around 70°C due to removal of moisture and impurities that adsorbed on the surface weakly (physical adsorption). There was no significant loss between 100-500°C because silica can not be reduced in this temperature range. If a reduction peak appears between 100 and 500°C, it must be from reduction of metal oxide.

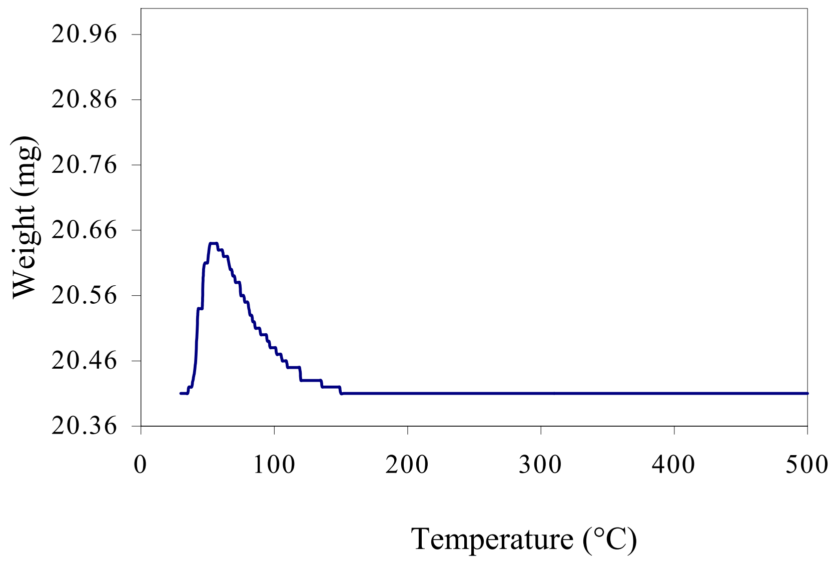


Figure 4.17 TPR of silica reduction in 5%H_2 + Helium balance Heating rate 2°C/min.

The Pd/SiO_2 Catalyst was tested for TPR in the temperature ranged from room temperature from 100°C to 500°C. The TPR profile is shown in Figure 4.18. At the beginning the weight increased slightly due to hydrogen and helium physical adsorption. Then the weight dropped quickly from room temperature to near 100°C. The weight loss for Pd/SiO_2 catalyst was relatively higher than that of silica support indicating that palladium oxide was reduced completely at this temperature range. The reduction of palladium oxide can be described by equation (1).

$$PdO + H_2 \longrightarrow Pd + H_2O \qquad \text{.........(1)}$$

From the derivative of weight loss present in Figure 4.19, there was only one peak began from room temperature and 50°C indicating that there was only one form of palladium oxide on silica support. Since the reduction produced water, some water could adsorb chemically (chemisorption) on resulting palladium metal and silica support. This chemisorbed water could be removed thermally and some weight loss was observed from this process.

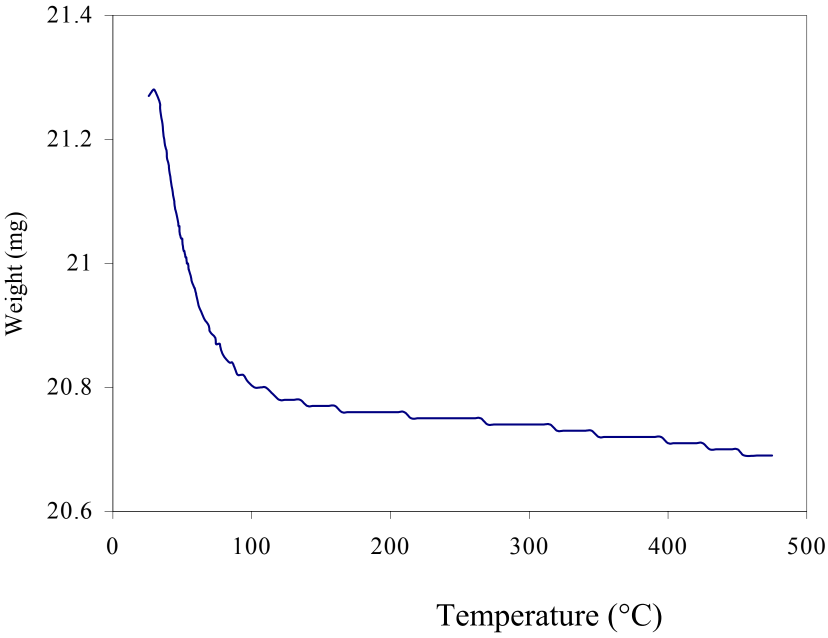


Figure 4.18 Weight loss during TPR of Pd/SiO_2 reduction in 5%H_2 + Helium balance Heating rate 2°C/min.

In general noble metals prefer to be in metallic from and, thus, their oxides can be reduced easily. A metal oxide which is reduced easily has low reduction potential (E°) and the temperature required for reduction is low. The trend of reduction temperature for noble metals is shown below:

$Au_2O < PtO < PdO < RhO, Ag_2O < CuO < NiO < CoO$. (Chou et al, 2001)

The reduction of a noble metal oxide can be retarded when it is mixed with an element which forms stable oxide. The example of this behavior was reported in Pd/La_2O_3/Al_2O_3 (Seoane et al, 1997).

The reduction temperature of metal oxides also depends on the nature of metal. Nanoparticles of palladium oxides have reduction temperature of only 8°C because the particle size is small and hydrogen can access and reduce the whole particle easily (Chou et al, 2001). As the particle size increased, the reduction temperature increases significantly. The reduction at the surface of metal oxides is relatively fast but after the outer surface is reduced, hydrogen has to penetrate into the bulk to complete reduction. An increase of metal oxide particle size results in broadening of derivative plot of weight loss. From this study, the reduction temperature of Pd/SiO_2 in Figure 4.19 was 50°C. The reduction peak was narrow indicating that the metal particles were uniform in size.

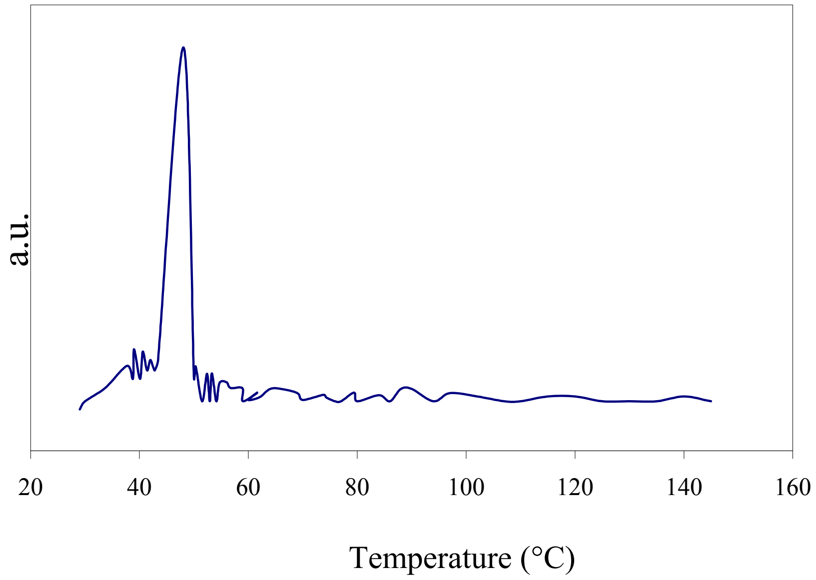


Figure 4.19 Derivative of weight loss from TPR of Pd/SiO_2 reduction in $5\%H_2$ in helium balance at the heating rate of 2°C/min.

The reduction temperature also depends strongly on the type of support. In supported catalyst, the metal-support interaction alters the nature of metal particles. For example, the reduction temperature of palladium on alumina was reported to be 144°C (Berry et al, 2000). It was possible that the metal-support interaction between palladium and silica is weaker than that between palladium and alumina. Lietz and coworkers studied the reduction of Pd/SiO_2 prepared from palladium nitrate by 5% hydrogen in argon. They suggested that palladium oxides were reduced at lower temperature than room temperature. Even though they did not mentioned about the metal loading, such character was characteristic of very low metal laoding well dispersed on the support. In addition, they observed negative peaks of hydrogen consumption. Such peaks were due to the decomposition of β-palladium hydride phase in the catalyst.

The TPR was also studied on Ni/SiO_2 with similar conditions in the same temperature range. The weight loss is shown in Figure 4.20. There were two steps of weight loss between room temperature and 100°C and between 350 and 420°C. The weight loss was more clearly seen by considering the derivative in Figure 4.21. There were 2 main peaks at 50°C and 400°C. Again, the first peak may be resulted from loss of weakly adsorbed impurity as well as partial reduction of nickel oxide. There could be at least two Forms of nickel oxides and they can be reduced completely after 400°C. The reduction temperature of nickel was reported to be 327°C (Chen, 1985) and it was harder to reduce compare to palladium. There are two forms of nickel oxide: NiO and Ni_2O_3. Because the oxidation states of Nickel in NiO and Ni_2O_2 are +2 and +3, respectively, the first reduction must be on Ni_2O_3 and the second reduction is NiO. The reduction of nickel oxide can be written as in equations 2 and 3.

$$Ni_2O_3 + H_2 \xrightarrow{\qquad} NiO + H_2O \qquad \text{.....(2)}$$

$$NiO + H_2 \xrightarrow{\qquad} Ni + H_2O \qquad \text{.....(3)}$$

The reduction temperature of nickel and other metal oxides depend strongly on many factors such as precursor, preparation method, and reduction conditions. $2\%Ni/SiO_2$ prepared by impregnation of nickel nitrate on silica gel showed reduction peak by hydrogen in argon at 307°C and the reduction shifted to lower temperature when nickel was co-impregnated with ruthenium (Crisafulli et al, 2002). Bhering et al (2002) studied Ni/SiO_2 by precipitation method at precipitation and aging temperature of 90°C. When the catalysts cooled down quickly, two reduction peaks were observed at 350 and 377°C along with a very broad and small peak at 500°C. If the precipitated Ni/SiO_2 was aged for 20 minutes, the reduction peak was broad and shifted to higher temperature beginning at 427 and completed 750°C with the peak around 600°C.

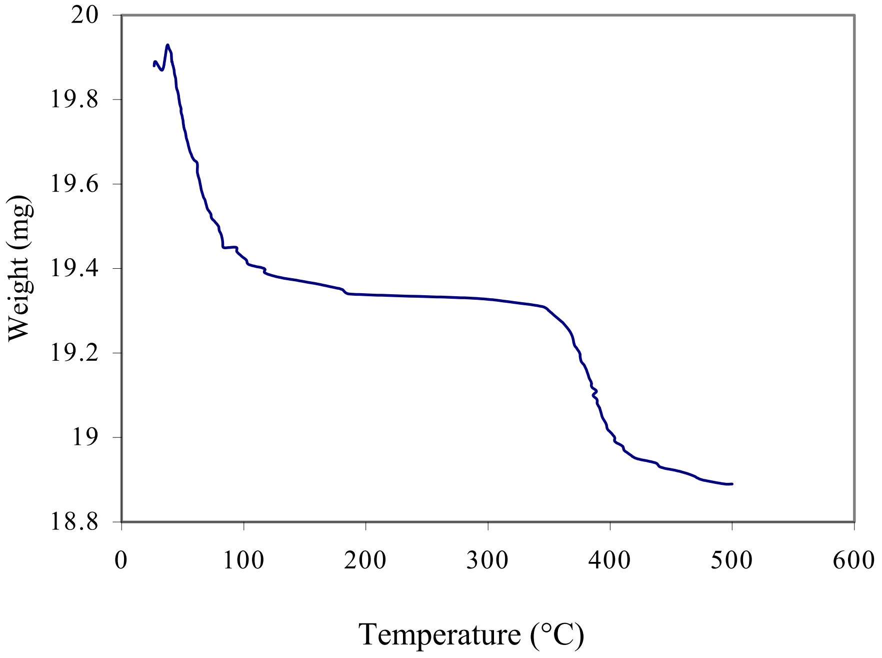


Figure 4.20 Weight loss of Ni/SiO$_2$ during the reduction with 5%H$_2$ in helium balance with heating rate of 2°C/min

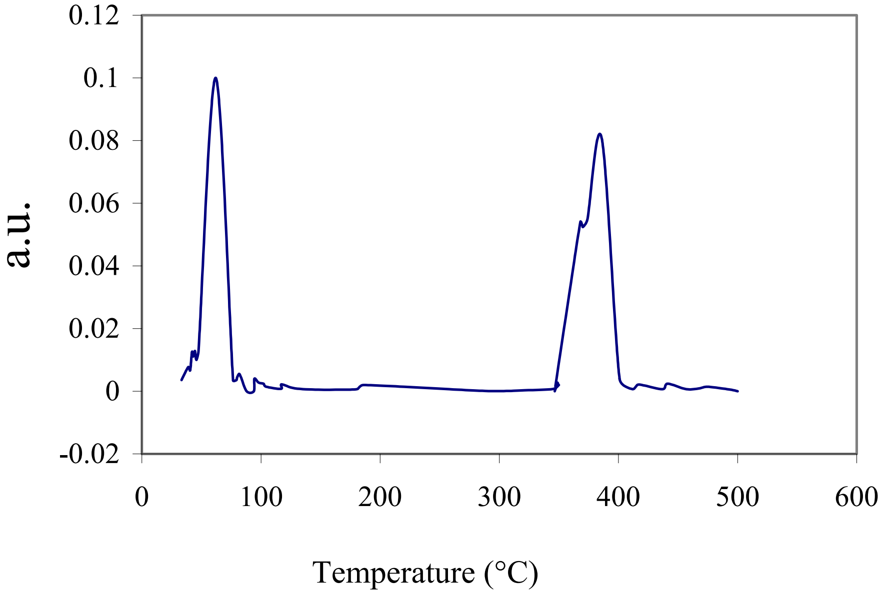


Figure 4.21 Derivative of weight loss during TPR of Ni/SiO$_2$ reduction in 5%H$_2$ in helium balance with heating rate of 2°C/min

The most important TPR experiments for this study were those of PdNi/SiO$_2$ catalysts prepared from cluster and from a mixture of metal salt. All conditions used were similar to those of the reference materials. The weight loss of PdNi catalysts from both precursors were recorded and shown in Figure 4.22 and 4.23. However, the derivative of weight loss of PdNi catalysts did not show clear peaks as those of the monometallic catalysts. Thus, only the plots of weight loss were displayed here.

The weight loss of PdNi/SiO$_2$ prepared from cluster during TPR by 5%H$_2$ in helium is displayed in Figure 4.22. At the beginning there was a reduction of palladium oxide and the weight was dropped continuously and became almost constant between 100 and 240°C. Then the weight dropped again at 240 and became constant again at 300°C. The weight change in this range was from the reduction of nickel oxide to nickel. However, the reduction temperature was lower than that of supported nickel oxide. It was possible that PdNi/SiO$_2$ catalysts contain nickel oxide that partially attached to palladium oxide. Because palladium oxide was reduced at lower temperature and became adsorption sites for hydrogen. With continuous flow of hydrogen over the catalysts, the adsorption sites on palladium became fully occupied by surface hydrogen. Then hydrogen spillover to reduce neighboring nickel oxide to nickel. When this happened, the reduction temperature of nickel was lower than the monometallic nickel catalyst. Since the reduction of nickel oxide was lower than that of monometallic oxide, it was concluded that the majority of nickel stayed intact with palladium. Thus, the preparation of PdNi//SiO$_2$ catalyst from a mix-metal PdNi cluster was an effective method to keep both metal intact.

When two metal oxides were mixed, the more noble metal could assist the reduction of the other metal. For example, Rh/SiO$_2$ was reduced in the temperature range of 25-175°C while the reduction of Fe/SiO$_2$ started at 225°C and had two peaks at 300 and 350°C. Because there are many forms of iron oxides and many forms are very stable, the reduction of iron oxide was not complete even after 500°C. When both metal oxides were mixed, the reduction temperature of iron oxide was lower with an assistance of hydrogen spillover from rhodium (Niemantsverdriet, 2000). Moreover, if FeRh/SiO$_2$ catalyst was reduced after it was re-oxidized, the reduction became easier and more complete because both metals were mixed better after oxidation.

The reduction assistance of palladium to other metal was also reported on PdAg nanoparticles in which the reduction temperature of Ag was lower than monometallic particles (Chou et al, 2001). Similar behavior was also expected on supported bimetallic catalysts. For example, iron oxides in Fe-Pd/Al_2O_3 were reduced easier when they were mixed with palladium (Berry et al, 2000). Feeley and Sachtler reported that palladium and nickel formed PdNi alloy in the cages of zeolite NaY enhanced each other reproducibility.

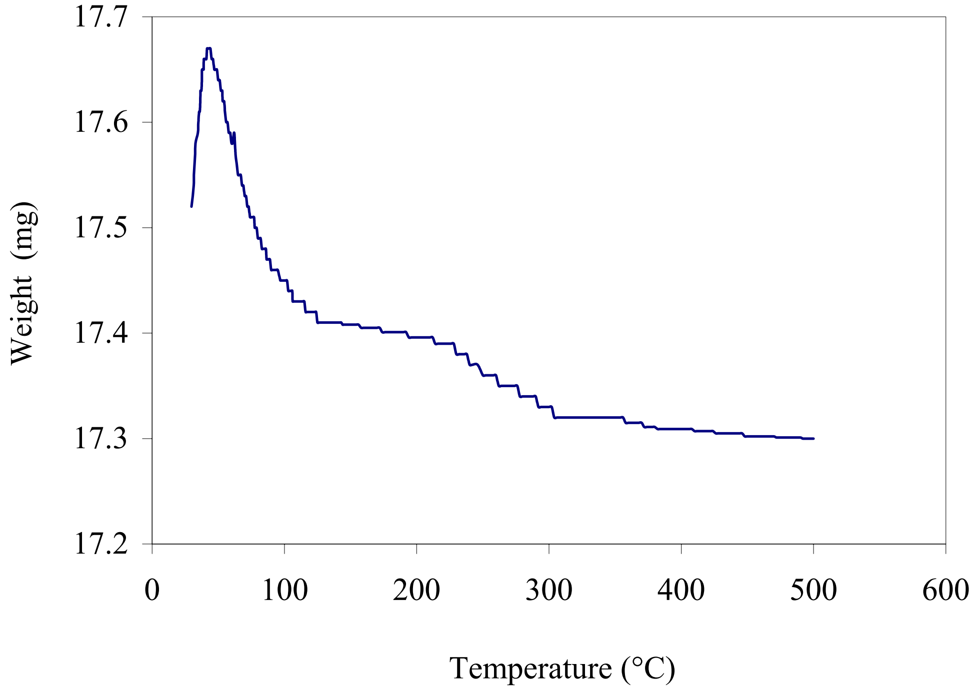


Figure 4.22 Derivative of weight loss during TPR of PdNi/SiO_2 prepared from cluster by 5%H_2 in helium balance with heating rate of 2°C/min

The TPR profile of PdNi/SiO_2 catalyst prepared from metal salts in Figure 4.23 was almost similar to that of the catalyst from cluster. The weight loss at the beginning represented the reduction of palladium oxide which was completed near 150°C. The weight was then dropped continuously and became almost constant at

400°C without a dramatic dropped as seen in Ni/SiO_2 or PdNi/SiO_2 catalysts. This result indicated that the form and distribution of nickel oxide in PdNi/SiO_2 catalyst prepared from metal salts is random. There were isolated nickel particles on silica support corresponding to the reduction near 400°C. Some nickel oxides that attached to palladium particles had reduction temperature lower than 400°C.

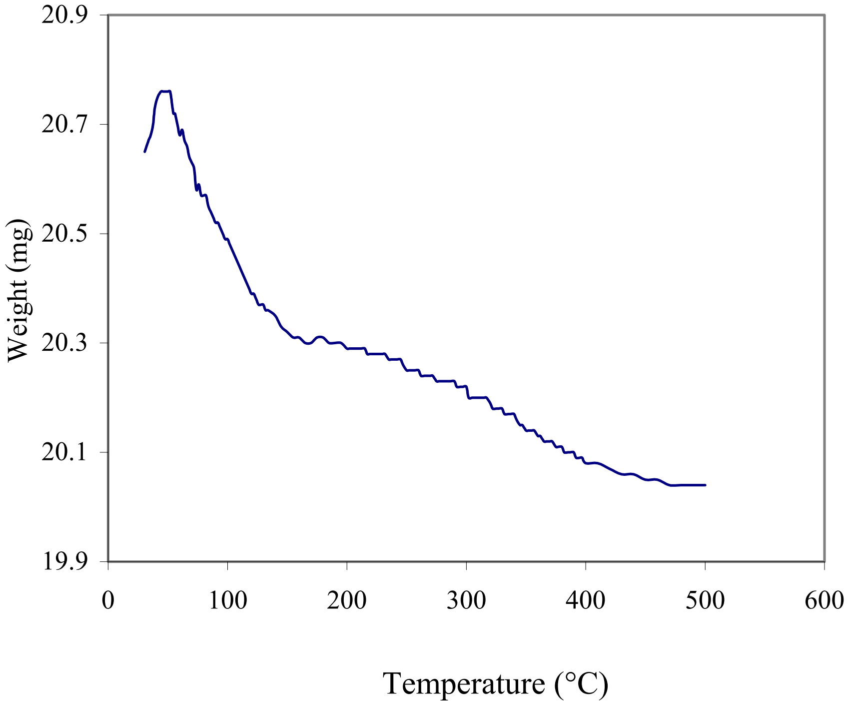


Figure 4.23 Weight loss during TPR of PdNi/SiO_2 prepared from salt by 5%H_2 in helium balance with heating rate of 2°C/min

The shift in reduction temperature of nickel oxide in the presence of palladium could also cause by the change in core-level binding energy. Harikumar, Ghost, and Rao (2002) studied binding energy of bimetallic clusters by X-ray photoelectron spectroscopy and reported the shift in binding energy of core electrons of both palladium and nickel. The shift was also depending on the cluster size.

In conclusion, alloy particles of palladium and nickel were formed and palladium enhanced the reduction of nickel oxides.

4.8 Catalyst Characterization by Hydrogen Adsorption and BET

The active sites of the catalysts were then determined by hydrogen adsorption. The amount of hydrogen adsorbed is related directly to the number of active sites on the catalyst. The ratio between hydrogen and metal atom can imply the metal dispersion. Catalysts with good metal dispersion have small metal particles on the support, have higher surface area, and can accommodate more hydrogen.

To determine the amount of hydrogen adsorbed, a known amount of Pd-Ni/SiO_2 catalyst was place in a U-tube reactor connected to a thermal conductivity detector (TCD) and gases. Catalyst was heated from room temperature to 450°C at a 5°C/min rate under hydrogen atmosphere and held for one hour in order to complete catalyst reduction. Then the temperature was lowered to 400°C, held for 30 minutes and cooled down to room temperature and hydrogen injection was tested on the TCD. The catalysts was then cooled down to room temperature in nitrogen.

For this part the amount of Pd and Ni was determined by ICP technique and the results are shown in Table 1.1. The catalysts prepared from cluster were labeled CC1, CC2, and CC3, which had total loading of 1.468, 1.858, and 1.594, respectively. According to their weight percent of Pd and Ni, the mole ratio of Pd/Ni were 0.31, 0.39, 0.37 which were not 1 as expected from the cluster precursor, $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$. The possible explanation for this ratio might be from crystallographic disorder in which palladium atomic positions were substituted by nickel. As reported by Tran et al (2000), the Pd/Ni ratios of occupancy at some positions were 0.23/0.77, 0.22/0.78 and 0/1.00.

The catalysts prepared from salts were labeled SC1, SC2, and SC3 for loading of 1.634, 5.114, and 8.364% respectively. The only catalyst with comparable loading to catalysts from cluster was SC1. From hydrogen adsorption experiment, SC1 had higher hydrogen adsorption and higher H/Pd ratio than CC1, CC2, and CC3. Because Pd is known to adsorb hydrogen better than Ni, it was possible that Pd and Ni in catalysts prepared from cluster were still intact resulting in lower hydrogen adsorption of Pd. When compare the SC series, the ratio H/Pd of SC3 was lower than others due to higher loading in which larger metal particle (i. e., lower surface area) was expected. Surface areas of all catalysts were in the same range.

Table 4.2 Metal loading on PdNi/SiO_2 catalysts prepared from cluster and metal salts determined by ICP technique, results from hydrogen adsorption experiment, and BET surface area (CC = catalyst prepared from cluster, SC = catalyst prepared from salt)

Cat.	Total	Pd	Ni	H atom/g cat	H/Pd	H/M	BET surface area (m^2/g)
CC1	1.468	0.685	0.782	1.20665E-06	0.0187	0.0061	282.02
CC2	1.858	0.928	0.931	2.8640E-06	0.0328	0.0117	277.50
CC3	1.594	0.781	0.813	0.0000E+00	0.0000	0.0000	275.31
SC1	1.634	0.523	1.111	3.0559E-06	0.0621	0.0128	277.12
SC2	5.113	1.857	3.256	1.1267E-05	0.0645	0.0154	277.45
SC3	8.364	4.590	3.774	1.9870E-05	0.0461	0.0185	262.19

The surface area of PdNi/SiO_2 catalysts were determined by BET method using nitrogen adsorption at liquid nitrogen temperature. The results were also shown in Table 4.1. It was found that in catalyst CC1, CC2, CC3, and SC1 there was not much difference in BET surface area with metal loading. However, if the loading increased, the metal particles were larger and could clog the pores of the support and lower the surface area.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions were made from this study.

1. Cluster $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ was synthesized successfully under nitrogen atmosphere and characterized by FTIR which was enough to confirm CO ligands in the cluster.
2. After impregnation the solution of cluster $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ on silica, the carbonyl ligands were removed easily be heating at 50°C for a few minutes. However, further heat to 400°Cwas required to remove $[PPh_4]^+$ cation whose phosphorus could cause catalyst poisoning.
3. The metal particle size of bimetallic PdNi/SiO_2 catalysts increased with calcination temperature as confirmed by XRD. The size of metal particles also increased with loading. For the same loading, the bimetallic catalysts prepared from cluster had better metal dispersion.
4. The particle sizes of metal particles in the bimetallic catalysts were small and could not be seen by SEM with magnification of 20,000. Both palladium and nickel were detected together in all surface position by EDX analysis indicating the closeness of both metals.
5. From TPR study, PdNi catalysts prepared from cluster had lower reduction temperature compared to catalyst prepared from mixed salt. The catalysts from cluster precursor revealed that palladium and nickel were still intact and the reduction temperature of nickel was reduced by hydrogen spillover from palladium.
6. Judging from TPR results, the alloy formation of catalysts prepared from cluster was more uniform than those prepared from salt which were more random.
7. The adsorption capacity of bimetallic PdNi catalysts prepared from cluster was lower than that of catalysts prepared from salt because the metal intacity.

8. By impregnation of cluster solution on silica support, the surface area did not chance much due to good metal distribution.

5.2 Recommendations

If other researchers are interested to further this research, the following suggestions should be considered.

1. The catalysts prepared from cluster and salt should be tested for chemical reactions such as hydrogenation of unsaturated hydrocarbon. The activity and selectivity from both catalysts should be compared.
2. This study only used impregnation technique for catalyst preparation. It might be worthwhile to investigate the preparation by other methods such as adsorption, or sol-gel method.

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APPENDIX

APPENDIX A

Abstract of an Oral Presentation at
PACCON2002
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30-AMSC-08

PREPARATION AND CHARACTERIZATION OF BIMETALLIC Pd-Ni/SiO$_2$ CATALYSTS FROM AN ORGANOMETALLIC CLUSTER PRECURSOR

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Bimetallic catalysts prepared from bimetallic cluster precursors have several advantages. They provide the formation of bimetallic particles of desired metal composition under mild activation conditions. Combination of metals in the precursor clusters with different oxophilicities may lead to strong anchoring on support and prevent sintering [1]. In this study, bimetallic Pd-Ni/SiO2 catalysts were prepared by impregnation of an acetonitrile solution of [PPh4]4[Pd13Ni13(CO)34] cluster (**1**) on silica and a solution of mixed palladium and nickel salts. FTIR spectrum of carbonyl ligands of the cluster impregnated on silica showed the decrease of terminal carbonyl compared to the spectrum of the cluster in acetonitrile [2]. This may indicated that cluster lost terminal carbonyl upon anchoring to silica support by oxidative displacement. Upon catalyst activation, the cluster cations, [PPh4]$^+$, and carbonyl ligands on the cluster **1** can be effectively removed thermally. Catalysts from both precursors were studied by temperature-programmed reduction (TPR) which can distinguish the interaction between Pd and Ni from different precursors. The Ni reduction temperature of catalysts prepared from cluster **1** was significantly lowered than that of the Ni/SiO2 reference indicating that Pd and Ni were still intact. On the other hand, the Ni reduction temperature of the catalysts prepared from mixed-metal salt was not different from that of Ni/SiO2 reference material indicating the preference of metal aggregation to its own kind. In addition, the catalysts from both precursors were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET surface area analysis. Results showed that bimetallic catalysts from cluster precursor have slightly better metal dispersion on the silica support.

APPENDIX B

Extended Abstract of Poster Presented in the 3nd National Symposium on Graduate Research

การเตรียมและการวิเคราะห์ลักษณะของตัวเร่งปฏิกิริยา Pd-Ni/SiO2 จากคลัสเตอร์ของโลหะ

PREPARATION AND CHARACTERIZATION OF Pd-Ni/SiO_2 FROM METAL CLUSTER

Research/Presenter Jarunan Wongwiwattana*, Jatuporn Wittayakun*, Tohru Mori**, and Yutaka Morikawa**
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Introduction (Background Rationale Objectives and Scope of Research work)

Metal clusters are complexes containing at least three metal-metal bonds that form triangular or larger metal-core structure [1]. They may be considered as intermediates between molecular compounds and solid-state materials. Large clusters such as $[Rh_{13}(CO)_{24}H_3]^{2-}$ and $[Os_{20}(CO)_{40}]^{2-}$ have metal-core geometries that resemble close-packed metal atoms in small naked metal crystallites [2]. The metal-core atoms of each of these large metal carbonyl clusters can be thought of as a metal aggregate that is stabilized by CO ligands on its metal surface. Such clusters can be used as precursors for preparing heterogeneous catalysts [3].

Recently, $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ (1) was successfully separated in high yield (> 90%) from reduction of $Pd(OAc)_2$ by $[NMe_4]_2[Ni_6(CO)_{12}]$ in DMF [4]. The cluster metal core consists of 26 metal polyhedron with close-packed arrangement. Since the preparation procedure was simple, cluster 1 is selected a precursor for Pd-Ni/SiO_2 catalyst preparation. An acetonitrile solution of cluster 1 was used to impregnate silica support. After drying under nitrogen, heated to remove CO ligands, and calcined to removed $[PPh_4]^+$, the PdNi/SiO_2 catalysts were characterized by powder X-ray diffraction, scanning electron microscopy, BET surface area analysis, and temperature-programmed reduction. The metal loading on each catalyst was determined by ICP and the active site was calculated from hydrogen adsorption experiment. All results will be compared with catalysts prepared from mixtures of palladium and nickel salt solution.

Methodology / Equipment and Experiment

The amount of acetonitrile required to wet the silica support (incipient wetness) was determined prior to the impregnation. An acetonitrile solution of **1** was dropped slowly onto oven-dried silica under nitrogen atmosphere. The samples were then dried under dry nitrogen flow at room temperature, heated at 80°C for 10 minutes to remove carbonyl ligands, and then calcined at 400ºC for 3 hours to remove $[PPh4]^+$. The metal loading in each catalyst was confirmed by ICP while the surface area was measured by BET analysis. The number of active sites was determined by hydrogen adsorption experiments. Metallic phase and morphology were evaluated by XRD and SEM, respectively. In addition, metal reduction temperature was studied by temperature-programmed reduction (TPR).

For hydrogen adsorption experiment, a known amount of Pd-Ni/SiO_2 catalyst was place in a U-tube reactor connected to a thermal conductivity detector (TCD) and gases. Catalyst was heated from room temperature to 450°C at a 5°C/min rate under hydrogen atmosphere and held for one hour in order to complete catalyst reduction. Then the temperature was lowered to 400°C, held for 30 minutes and cooled down to room temperature and hydrogen injection was tested on the thermal conductivity detector (TCD). The catalysts was then cooled down to room temperature in nitrogen.

TPR studied was done in a thermogravimetric analyzer (TGA). Each catalyst sample was loaded into a sample pan, heated under nitrogen flow at 110ºC to remove moisture and air in the pores, and cooled down to room temperature. Then flow gas was then switched to hydrogen as the temperature was raised to 900ºC at the rate 10ºC/min and held for 30 minutes. Each sample weight loss as well as its derivative from reduction was recorded.

Research Findings

An amount of Pd and Ni was determined by ICP technique and the results are shown in Table 1. The catalysts prepared from cluster were labeled CC1, CC2, and CC3 with total loading of 1.468, 1.858, and 1.594, respectively. According to their weight percent of Pd and Ni, the mole ratio of Pd/Ni were 0.31, 0.39, 0.37 which were not 1 as expected from the cluster precursor, $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$. The possible explanation for this ratio might be from crystallographic disorder in which palladium atomic positions were substituted by nickel. As reported by Tran [4], the Pd/Ni ratios of occupancy at some positions were 0.23/0.77, 0.22/0.78 and 0/1.00.

The catalysts prepared from salts were labeled SC1, SC2, and SC3 for loading of 1.634, 5.114, and 8.364% respectively. The only catalyst with comparable loading to catalysts from cluster was SC1. From hydrogen adsorption experiment, SC1 had higher hydrogen adsorption and higher H/Pd ratio than CC1, CC2, and CC3. Because Pd is known to adsorb hydrogen better than Ni, it is possible that Pd and Ni in catalysts prepared from cluster were still intact resulting in lower hydrogen adsorption of Pd. When compare the SC series, the ratio H/Pd of SC3 was lower than others due to higher loading in which larger metal particle (i. e., lower surface area) was expected. Surface areas of all catalysts were in the same range.

Table 1 Metal loading on PdNi/SiO_2 catalysts prepared from cluster and metal salts determined by ICP technique, results from hydrogen adsorption experiment, and BET surface area (CC = catalyst prepared from cluster, SC = catalyst prepared from salt)

Cat.	Total	Pd	Ni	H atom/g cat	H/Pd	H/M	BET surface area (m^2/g)
CC1	1.468	0.685	0.782	1.20665E-06	0.0187	0.0061	282.02
CC2	1.858	0.928	0.931	2.8640E-06	0.0328	0.0117	277.50
CC3	1.594	0.781	0.813	0.0000E+00	0.0000	0.0000	275.31
SC1	1.634	0.523	1.111	3.0559E-06	0.0621	0.0128	277.12
SC2	5.113	1.857	3.256	1.1267E-05	0.0645	0.0154	277.45
SC3	8.364	4.590	3.774	1.9870E-05	0.0461	0.0185	262.19

From XRD spectrum of catalysts prepared from the cluster and salt mixture, there was a slight shift of peaks in Figure 2a compared to Figure 2b which might cause by alloy formation. From the shape of the peaks, the metal particle size increased in the order CC3 > CC2 > CC1. Thus, it agreed well with hydrogen adsorption experiment of CC3 which was unable to detect. Similarly, metal particle size of catalysts prepared from salts were in the order SC3 > SC2 > SC1. Even though the total hydrogen adsorption increased with loading, the H/Pd ratio was smallest for SC3.

Morphology of all catalysts was studied by scanning electron microscopy and the surface images taken with 20,000 magnification. There was no distinction among catalysts prepared from clusters. It was hard to conclude the existence of metal particle. When an electron beam was directed at random areas for EDX measurements, at what seemed to be metal particles or smooth areas, both Pd and Ni were detected in all areas. Thus, the only conclusion to be made is that those catalysts contain good metal dispersion. Similar EDX results were obtained from catalysts from salt mixtures despite the more messy appearance of the surface.

Temperature-programmed reduction of PdNi/SiO_2 was investigated on a TGA compared to Pd/SiO_2 and Ni/SiO_2. The peak of weight loss was obtained from derivative TG curve. The weight loss of Pd/SiO_2 was between 30-80°C which could be contributed from loss of surface water as well as reduction. The weight loss over Ni/SiO2 took place at two temperature ranges: 30-80 and 275-350°C. The loss during first range caused by elimination of surface water while that during the second range was caused by reduction. This result agreed with the fact that palladium oxide is reduced easier than nickel oxide.

The weight loss of PdNi/SiO_2 took place at the 30-160°C range with two peaks which were between that of Pd/SiO_2 and Ni/SiO_2. This result indicated that Pd and Ni in PdNi/SiO_2 were still intact. Hydrogen first dissociatively adsorbed on palladium oxide and reduced it to palladium metal which was active site for further hydrogen adsorption. Hydrogen on palladium then migrated to reduce nickel oxide next to palladium on the same particle. Thus, the reduction temperature of nickel was decreased.

Discussion and Recommendations

High-nuclearity $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ was synthesized successfully and used as a precursor for PdNi/SiO2 catalysts preparation by impregnation. Removal of carbonyl ligands was completed by heating at 80°C for 10 minutes while removal of $[PPh_4]^+$ was done by heating at 400°C. The catalysts prepared from cluster had lower hydrogen adsorption than those prepared from metal salts. In addition, The catalysts prepared from cluster showed high metal dispersion and evidence of Pd-Ni alloy formation from XRD peak shifts and lower Ni reduction temperature.

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Key Words bimetallic PdNi catalyst, PdNi/SiO_2, Catalyst from cluster, cluster catalyst

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APPENDIX C

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Characterization of Pd-Ni/SiO$_2$ Catalysts Prepared from Organometallic Cluster Precursor

Paper # 485

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ABSTRACT

The Pd-Ni/SiO$_2$ catalysts were prepared by impregnation of two precursors on silica: an acetonitrile solution of $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ (1) and a mixture of palladium and nickel salts. Both catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area analysis, and temperature-programmed reduction (TPR). In addition, the metal loading was determined by ICP and the number of active sites was measured by hydrogen adsorption experiment. The cluster's carbonyl ligands were removed by heating at the 80°C for 10 minutes while the counter cations, $[PPh_4]^+$ on were removed by heating at 400°C. XRD peaks of Pd-Ni/SiO$_2$ prepared from the cluster was shifted slightly possibly due to Pd-Ni alloy formation. It was found from TPR experiment that the Ni reduction temperature of Pd-Ni/SiO$_2$ catalysts from cluster was significantly lowered than that of the Ni/SiO$_2$ reference indicating that Pd and Ni are still intact. However, Pd-Ni/SiO$_2$ prepared from salts solution adsorbed hydrogen better than that from cluster

INTRODUCTION

Metal clusters are complexes containing at least three metal-metal bonds that form triangular or larger metal-core structure.[1] They may be considered as intermediates between molecular compounds and solid-state materials. Large clusters like $[Rh_{13}(CO)_{24}H_3]^{2-}$ and $[Os_{20}(CO)_{40}]^{2-}$ have metal-core geometries that resemble close-packed metal atoms in small naked metal crystallites.[2] The metal-core atoms of each of these large metal carbonyl clusters can be thought of as a metal aggregate that is stabilized by CO ligands on its metal surface. Such clusters can be used as precursors for preparing heterogeneous catalysts.[3]

In general, heterogeneous catalysts are usually obtained by using inorganic metal salts adsorbed on supporting materials by techniques such as impregnation, followed by calcination which is an oxidation at high temperatures. The resulting metal oxide crystals are then reduced into metal particles by reductants such as hydrogen. However, catalysts prepared by this general method do not provide good control of particle size distribution and metal composition.[4] Metal clusters have been used instead of metal salts to impregnate a support in order to prepare heterogeneous catalysts and such clusters possess attractive features such as solubility in organic solvents. Milder conditions can be used to activate the catalysts prepared from metal clusters because metal atoms in the clusters are in low oxidation states and can be reduced more easily than conventional metal salt precursors. Clusters of Pt, Rh, Ir, Ru can be synthesized in the cavity of zeolites by a procedure called "ship-in-bottle" which includes carbonylation of ion-exchanged metals in zeolites. After decarbonylation, removal of carbonyl ligands, the metal atoms are still intact and are active catalysts.[5]

One method to modify the activity and selectivity of supported metal catalysts is to form alloy with another element. There are several reports that bimetallic catalysts show better catalytic performance than monometallic catalysts of the same metals. Bimetallic catalysts can be prepared by several methods such as coimpregnation, ion-exchange, or of two metal salts on inorganic support.[6]

Our interest is on supported bimetallic Pd-Ni catalysts. Both Pd and Ni are active for several catalytic reactions but there are only a few examples of bimetallic Pd-Ni catalysts. Bimetallic $PdNi_x$/zeolite NaY was prepared by simultaneous exchange of the two metal ions and washed with either dilute nitric acid (pH = 6) to give loading 10.3Pd + 8.6Ni or with dilute sodium hydroxide (pH = 10.5) to give loading 10.0Pd + 9.2Ni. The evidence from TPR and TPD indicated that Pd and Ni in the same zeolite formed bi-metallic particles and enhanced each other's reducibility in which both Ni and Pd reduction temperature decreased.[7] The bimetallic alloy catalysts were reported to have significantly higher selectivity for methane formation from CO hydrogenation.[8] Polymer-supported PVP-$PdCl_2$-$4NiCl_2$-PPh_3 bimetallic catalyst [PVP=poly(*N*-vinyl-2-pyrrolidone)] was an efficient catalyst for the hydroesterification of styrene.[9] The high activity and selectivity of the catalyst are achieved by the synergic effect of Pd-Ni bimetallic system and the effect of polymer protection.[10] However, it is difficult to keep two metals intact. To solve this problem, bimetallic cluster precursor should be considered.

Recently, $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ (1) was successfully separated in high yield (> 90%) from reduction of $Pd(OAc)_2$ by $[NMe_4]_2[Ni_6(CO)_{12}]$ in DMF.[11] The cluster metal core consists of 26 metal polyhedron with close-packed arrangement. Since the preparation procedure was simple, cluster 1 is selected a precursor for Pd-Ni/SiO_2 catalyst preparation. An acetonitrile solution of cluster 1 was used to impregnate silica support. After drying under nitrogen, heated to remove CO ligands, and calcined to removed $[PPh_4]^+$, the PdNi/SiO_2 catalysts were characterized by powder X-ray diffraction, scanning electron microscopy, BET surface area analysis, and temperature-programmed reduction. The metal loading on each catalyst was determined by ICP and the active site was calculated from hydrogen adsorption experiment. All results will be compared with catalysts prepared from mixtures of palladium and nickel salt solution.

EXPERIMENTAL PROCEDURES

A. Synthesis of $[PPh_4]_4[Ni_{13}Pd_{13}(CO)_{34}]$ (1)

1 was used as a catalyst precursor. It was prepared and separated in high yields under nitrogen atmosphere by small modifications of the procedure, described by Tran et al in reference 11. A solution of $Pd(OAc)_2$ in DMF was added dropwise via a stainless steel canula into a stirred DMF solution of $[NMe_4]_2[Ni_6(CO)_{12}]$ over approximately 20 minutes. The color of the solution quickly changed from cherry red to dark brown. After this solution was stirred at room temperature for six hours, a solution of PPh4Br in methanol was added quickly. The mixture was cooled in an ice bath, after which the slow addition of deoxygenated water gave rise to a dark brown precipitate. This precipitate was separated by filtration, washed several times with methanol, and the remaining solid was extracted with of acetonitrile. The IR absorption bands of the

acetonitrile solution was at 2024(s), 2000(sh), 1883(s), and 1860(s) cm^{-1} in accordance with those reported by Tran for **1**.

B. Preparation of Pd-Ni/SiO$_2$ by Impregnation of 1 on Silica

The amount of acetonitrile required to wet the silica support (incipient wetness) was determined prior to the impregnation. An acetonitrile solution of **1** was dropped slowly onto oven-dried silica under nitrogen atmosphere. The samples were then dried under dry nitrogen flow at room temperature, heated at 80°C for 10 minutes to remove carbonyl ligands, and then calcined at 400ºC for 3 hours to remove [PPh$_4$]$^+$. The metal loading in each catalyst was confirmed by ICP while the surface area was measured by BET analysis. The number of active sites was determined by hydrogen adsorption experiments. The metallic phase and morphology were evaluated by XRD and SEM, respectively. In addition, metal reduction temperature was studied by temperature-programmed reduction (TPR).

C. Preparation of Pd-Ni/SiO$_2$, Pd/SiO$_2$, and Ni/SiO$_2$ from Metal Salts

Pd-Ni/SiO$_2$ catalysts were also prepared by impregnation of a mixture of Pd (OAc)$_2$ and Ni(OAc)$_2$ on silica with the Pd:Ni mole ratio of 1:1 and loading similar to those of catalysts from cluster precursors. The metal solution was slowly dropped onto oven-dried silica, dried at 110ºC and calcined at 400ºC for 3 hours.

Pd/SiO$_2$ and Ni/SiO2 reference catalysts were prepared by impregnation of Pd (OAc)$_2$ and Ni(OAc)$_2$ solution to silica, respectively. The preparation procedure was similar to that of Pd-Ni/SiO$_2$ catalysts from mixed metal salt.

D. Hydrogen Adsorption Experiment

A known amount of Pd-Ni/SiO$_2$ catalyst was place in a U-tube reactor connected to a thermal conductivity detector (TCD) and gases. Catalyst was heated from room temperature to 450°C at a 5°C/min rate under hydrogen atmosphere and held for one hour in order to complete catalyst reduction. Then the temperature was lowered to 400°C, held for 30 minutes and cooled down to room temperature and hydrogen injection was tested on the thermal conductivity detector (TCD). The catalysts was then cooled down to room temperature in nitrogen.

E. Temperature-Programmed Reduction (TPR)

TPR studied was done in a thermogravimetric analyzer (TGA). Each catalyst sample was loaded into a sample pan, heated under nitrogen flow at 110ºC to remove moisture and air in the pores, and cooled down to room temperature. Then flow gas was then switched to hydrogen as the temperature was raised to 900ºC at the rate 10º C/min and held for 30 minutes. Each sample weight loss as well as its derivative from reduction was recorded.

Cluster **1** was prepared and separated in high yields by small modifications of the procedure described by Tran and coworkers[11] under nitrogen atmosphere. The procedures involved reduction of Pd(OAc)$_2$ with [NMe$_4$]$_2$[Ni$_6$(CO)$_{12}$] in DMF followed by addition of PPh$_4$Br, precipitation the cluster product with water, filtered, washed with methanol and dried in nitrogen flow. The dark-brown solid product gave IR absorption bands at 2024(s), 2000(sh), 1883(s), and 1860(s) cm^{-1} in accordance with those reported by Tran.

F. Preparation of Pd-Ni/SiO$_2$ by Impregnation of 1 on Silica

The amount of solvent required to wet the silica support (incipient wetness) was determined prior to the impregnation. An acetonitrile solution of **1** was dropped slowly onto oven-dried silica under nitrogen atmosphere. The samples were then dried under nitrogen flow at room temperature and calcined at 400ºC for 1, 2, and 3 hours to remove carbonyl ligands and $[PPh_4]^+$ cation. The metal phase, morphology, and surface area of all catalysts were evaluated by XRD, SEM, and BET, respectively. Metal loading was confirmed by X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS).

G. Preparation of Pd-Ni/SiO_2, Pd/SiO_2, and Ni/SiO_2 from Metal Salts

Pd-Ni/SiO_2 catalysts were prepared by impregnation from a mixed solution of $Pd(OAc)_2$ and $Ni(OAc)_2$ with the Pd:Ni mole ratio of 1:1 and loading similar to those of catalysts from cluster precursors. The metal solution was slowly dropped onto oven-dried silica, dried at 110ºC and calcined at 500ºC for 3 hours.

Pd/SiO_2, and Ni/SiO_2 were prepared from $Pd(OAc)_2$ and $Ni(OAc)_2$, respectively. The preparation procedure was similar to that of Pd-Ni/SiO_2 catalysts from mixed metal salt.

RESULTS AND DISCUSSION

An amount of Pd and Ni was determined by ICP technique and the results are shown in Table 1. The catalysts prepared from cluster were labeled CC1, CC2, and CC3, which had total loading of 1.468, 1.858, and 1.594, respectively. According to their weight percent of Pd and Ni, the mole ratio of Pd/Ni were 0.31, 0.39, 0.37 which were not 1 as expected from the cluster precursor, $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$. The possible explanation for this ratio might be from crystallographic disorder in which palladium atomic positions were substituted by nickel. As reported by Tran [11], the Pd/Ni ratios of occupancy at some positions were 0.23/0.77, 0.22/0.78 and 0/1.00.

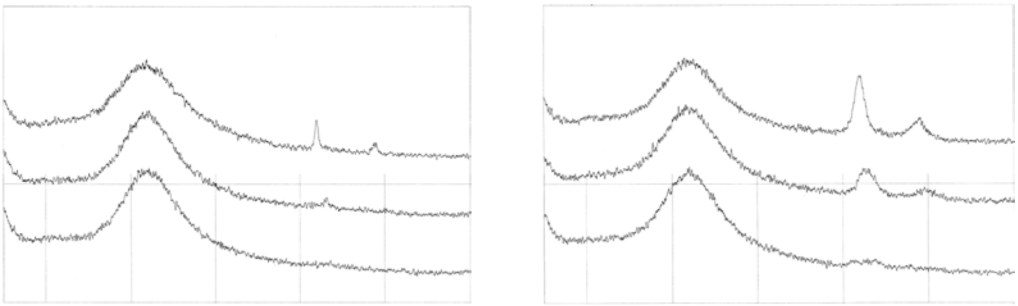
The catalysts prepared from salts were labeled SC1, SC2, and SC3 for loading of 1.634, 5.114, and 8.364% respectively. The only catalyst with comparable loading to catalysts from cluster was SC1. From hydrogen adsorption experiment, SC1 had higher hydrogen adsorption and higher H/Pd ratio than CC1, CC2, and CC3. Because Pd is known to adsorb hydrogen better than Ni, it is possible that Pd and Ni in catalysts prepared from cluster were still intact resulting in lower hydrogen adsorption of Pd. When compare the SC series, the ratio H/Pd of SC3 was lower than others due to higher loading in which larger metal particle (i. e., lower surface area) was expected. Surface areas of all catalysts were in the same range.

Table 1 Metal loading on PdNi/SiO_2 catalysts prepared from cluster and metal salts determined by ICP technique, results from hydrogen adsorption experiment, and BET surface area (CC = catalyst prepared from cluster, SC = catalyst prepared from salt)

Cat.	Total	Pd	Ni	H atom/g cat	H/Pd	H/M	BET surface area (m^2/g)
CC1	1.468	0.685	0.782	1.20665E-06	0.0187	0.0061	282.02
CC2	1.858	0.928	0.931	2.8640E-06	0.0328	0.0117	277.50
CC3	1.594	0.781	0.813	0.0000E+00	0.0000	0.0000	275.31
SC1	1.634	0.523	1.111	3.0559E-06	0.0621	0.0128	277.12
SC2	5.113	1.857	3.256	1.1267E-05	0.0645	0.0154	277.45
SC3	8.364	4.590	3.774	1.9870E-05	0.0461	0.0185	262.19

XRD spectrum of catalysts prepared from the cluster and salt mixture are shown in Figure 2. There was a slight shift of peaks in Figure 2a compared to Figure 2b which might cause by alloy formation. From the shape of the peaks, the metal particle size increased in the order CC3 > CC2 > CC1. Thus, it agreed well with hydrogen adsorption experiment of CC3 which was unable to detect.

Similarly, metal particle size of catalysts prepared from salts were in the order SC3 > SC2 > SC1. Even though the total hydrogen adsorption increased with loading, the H/Pd ratio was smallest for SC3.

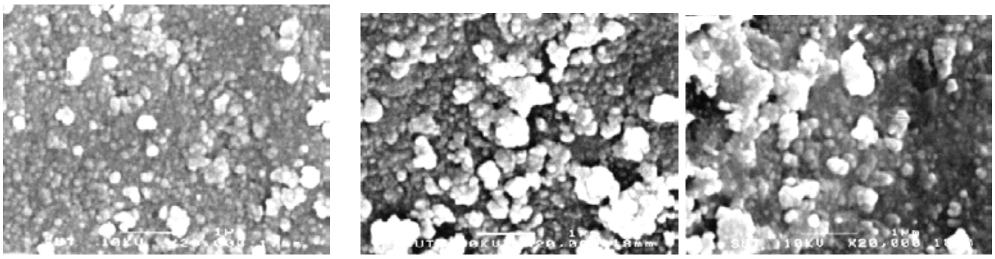


(a) (b)

Figure 1 XRD spectrum of (a) PdNi/SiO_2 cluster-catalysts reduced at 450°C for 1 hour, from top to bottom, CC3, CC2, and CC1. (b) PdNi/SiO_2 salt-catalysts reduced at 450 °C for 1 hour, from top to bottom, SC3, SC2, and SC1. Note the d of pure Pd and pure Ni are 2.25 and 2.03, respectively.

Morphology of all catalysts was studied by scanning electron microscopy and the surface images taken with 20,000 magnification are displayed in Figure 2 and 3. In Figure 2 there was no distinction among catalysts prepared from clusters. It was hard to conclude the existence of metal particle. When an electron beam was directed at random areas for EDX measurements, at what seemed to be metal particles or smooth areas, both Pd and Ni were detected in all areas. Thus, the only conclusion to be made is that those catalysts contain good metal dispersion.

Similar EDX results were obtained from catalysts from salt mixtures despite the more messy appearance of the surface (Figure 3).



(a) (b) (c)

Figure 2 SEM picture (x 20,000) of PdNi/SiO_2 prepared by impregnation of **1** on silica. (a) 1.468%PdNi/SiO_2 (Pd = 0.685%, Ni = 0.782%), (b) 1.858 %PdNi/SiO_2 (Pd = 0.928%, Ni = 0.931 %), and (c) 1.594 %PdNi/SiO_2 (Pd = 0.7818%, Ni = 813%)

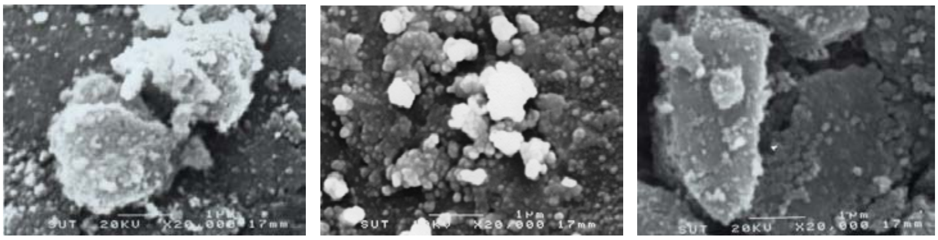

(a) (b) (c)

Figure 3 SEM picture (x 20,000) of PdNi/SiO_2 prepared by impregnation of **1** on silica. (a) 1.634%PdNi/SiO_2 (Pd = 0.523%, Ni = 1.111%), (b) 5.113 %PdNi/SiO_2 (Pd = 1.857%, Ni = 3.256%), and (c) 8.364 %PdNi/SiO_2 (Pd = 4.590%, Ni = 3.774%)

Temperature-programmed reduction of PdNi/SiO_2 was investigated on a TGA compared to Pd/SiO_2 and Ni/SiO_2 and the results are listed in Table 2. The peak of weight loss was obtained from derivative TG curve. The weight loss of Pd/SiO2 was between 30-80°C which could be contributed from loss of surface water as well as reduction. The weight loss over Ni/SiO_2 took place at two temperature ranges: 30-80 and 275-350°C. The loss during first range caused by elimination of surface water while that during the second range was caused by reduction. This result agreed with the fact that palladium oxide is reduced easier than nickel oxide.

The weight loss of PdNi/SiO_2 took place at the 30-160°C range with two peaks which were between that of Pd/SiO_2 and Ni/SiO_2. This result indicated that Pd and Ni in PdNi/SiO_2 were still intact. Hydrogen first dissociatively adsorbed on palladium oxide and reduced it to palladium metal which was active site for further hydrogen adsorption. Hydrogen on palladium then migrated to reduce nickel oxide next to palladium on the same particle. Thus, the reduction temperature of nickel was decreased.

Table 2 Ranges and peaks of weight loss and of Pd/SiO_2, Ni/SiO_2, and PdNi/SiO_2 from TPR experiment

Catalyst	Weight loss Temperature (°C)	Peak of weight loss (°C)
Pd/SiO_2	30-80	43
Ni/SiO_2	30-80 and 275-350	43 and 307
PdNi/SiO_2 from cluster	30-160	52 and 103

CONCLUSIONS

In this research cluster $[PPh_4]_4[Pd_{13}Ni_{13}(CO)_{34}]$ was utilized as a precursor for heterogeneous catalyst preparation in which the solution of cluster was deposited on silica by impregnation technique. The catalysts prepared from clusters have desired properties including small metal particles with good metal dispersion. Calination temperature of 400°C is enough to remove carbonyl ligands and phosphonium cation. In addition, TPR results indicated that palladium was still intact with nickel and lower the reduction temperature of nickel. The catalysts prepared from cluster have good metal dispersion with small metal particles.

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