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Synthesis Characterization and Applications of Colloidal Supported Metal Nanoparticles

Kalyani Gude
University of Rhode Island, kalyanigude@gmail.com

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SYNTHESIS CHARACTERIZATION AND APPLICATIONS OF COLLOIDAL
SUPPORTED METAL NANOPARTICLES

BY
KALYANI GUDE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
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OF
KALYANI GUDE

APPROVED

Thesis Committee:

Major Professor

Radha Narayanan

Louis J. Kirschenbaum

Vinka Craver

Nasser H. Zawia

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

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ABSTRACT

Nanocatalysts show excellent catalytic activity because of their immense surface-to-volume ratio. In homogeneous nanocatalysis, the catalyst remains in the same phase as the reactants and products. Traditionally available homogeneous nanocatalysts include colloidal suspensions of transition metal nanoparticles. In heterogeneous nanocatalysis, the catalyst and the reactants are in different phases. Traditionally available heterogeneous nanocatalysts include metal nanoparticles adsorbed onto bulk supports such as silica, alumina, carbon etc. The main advantage associated with homogeneous nanocatalysts is that they have high selectivities compared to heterogeneous nanocatalysts. The main disadvantages associated with homogeneous nanocatalysts include poor thermal stability, metal contamination and difficulty recovering the catalyst. The heterogeneous nanocatalysts on the other hand have good thermal stabilities and good catalyst recoveries. We focused on synthesizing a new type of catalyst that we termed as colloidal supported metal nanoparticles (CSMNs). The CSMNs act as an intermediate class of nanocatalysts that have properties associated with both homogeneous and heterogeneous nanocatalysts. The synthesized CSMNs are characterized using TEM and EDS. The CSMNs are used as nanocatalysts for the Suzuki and Heck cross-coupling reactions. The kinetics of these reactions is monitored using high performance liquid chromatography (HPLC). The catalytic activity, stability and the recycling potential of the CSMNs is investigated in our study.

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PREFACE

This dissertation is written utilizing a manuscript format. The first chapter is an introduction about nanocatalysis. The second chapter entitled “Synthesis and Characterization of Colloidal Supported Metal Nanoparticlees (CSMNs) as Potential Intermediate Nanocatalysts” was published in Journal of Physical Chemistry C. (*Journal of Physical Chemistry C*, **2010**, *114*, 6256-6362) in March 2010. The third chapter entitled “Colloidal Supported Metal Nanoparticles (CSMNs) as Effective Nanocatalysts for Liquid-Phase Suzuki Cross-Coupling Reactions” was published in the Journal of Physical Chemistry C. (*Journal of Physical Chemistry C*, **2011**, *115*, 12716-12725) in June 2011. The fourth chapter entitled “Functionalized Colloidal Supported Metal Nanoparticles (CSMNs) as efficient Recyclable Nanocatalysts for Liquid-Phase Cross-Coupling Reactions” is submitted for publication in Journal of Physical Chemistry C.

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Chapter 1: INTRODUCTION TO NANOCATALYSIS

Catalyst is a substance that increases the rate of a reaction by lowering the activation energy (E_a) that is required to convert reactants into products. By using a catalyst, the desired product can be obtained faster than without the presence of the catalyst. They are used to make chemicals, medicines, fuels and many other important products. Catalysts also play a major role in improving the quality of our life from environmental perspective. Catalysts containing platinum, palladium, rhodium and other metals are used to control the emission levels of toxic gases emitted from automobiles.

Only a portion of catalysts used today can be termed as nanocatalysts. The small particle size leads to many unique properties of the nanoparticles. The term nanocatalyst is defined as a material that has catalytic properties on at least one nanoscale dimension. They possess immense surface-to-volume ratio because of their small size, which is why they act as attractive catalysts. They also have potential applications in the field of photochemistry, nanoelectronics, optics etc. Although the term nano was used until recent times, researchers traditionally focused on producing very small particles of active catalytic agents in order to maximize the reaction efficiency and to reduce the overall cost of the chemical process. Recent advances in synthetic methods for the production of nanomaterials has produced new nanocatalysts with novel properties and reactivity.

Metal nanoparticles are attractive catalysts compared to the bulk materials due to high surface to volume ratio. Because of their small size, the nanoparticles will have

more percentage of atoms on the surface, which leads to increased catalytic activity. However, the problem associated with these catalysts is that they tend to aggregate at higher temperatures and harsh reaction conditions. In most of the cases, aggregation leads to loss of properties associated with the colloidal transition metal nanoparticles. During catalysis, aggregation or coagulation of metal nanoparticles leads to significant loss of catalytic activity. The stabilization of the metallic nanoparticles in colloidal solution and the means to preserve the catalytic activity is an important aspect to be considered while synthesizing these catalysts.

Synthesis of Colloidal Metal Nanoparticles

There are many ways to synthesize metal nanoparticles and can be mainly divided into two categories: top down approach and bottom up approach. In the top down process, the bulk materials are used as the starting materials and treated by physical means such as mechanical grinding¹, mechanical alloying² and sputtering techniques³⁻⁶ etc. to synthesize nanomaterials. The particles synthesized by this method generally have a size distribution that is broad.⁶ The metal nanoparticles synthesized by this method are typically larger and cannot be reproduced resulting in irreproducible catalytic activity. In the bottom up process, the single atoms or ions are allowed to grow into clusters or nanoparticles using wet chemical synthetic methods such as chemical reduction of metal salts^{7, 9} and the decomposition of precursors using thermal^{10, 11}, photolytic⁸ or sonochemical treatment.^{12, 13} The particles synthesized by this method have narrow size distribution of the particles.

The method used for the synthesis of metal nanoparticles has control over the size and shape of the particles. To have better control over the particle size and shape, chemical synthesis methods are found to be more suitable than physical synthesis methods. Three major routes used to synthesize transition metal nanoparticles include chemical reduction of metal salts, thermal and photochemical decomposition of metal complexes and electrochemical reduction of metal salts.

Chemical Reduction

The chemical reduction of metal salts is one of the most widespread methods used for the synthesis of transition metal nanoparticles.^{7, 9} In this method, the metal salts dissociate to form metal ions. The metal ions are then reduced by a reducing agent to form metal nanoparticles that are stabilized by a stabilizer. Most commonly used reducing agents include solvents such as alcohol^{14, 15, 17}, salts such as sodium borohydride¹⁸⁻²⁶ or sodium citrate²⁷⁻²⁹ and gases such as carbon monoxide³³ and hydrogen.³⁰⁻³²

The alcohols mainly used for the reduction of metal salts include ethanol, methanol and isopropanol. The alcohols act both as a reducing agent and solvent. The transition metal nanoparticles are formed by the reduction of metal salts in the refluxing alcohol and the alcohols are oxidized to form corresponding carbonyl compounds (for example, methanol to formaldehyde, ethanol to acetaldehyde). The size distribution of the metal nanoparticles is dependent on the structure and quantity of the alcohol, the stabilizing agent, metallic precursor, temperature and the base used.¹⁴⁻¹⁷

Miyake and co-workers reported that the size of palladium nanoparticles can be controlled by varying the amount of the protective polymer, PVP and the kind or concentration of the alcohol used.^{14, 15} The smaller sized palladium and platinum nanoparticles were obtained in case of reduction of H_2PdCl_4 or H_2PtCl_4 with increase in the amount of the polymer used.^{14, 15} Also, the particle size and standard deviation became smaller when the alcohol used has higher boiling point.¹⁵ It was also reported that smaller size of the particles is observed during the reduction of H_2PtCl_6 or PdCl_2 in the presence of sodium hydroxide and methanol.¹⁷

Borohydrides are the most commonly used reducing agents to synthesize colloidal transition metal nanoparticles. Sodium borohydride is dissolved in aqueous solution and used immediately to avoid decomposition of borohydride to borane and gaseous hydrogen that could escape from the solution. Sodium borohydride is also used as a reducing agent to synthesize platinum and palladium nanoparticles stabilized by PAMAM dendrimers.²² Phosphine dendrimer stabilized nickel nanoparticles²⁰ and dendrimer encapsulated iron-oxide nanoparticles¹⁹ were synthesized using sodium borohydride as reducing agent. PEGylated dendrimer stabilized gold nanoparticles were synthesized using sodium borohydride as reducing agent in methanol.²⁶

Sodium citrate is used as a reducing agent to synthesize Ir and Pt nanoparticles.²⁸⁻²⁹ Turkevitch and co-workers used sodium citrate as reducing agent to synthesize Au nanoparticles.²⁷ The citrate anion acts both as a reducing agent and stabilizer. The decrease in the amount of sodium citrate results in larger size particles. The reduction in the amount of sodium citrate will result in less number of citrate ions

available for stabilizing the particles. This causes the aggregation of smaller particles to form bigger ones.²⁷

The hydrogen gas is another commonly used reducing agent to synthesize colloidal transition metal nanoparticles.³⁰⁻³² This method involves bubbling of hydrogen gas into a solution containing precursor metal salt and a slow reduction process allows the formation of colloidal metal nanoparticles. Hydrogen gas is used as a reducing agent to synthesize Au, Ag, Pt, Pd, Ir, Rh and Ru colloids in the presence of polyvinylalcohol.³⁰ Polyphosphate is used as a stabilizer to synthesize Ag nanoparticles using hydrogen as reducing agent.³² Carbon monoxide is used as a reducing agent to synthesize Au nanoparticles in the presence of polyvinylsulfate.³³

Thermal and Photochemical Decomposition

Thermal decomposition involves the decomposition of organometallic salts to respective zero-valent species in high boiling point solvents. Meguro and co-workers reported the synthesis of palladium nanoparticles by heating a solution of palladium acetate to 110⁰ C.³⁴ Using this method, broad size distribution of particles is obtained if secondary stabilizers are not used.

Photochemical decomposition of metal salts was found to be a promising method for the synthesis of monodisperse transition metal nanoparticles. Using this method, metal salts are reduced by radiolytically produced reducing agents or radio induced degradation of organometallic complexes. The main advantage of this method is that a large number of atoms are homogeneously and instantaneously produced during irradiation. This allows the formation of monodisperse nanoparticles. Au, Ag,

Pd, Pt, Cu, and Ir nanoparticles have been synthesized by this method.³⁵⁻³⁸ During radiolysis of transition metal salts in aqueous solution, solvated electrons or radicals are formed which react with other molecules in solution to form new radicals. These solvated electrons and newly formed radicals act as reductant to reduce the metal salts forming the nanoparticles. The ionization radiation sources used include UV-Vis, x-ray or γ -ray generators. Au, Ag, and Pt nanoparticles have been synthesized by irradiating the corresponding transition metal salt with UV-Visible light in the presence of polymers or surfactants.³⁹⁻⁴¹

The irradiation time used was quite long using photochemical decomposition methods. To solve this problem, Scaiano and co-workers developed methods in which the irradiation time was reduced to several minutes.⁴²⁻⁴⁵ Ag nanoparticles were synthesized using hydroxydiphenylmethyl as a source of radical species and the irradiation time required to reduce the metal salt to Ag was decreased to few minutes.⁴²

Electrochemical Reduction

Reetz *et al* developed electrochemical method for the synthesis of monodisperse transition metal nanoparticles.^{46, 47} The mechanism proposed by authors include the following steps: oxidative dissolution of anode to form metal ions, migration of metal ions to cathode, reduction of metal ions at the cathode, nucleation and growth of metal particles, and stabilizing the metal nanoparticles with protecting agents such as tetraalkyl ammonium salts. Adjusting the distance between electrodes, reaction time, temperature and the polarity of solvent can control the size of the nanoparticles. The

particle size can also be controlled by the current intensity. The increase in current intensity resulted in smaller transition metal nanoparticles. Pd, Ni, Co, Fe, Ag and Au nanoparticles were synthesized using this method.^{46, 47}

Stabilization of Metal Nanoparticles

Transition metal nanoparticles in colloidal solution have been used as catalysts for a variety of organic reactions because of their excellent catalytic activity. In general, it is difficult to separate and recycle the catalyst from the suspension of the reaction mixture. Furthermore, they tend to aggregate or coagulate which leads to the loss of catalytic activity. Hence, in order to prevent the aggregation of particles, they have to be stabilized using stabilizers. The selection of the stabilizers is important while synthesizing transition metal nanoparticles. The size and shape of the metal nanoparticles depend on the chemical structure of the stabilizer used. Based on the nature of protective agents used, it is possible to identify five different kinds of stabilization. (i) electrostatic stabilization due to adsorbed ions, (ii) steric stabilization due to the presence of bulky groups, (iii) electrosteric stabilization by the presence of surfactants, (iv) stabilization by ligands and (v) stabilization by dendrimers.

Electrostatic Stabilization

The stabilization of transition metal nanoparticles can be achieved by means of electrostatic stabilization. Ionic compounds such as halides, carboxylates and polyoxoanions when dissolved in solution can produce electrostatic stabilization. The

adsorption of these compounds and their related counter ions on the metallic surface will generate an electrical double layer around the particles. This results in Coulombic repulsion between the nanoparticles that prevents the aggregation of the particles.⁴⁸⁻⁵¹

Steric Stabilization

The stabilization of metal nanoparticles can also be achieved by the use of macromolecules such as polymers or oligomers.^{52, 53} The steric stabilization of metal nanoparticles can be achieved by the steric bulk framework of polymers.⁵² Most commonly utilized polymers include PVP^{54-56, 58, 59}, polyacrylate^{57, 60, 61}, polystyrene^{62, 63} etc. Polyacrylate has also been used to stabilize cubic shaped platinum nanoparticles⁶⁰. The bulky groups of PVP, polyacrylate and polystyrene will form a protective layer around the surface of nanoparticles thereby preventing the aggregation of the particles.

Of all the polymers, PVP is mostly used because of its low cost and its ability to stabilize nanoparticles with accessible surface areas in polar solvents such as water. PVP do not completely passivate the nanoparticle surface. It was speculated that one part of PVP chain adsorbs to the surface of nanoparticle and other part suspends freely in solution forming a protective layer.⁵⁸ One of the disadvantage associated with the PVP is the problematic separation of nanoparticles from the polymer.^{64, 65}

PVP has been used to stabilize platinum^{56, 57}, palladium^{54, 55, 64} and rhodium⁵⁹ spherical shaped nanoparticles. PVP stabilized nanoparticles have been used as catalyst for various reactions. El-Sayed and co-workers reported that palladium nanoparticles stabilized by PVP acts as efficient catalysts for Suzuki cross-coupling

reactions.⁶⁷ They reported that by varying the PVP/metal ratio, the size of the nanoparticle can be varied.⁶⁶ They have also shown that the decrease in palladium nanoparticle size down to 3 nm improved the catalytic activity in the Suzuki reaction.^{64, 67}

Electrosteric Stabilization

The electrostatic and steric stabilization can be provided by the use of ionic surfactants such as polyoxoanions.^{68, 69} These compounds have a polar head group that generates electrical double layer and lyophobic side chain that provide steric repulsion. Surfactant such as ammonium (Bu_4N^+)/polyoxoanion has bulky ammonium counterions with a highly charged polyoxoanion that provide electrosterical stabilization towards agglomeration.^{68, 69}

Stabilization by Ligands

The stabilization of metal nanoparticles can also be achieved by the use of ligands such as phosphines^{53, 70-71}, thiols^{53, 72, 73} or amines⁵³ etc. The stabilization occurs by coordination of nanoparticles with ligand molecules. Platinum, palladium and gold nanoparticles in colloidal solution have been stabilized using phosphine ligands.^{70, 71} Gold nanoparticles have been stabilized using alkanethiols and functionalized thiols that were referred to as monolayer-protected clusters (MPCs).^{72, 73} Thiol stabilized nanoparticles are often shown to be less catalytically active or inactive due to passivation of metal surface. Astruc and coworkers synthesized palladium nanoparticles stabilized by dodecanethiolate ligands.⁷⁴ Thiol stabilized

palladium nanoparticles are reported to be stable and recyclable catalysts for the Suzuki reaction of aryl halides under ambient conditions.

Stabilization using Dendrimers

Recently, dendrimers are used as stabilizers to synthesize transition metal nanocatalysts.^{18, 22-24, 75-76} Dendrimers are a class of polymeric materials that are highly branched monodisperse macromolecules. Dendrimers become densely packed as the chain grows and forms a closed membrane-like structure. Most commonly used dendrimers include PAMAM poly(amido amine)⁷⁶ and PPI poly(propylene imine) dendrimers⁷⁵. The nanoparticles synthesized by this method do not agglomerate and are stabilized by encapsulation within the dendrimer.

Crooks and co-workers synthesized Cu, Au, Pt, Pd, Fe, and Ru nanoparticles using poly(amidoamine) (PAMAM) dendrimers.^{22, 23} Dendrimers with higher steric bulk play an important role in the stability and catalytic activity exhibited by the dendrimer encapsulated nanoparticles. El-Sayed and co-workers have shown that Generation 3 and Generation 4 PAMAM dendrimers act as good stabilizers for palladium nanoparticles as higher generation dendrimers encapsulate the nanoparticles more strongly.⁷⁷ They also reported that fourth generation PAMAM-OH dendrimer encapsulated palladium nanoparticles being more stable than PVP-Pd nanoparticles and can be recycled several times before aggregating out of solution.⁷⁸

Supported Nanoparticle Catalysts

The smaller nanoparticles (< 10 nm) are thermodynamically unstable because of their high surface energies and large surface areas. It is difficult to stabilize the nanoparticles by maintaining the small size range while retaining sufficient catalytic activity. Also, the separation of catalyst from unused reactants and products at the end of the reaction is difficult. To overcome this problem, transition metal nanoparticles can be supported onto a heterogeneous solid support.

In heterogeneous catalysis, transition metal nanoparticles supported on various substrates such as silica, carbon and alumina are used as catalysts. Supported metal nanoparticles have been used as catalysts for a variety of industrially important catalytic reactions such as hydrogenations^{79, 80}, dehydrogenations⁸¹⁻⁸³ and oxidation reactions.⁸⁰ The supported metal nanocatalysts have advantages such as enhanced activity, selectivity and prevention of aggregation by immobilization on solid support. Several strategies have been developed for the synthesis of supported metal nanoparticles. Some of the major routes used for the synthesis of supported metal nanocatalysts are described below.

The impregnation method is mostly used method for the synthesis of supported metal catalysts. This process involves wetting of solid support with the precursor metal solution. In the first step, metal salts are dissolved in minimum amount of solvent, followed by the addition of solid support to form slightly wet powder. The solvent is then removed by drying and calcination under oxidizing and reducing

conditions.⁸⁴ The supported catalysts synthesized by this method are polydisperse and the dispersity depends on the metal, metal loading and support.^{85, 86}

Deposition/Precipitation or co-precipitation is another way that is used to synthesize supported metal catalysts.⁸⁷ This method involves dissolution of precursor metal salt in appropriate solvent, followed by adjustment of pH to achieve complete precipitation of precursor. The precipitate is then deposited on the surface of support followed by calcination. Highly dispersed gold catalysts on different supports have been synthesized using this method.⁸⁹ The size distribution of nanoparticles and the degree of dispersion depends on the nature of the support, pH and concentration of the precursor solution, the temperature conditions used for drying and calcination.⁸⁷

Grafting is another method that is used to synthesize supported metal catalysts.^{90, 91} This method involves formation of covalent bond between the metal precursor and the functional groups on the support. The supports that are used for grafting include polyacrylamide gels⁹²⁻⁹⁵ and polystyrene microspheres^{96, 97} etc. Platinum and rhodium colloids have been grafted onto polyacrylamide gel having aminoethyl groups.⁹¹⁻⁹³

Microwave irradiation exposure is another method that is used synthesize supported metal catalysts.⁹⁸⁻¹⁰⁰ Silver nanoparticles are reduced on graphene oxide under microwave irradiation conditions using starch as a stabilizer.⁹⁸ Gold, silver and palladium nanoparticles are supported on mesoporous silica by microwave irradiation of metal salts.⁹⁹ These catalysts were found to be highly active in oxidation reactions. This method allows shorter reaction times compared to the conventional heating

methods that take longer. This method also allows the formation of smaller particles and narrow particle size distributions.¹⁰⁰

Supports

The supports used for the synthesis of supported metal nanocatalysts include a variety of solid materials. The solid materials generally used for the synthesis of supported metal catalysts include carbon, silica, alumina, titania¹⁰¹⁻¹⁰⁹ etc.

Transition metal nanoparticles supported on carbon have been used for a variety of heterogeneous catalytic applications. Carbon materials are most widely used as supports for metal nanoparticles because of their low cost, thermal and chemical stability. The surface of the carbon can be tuned using different approaches such as acid base treatment or heat treatment to optimize catalyst support interactions. Different kinds of carbon supports used include carbon nanotubes^{108, 109}, carbon black¹¹¹, diamond¹¹⁰, nanoporous carbon etc. Activated charcoal is most widely used carbon support for the synthesis of supported metal nanocatalysts.^{112, 113} Gold, palladium, platinum and bimetallic platinum-ruthenium nanoparticles have also been supported on carbon.¹¹⁴

Transition metal nanoparticles supported on metal oxides have been used as catalysts for a variety of organic reactions. Metal oxides supports have high surface areas, high thermal stabilities and organized pore structures. Silica^{103, 104}, alumina^{106, 107} and titania^{105, 106} are the most commonly used metal oxide supports. Different kinds of silica supports used include silica gel¹²⁵, silica monoliths^{115, 116}, mesoporous

silica^{103, 104, 135} etc. Silica supported transition metal nanoparticles have been used to catalyze reactions such as hydrogenations^{117, 118}, Heck cross coupling reactions^{119, 120} etc.

Nanocatalysts for Suzuki and Heck Cross-Coupling Reactions

In recent times, carbon-carbon bond forming reactions discovered by Noble laureates Suzuki, Heck and Negishi have been catalyzed using a wide variety of homogeneous and heterogeneous nanocatalysts.¹²¹ The homogeneous catalysts were used because of their high activity and selectivity, however it is difficult to separate the catalyst at the end of the reaction. It is important to separate the catalyst and reuse it several times to recover the cost of metal in reasonable time. Catalysts that are active but difficult to recover are not generally preferred in chemical industries. To overcome this issue associated with homogeneous catalysts lot of research is done on synthesizing heterogeneous nanocatalysts where the metal is loaded on solid supports such as silica, alumina, carbon etc. However, the active sites on the solid support are not easily accessible to the reactants resulting in decreased catalytic activity. Therefore it is important to synthesize catalysts that are highly active, stable, easily recoverable and reusable.

Suzuki Reaction

The Suzuki cross-coupling reaction is the reaction of aryl or vinyl boronic acids with aryl or vinyl halides in the presence of palladium that result in the

formation of biaryls. Reetz et al used Pd, Pd/Ni clusters stabilized by tetraalkyl ammonium salts or PVP as catalysts for Suzuki reaction.¹²² They observed that bromo aromatics showed better catalytic activity compared to chloro aromatics. El-Sayed and co-workers catalyzed the Suzuki reaction on aryl iodide and phenylboronic acid using palladium nanoparticles stabilized by PVP in water.¹²³ They observed the precipitation of palladium black during the reaction.

Rothenburg and co-workers synthesized Pd, Pt, Cu, Ru and mixed bimetallic nanoparticles and used them as catalysts for Suzuki reaction between phenylboronic acid and iodobenzene in DMF using K_2CO_3 as a base.¹²⁴ Palladium nanoparticles showed higher activity among the monometallic catalysts and no reaction was observed with platinum nanoparticles. But, ruthenium and copper showed some catalytic activity and are found to be stable. Among the bimetallic ones, Cu/Pd showed most activity on par with palladium nanoparticles.¹²⁴

The problem associated with these homogeneous catalysts is difficulty recycling and metal contamination. The heterogenization of homogeneous catalysts is extensively being done in recent years by incorporation of metal nanoparticles in inorganic supports such as silica, carbon, zeolites etc. Palladium nanoparticles immobilized on PEG functionalized silica gels were used as heterogeneous catalysts for Suzuki reaction and are recycled several times without much loss in catalytic activity.¹²⁵ Palladium nanoparticles embedded in carbon thin film lined SBA-15 (mesoporous silica)¹²⁶ were used as heterogeneous catalysts for Suzuki reaction between iodobenzene and phenylboronic acid. It was found that the catalyst can be reused five times without any significant loss in activity.

Heck Reaction

The palladium catalyzed reaction between an aryl halide and alkene was first reported by Mizoroki¹²⁷ and Heck¹²⁸ in early 1970s. The Mizoroki-Heck reaction has been most widely used for the carbon-carbon bond formation reactions that allow alkylation, arylation, vinylation of various alkenes through their reaction with alkyl, aryl and vinyl halides in the presence of palladium and base in a single step reaction. This reaction is mostly carried out in the presence of palladium catalysts involving phosphine ligands. But, these ligands are air-sensitive, poisonous and unrecoverable from the reaction medium. Later, researchers tried to test phosphine-free catalytic systems and were successful.^{129, 130}

Beller and Reetz for the first time showed that the Heck and Suzuki reaction can also be catalyzed by preformed palladium nanoparticles that are stabilized by tetraalkyl ammonium halides or PVP.^{131, 132} But, the problems with these homogeneous catalysts is extreme difficulty of separation, recycling, loss of metal or deactivation via aggregation of palladium nanoparticles formed in situ during heck reaction. To overcome these problems, many chemists have tried designing heterogeneous catalytic systems. This system allows easy catalyst recovery, product separation and inhibits loss of metal. In this regard, the homogeneous palladium nanoparticles are supported or immobilized on PVP-grafted silica¹³³, PVI grafted silica¹³⁴ and amine functionalized mesoporous silica¹³⁵ and are used as catalysts for Heck reaction. All the studies have shown leaching of palladium metal into the solution from the support.

Homogeneous and Heterogeneous Catalysis

In homogeneous catalysis, the catalyst remains in the same phase as the reactants and products. In this type of catalysis, colloidal transition metal nanoparticles finely dispersed in organic or aqueous solutions are used. In heterogeneous nanocatalysis, the catalyst and the reactants are in different phases. Usually, the nanocatalyst will be a solid and the reactants will be either liquids or gases. Traditionally available heterogeneous nanocatalysts include metal nanoparticles adsorbed onto bulk supports such as silica, alumina or carbon.¹⁰¹⁻¹⁰⁹ The main advantage associated with homogeneous nanocatalysts is that they have high selectivity compared to the heterogeneous nanocatalysts. The disadvantage associated with homogeneous catalysts includes difficulty recycling the catalyst, metal contamination and poor thermal stability. The heterogeneous catalysts have good thermal stability and the catalyst can be recovered and recycled several times before losing its activity.

The main goal of our research is to synthesize colloidal supported metal nanoparticles (CSMNs) that acts as an intermediate between heterogeneous and homogeneous catalysts. The support that we used is silica colloids and the active catalyst is palladium nanoparticles. The CSMNs have a high surface area and highly active surface atoms. They have the ability to be suspended in solution during catalysis and can be easily separated from the reaction mixture. The CSMNs combine the advantages of heterogeneous catalysts in a near homogeneous format.

In Chapter 2 we focused on synthesizing Colloidal Supported Metal Nanoparticles. The CSMNs consists of palladium nanoparticles covalently attached to the surface of functionalized silica colloids. The surface of the silica colloids is functionalized with 3-mercaptopropyl trimethoxysilane (MPTMS) or 3-aminopropyl triethoxysilane (APTES). The CSMNs are characterized using TEM and EDS. The stability and catalytic activity exhibited by the CSMNs is investigated. For this purpose, the CSMNs are used to catalyze the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene that forms biphenyl. The amount of biphenyl formed is quantitatively analyzed using HPLC.

In Chapter 3 we focused on investigating the catalytic activity obtained for three types of nanocatalysts: colloidal supported metal nanoparticles (CSMNs) prepared with silica colloids in solution that are air-dried, CSMNs prepared with dry silica colloids resuspended in doubly deionized water that are air-dried, and palladium nanoparticles loaded onto bulk silica dispersed in doubly deionized water that are air-dried. The three types of catalysts are prepared with and without the aminopropyltriethoxysilane (APTES) linker. All the six different types of catalysts are characterized using TEM and EDS. The catalytic activity exhibited by six different catalysts is tested on Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene that results in the formation of biphenyl.

In Chapter 4 we focused on investigating the catalytic activity, stability and recycling potential of two different types of nanocatalysts: The palladium metal nanoparticles that are adsorbed onto the surface of unfunctionalized silica colloids, palladium nanoparticles covalently attached to the surface of functionalized silica

colloids. We used aminopropyltriethoxysilane (APTES) as the linker to functionalize silica colloids. Both these catalysts are used to catalyze Heck cross-coupling reaction between styrene and iodobenzene to form *trans*-stilbene. The fresh catalysts and recycled catalysts are characterized using TEM to observe any changes that might be happening to the catalysts after its use in the reaction.

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Synthesis and Characterization of Colloidal Supported Metal Nanoparticlees (CSMNs)
as Potential Intermediate Nanocatalysts

Kalyani Gude and Radha Narayanan^{*}

Department of Chemistry, University of Rhode Island, Kingston, RI, USA, 02881

Chapter 2

Synthesis and Characterization of Colloidal Supported Metal Nanoparticles (CSMNs) as Potential Intermediate Nanocatalysts

Abstract

We report the synthesis of a new type of intermediate nanocatalyst material that we term as colloidal supported metal nanoparticles (CSMNs). The CSMNs that we have synthesized consist of palladium nanoparticles covalently attached to functionalized silica colloids. The synthesis process involves four steps, which include the synthesis of the silica colloids, synthesis of the palladium nanoparticles, functionalization of the silica colloids with 3-mercaptopropyl trimethoxysilane (MPTMS) or 3-aminopropyl triethoxysilane (APTES), and covalent attachment of the palladium nanoparticles onto the functionalized silica colloids. We have characterized the size of the silica colloids and palladium nanoparticles by using transmission electron microscopy (TEM). In addition, we have characterized the attachment of the palladium nanoparticles onto the two types of functionalized silica colloids by using TEM as well as energy dispersive spectroscopy (EDS). In the case of the CSMNs prepared by using the silica colloids functionalized with MPTMS, we observed that there is significant amount of additional deposits between each of the functionalized silica colloids. This type of additional deposits is significantly diminished in the case of the CSMNs prepared by using silica colloids functionalized with APTES. We have conducted some initial studies to determine at what stage the additional deposits occur and discuss potential sources that give rise to this phenomenon. We have also

conducted initial kinetics study and assessment of the stability of the CSMNs after the catalytic process.

Keywords: transition metal nanoparticles, nanocatalysts, silica colloids, palladium nanoparticles, colloidal supported metal nanoparticles (CSMNs)

Introduction

Metal nanoparticles are very attractive catalysts compared to bulk catalytic materials due to their high surface-to-volume ratio. Some types of traditional nanocatalysts include transition metal nanoparticles in colloidal suspension¹⁻⁸, those adsorbed onto bulk supports⁹⁻¹⁴, and lithographically fabricated arrays of nanocatalysts¹⁵⁻¹⁹. Transition metal nanoparticles in colloidal suspension have been synthesized by using a wide variety of reducing agents²⁰ such as hydrogen²¹⁻²³, sodium borohydride²⁴, and ethanol²⁵⁻²⁷. Many different types of stabilizers have been used as capping agents to stabilize the nanoparticles such as surfactants^{28,29}, polymers^{29,30}, dendrimers^{28,30}, as well as different types of ligands^{28,29}. In the case of metal nanoparticles adsorbed onto bulk supports, a wide variety of support materials have been used such as carbon^{31,32}, mesoporous silica^{33,34}, titania^{35,36}, alumina^{36,37}, zeolites^{9,36}, and resins^{36,38}. Arrays of metal nanocatalysts have been fabricated by using electron beam lithography^{17,19} as well as colloidal lithographic techniques³⁹.

In this paper, we discuss the design of a new type of intermediate nanocatalyst that we term as colloidal supported metal nanoparticles (CSMNs). Some potential advantages of CSMNs as intermediate nanocatalysts include: 1.) being suspended in solution during liquid-phase catalytic reactions, 2.) having high metal loadings on the silica colloid surface resulting in a high surface area, and 3.) facile separation of the

reaction mixture from the CSMNs. The CSMNs combine the advantages of heterogeneous catalysts in a near homogeneous format. These advantages make using CSMNs particularly attractive nanocatalysts for liquid-phase reactions compared to their colloidal counterparts and those adsorbed onto bulk supports. We have utilized a four step process for synthesizing the palladium nanoparticles attached to silica colloids. The four steps in this process include synthesizing the silica colloids, synthesizing the PVP capped palladium nanoparticles, functionalizing the silica colloids, and attaching the PVP capped palladium nanoparticles to the silica colloids. We have characterized the CSMNs by using TEM and EDS. In the case of the CSMNs prepared with silica colloids functionalized with 3-mercaptopropyl trimethoxysilane (MPTMS), there is significant amount of additional deposits present between each of the silica colloids. This type of additional deposits is significantly diminished in the case of the CSMNs prepared with silica colloids functionalized with APTES. We have conducted some initial studies to determine at which stage the additional deposits are formed and discuss potential sources that give rise to this phenomenon.

Experimental

Synthesis of Silica Colloids

The silica colloids were synthesized by using the Stoeber synthesis method⁴⁰. First, 30 mL of ethanol and 2.4 mL of ammonium hydroxide was added to an Erlenmeyer flask and stirred for 5 minutes. Then, 1.2 mL of tetraethylorthosilicate (TEOS) was added to the solution containing ethanol and ammonium hydroxide and

this solution was stirred overnight. The solution was initially clear and after 15-20 minutes, the solution starts to turn cloudy and the final solution is very turbid and consists of a suspension of the silica colloids.

Synthesis of PVP Stabilized Palladium Nanoparticles

The palladium nanoparticles were synthesized by using the ethanol reduction method similar to that described previously^{25,41-43}. The palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887 g of PdCl_2 and 6 mL of 0.2 M HCl, and diluting to 250 mL with doubly distilled water. A solution containing 15 mL of 2 mM of H_2PdCl_4 , 21 mL of doubly deionized water, 0.0667 g of PVP, and 4 drops of 1 M HCl was heated. When the solution began to reflux, 14 mL of ethanol was added. The solution was then refluxed for 3 h, and this resulted in a dark brown suspension of Pd nanoparticles.

Functionalization of Silica Colloids

We have used two different linkers to functionalize the silica colloids: 3-mercaptopropyl trimethoxysilane (MPTMS) and 3-aminopropyl triethoxysilane (APTES). Two separate sets of functionalized silica colloids were prepared in which 100 μL of MPTMS or APTES is added to the silica colloid suspension.

Synthesis of Colloidal Supported Palladium Nanoparticles

The functionalized silica colloids were first centrifuged four times at 13,500 rpm for 3 minutes each time. During the first two-centrifugation cycles, the

functionalized silica colloids were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. Two mL of the centrifuged functionalized silica colloids and four mL of the PVP capped palladium nanoparticles are placed into a scintillation vial and this suspension is mixed for 24 hours to allow the palladium nanoparticles to bind to the functionalized silica colloids.

Characterization Studies with TEM and EDS

One drop of dilute suspensions of the palladium nanoparticles, silica colloids, and the colloidal supported palladium nanoparticles was placed on Formvar coated copper grids. The drop was allowed to air-dry for ~1 hour. The JEOL 2100EX TEM was used to obtain the TEM images of the palladium nanoparticles, silica colloids, and CSMNs. Energy dispersive spectroscopy (EDS) was used to determine what elements are present in the CSMNs.

Size Distribution Analysis

The UTHSCSA ImageTool for Windows—Version 3 image analysis software was used to determine the size distributions of the silica colloids and the palladium nanoparticles. The Distance tool in the Analysis pull-down menu is used to measure the number of pixels in the scale bar of the TEM image. Based on the number of pixels for the fixed size associated with the scale bar and measuring the number of pixels for ~200 nanoparticles in several TEM images, the size of the nanoparticles can be calculated by dividing the number of pixels for the nanoparticles by the number of

pixels of the scale bar and multiplying by the fixed size associated with the scale bar of the TEM image. We then plotted the histogram of % nanoparticles/colloids vs. nanoparticle/colloid size and obtained a Gaussian fit to the histogram. From the Gaussian fit, we can determine the average size and standard deviation of the palladium nanoparticles and the silica colloids.

Suzuki Cross-Coupling Reaction

The Suzuki reaction between phenylboronic acid and iodobenzene was catalyzed using the PVP-Pd nanoparticles as described previously^{25,26,44}. For this reaction, 0.49 g (6 mmol) of sodium acetate, 0.37 g (3 mmol) of phenylboronic acid, and 0.20 g (1 mmol) of iodobenzene was added to 150 mL of 3:1 acetonitrile:water solvent. The solution was heated to 100 °C and 5 mL of the PVP-Pd nanoparticles was added to start the reaction. The reaction mixture was refluxed for a total of 12 hours.

Results and Discussion

Synthesis of Colloidal Supported Metal Nanoparticles (CSMNs)

We discuss the design of a new type of intermediate nanocatalyst that we term as colloidal supported metal nanoparticles (CSMNs). Some important advantages of CSMNs include: 1.) being suspended in solution during liquid-phase catalytic reactions, 2.) having high metal loadings on the silica colloid surface resulting in a high surface area, and 3.) facile separation of the reaction mixture from the catalyst. The CSMNs combine the advantages of heterogeneous catalysts in a near-

homogeneous format. These advantages make using CSMNs particularly attractive nanocatalysts compared to their colloidal counterparts and those adsorbed onto bulk supports for liquid-phase reactions. Scheme 1 illustrates the four step process that we have used to synthesize the palladium nanoparticles supported onto the silica colloids: 1.) synthesizing the silica colloids, 2.) synthesizing the palladium nanoparticles, 3.) functionalizing the silica colloid surface, and 4.) attaching the palladium nanoparticles onto the silica colloid surface. The silica colloids were synthesized by using the Stoeber synthesis method and the palladium nanoparticles were synthesized by using the ethanol reduction method and polyvinylpyrrolidone as the stabilizer. The silica colloids were functionalized by using two different types of linkers: 3-mercaptopropyl trimethoxysilane (MPTMS) and 3-aminopropyl triethoxysilane (APTES). The palladium nanoparticles were covalently attached to the functionalized silica colloids via the Pd-S bond in the case of the silica colloids functionalized with MPTMS and Pd-N bond in the case of the silica colloids functionalized with APTES.

The silica colloids were synthesized by using the Stoeber synthesis method⁴⁰ and TEM was used to characterize the size of the silica colloids. Based on the size measurements obtained with ImageTool, we have plotted the size distribution histogram and calculated the average size of the silica colloids. Figure 1 shows a representative TEM image of the silica colloids as well as the size distribution histogram obtained based on the size measurements with the ImageTool image analysis software. The size distribution histogram is plotted as % silica colloids vs. silica colloid size. The average size of the silica colloids is 344 ± 19 nm and it can be seen that the silica colloids are relatively monodisperse.

The palladium nanoparticles were synthesized by using the ethanol reduction method as described previously²⁵. Figure 2 shows a representative TEM image of the palladium nanoparticles as well as the size distribution histogram obtained for the palladium nanoparticles. In this case, the size distribution histogram was also plotted as % palladium nanoparticles vs. palladium nanoparticle size. The average size of the palladium nanoparticles is 2.9 ± 1.4 nm based on the Gaussian fit of the size distribution histogram.

Figure 3 shows examples of TEM images of the palladium nanoparticles attached to the silica colloids functionalized with MPTMS. We also obtained the energy dispersive spectrum (EDS) of the CSMNs to determine if both Si and Pd peaks were present. The EDS spectrum can give valuable information on the elements present which can help determine whether we have formed CSMNs. As can be seen in Figure 3, there are peaks associated with both Pd and Si that are present which is evidence for the formation of the CSMNs since this is direct evidence of the attachment of the Pd nanoparticles onto the functionalized silica colloids. The silica colloids functionalized with MPTMS have mercapto groups available for the palladium nanoparticles to bind. This results in the Pd-S bond being formed. Also, from Figure 3, it can be seen that there is a significant amount of additional deposits that are present between each of the CSMNs with silica colloids functionalized with MPTMS. We will discuss this finding in more detail later on in another section of this paper.

We have also investigated the attachment of the palladium nanoparticles by using silica colloids functionalized with APTES. We chose this linker since this

would result in the silica colloids being functionalized with amine groups that would be available to bind to the palladium nanoparticles. Figure 4 shows examples of TEM images of CSMNs prepared by attaching the palladium nanoparticles to the silica colloids functionalized with APTES. From the TEM images, it can be seen that the palladium nanoparticles readily attach to the Pd nanoparticle surface since in this case the functionalized silica colloids have amine groups available for the Pd NPs to bind. The covalent attachment of the palladium nanoparticles occurs by formation of the Pd-N bond. Also, it can be seen that there is greatly diminished amount of additional deposits observed for the CSMNs prepared with silica colloids functionalized with APTES. This will be discussed in more detail in the next section of this paper.

Investigations on Additional Deposits Present in CSMNs Prepared with MPTMS Functionalized Silica Colloids.

As we briefly discussed earlier in this paper, we have observed significant additional deposits in the case of the CSMNs prepared with MPTMS functionalized silica colloids and very little or minimal amounts of these types of deposits in the case of the CSMNs prepared with the APTES functionalized silica colloids. As a result, we have conducted a set of investigations to determine at what stage the deposits are formed. These studies will help determine whether the deposits occurred after the functionalization process or after the stage in which the palladium nanoparticles were allowed to react with the functionalized silica colloids. To answer this question, we have conducted a set of experiments in which we obtained TEM images of the silica colloids before and after functionalization with MPTMS and APTES.

Figure 5 and 6 show the TEM images of the silica colloids before and after functionalization with MPTMS and APTES. It can be seen that the deposits are formed on the silica colloid surface after functionalizing the silica colloids with MPTMS, but not when the silica colloids are functionalized with APTES. As a result, it can be seen that the formation of the deposits occurs after the functionalization process in the case of the MPTMS functionalized silica colloids. This shows that in the case of the CSMNs prepared with silica colloids functionalized with MPTMS, the deposits are formed during the stage in the synthesis where the silica colloids are functionalized with the MPTMS. Also, it can be seen that there are very little or minimal amount of deposits observed after functionalizing the silica colloids with APTES. This is consistent with the observation that very little or minimal deposits are present in the case of the CSMNs prepared with the silica colloids functionalized with APTES.

This now raises the question of how these deposits are formed and also why there is significant amount of deposits formed when MPTMS is used as the linker and very little or minimal amount of deposits formed when the APTES is used as the linker. It is worth noting that the synthesis of the silica colloids occurs by base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS)⁴⁵. In the Stoeber synthesis method⁴⁰ to form silica colloids, ammonium hydroxide is used as the base. It is also worth noting that mesoporous silica materials containing mercaptopropyl or phenyl groups on their surface can be prepared by the sol-gel technique⁴⁶. This technique involves co-hydrolysis of TEOS with MPTMS or phenyltriethoxysilane (PTES) in the

presence of hexadecyltrimethylammonium bromide as a templating agent in aqueous sodium hydroxide⁴⁶.

This suggests that in our observations of additional deposits being present in MPTMS-functionalized silica colloids, there could be a side reaction that also takes place. After synthesizing the silica colloids, 100 microliters of the MPTMS is added directly to the silica colloid suspension. As a result, there could still be some TEOS and ammonium hydroxide also present in the silica colloid suspension. As a result, there are two reactions that can occur when the MPTMS is added to the silica colloid suspension. The main and desired reaction involves the functionalization of the MPTMS on the surface of the silica colloids and the mercapto groups being available for the palladium nanoparticles to bind to the MPTMS functionalized silica colloids. The secondary side reaction involves co-hydrolysis of MPTMS with excess unreacted TEOS still remaining in solution in the presence of the ammonium hydroxide base. This secondary reaction would result in the formation of amorphous silica materials and would explain the additional deposits that we observed in the TEM images of both the MPTMS functionalized silica colloids and the CSMNs prepared by using MPTMS functionalized silica colloids.

It is also interesting to observe that there are very little or minimal amounts of additional deposits present when the silica colloids are functionalized with APTES and when the palladium nanoparticles are attached to the APTES functionalized silica colloids. It is quite possible that the co-hydrolysis side reaction observed for the MPTMS functionalized silica colloids occurs at a much lower rate for the APTES functionalized silica colloids. It is worth noting that the co-hydrolysis reaction has

been reported to occur with many different silanes including MPTMS, APTES, and PTES^{46,47}. One reason that there is significantly diminished amount of additional deposits present in the APTES functionalized silica colloids and the CSMNs prepared with APTES functionalized silica colloids could be that the rate of functionalization onto the silica colloids is much faster than the rate of the co-hydrolysis process between TEOS and APTES in the presence of ammonium hydroxide base. In the case of MPTMS functionalized silica colloids, the functionalization onto the silica colloids occurs at a much slower rate compared to the co-hydrolysis process between TEOS and MPTMS in the presence of ammonium hydroxide base. Overall, the secondary co-hydrolysis side reaction occurs at a faster rate for the MPTMS functionalized silica colloids compared to the APTES functionalized silica colloids. This would also explain why there is very little or minimal amount of deposits present in the case of the APTMS functionalized silica colloids and a significantly large amount of deposits in the case of the MPTMS functionalized silica colloids. Overall, both types of CSMNS have the potential to be used as intermediate types of nanocatalysts for liquid-phase reactions that require palladium based catalysts.

Catalytic Activity and Stability of the CSMNs

We have used the CSMNs prepared with the amine functionalized silica colloids as catalysts for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl. Reversed phase HPLC was used to follow the kinetics of the biphenyl peak formed during the first hour of the Suzuki reaction between phenylboronic acid and iodobenzene. Figure 7 shows the reaction kinetics during the

first hour of the Suzuki reaction. It can be seen that biphenyl starts to form during the first five minutes of the reaction.

We have also examined the stability of the CSMNs after the full course of the Suzuki reaction (12 hours). Figure 8 shows TEM images of the CSMNs prepared with the amine functionalized silica colloids after the Suzuki reaction as well as the EDS spectra. It can be seen that there are structural changes in the silica colloids that takes place in which the silica colloids become porous. The observed changes in the silica colloids could be due to the high temperatures of the Suzuki reaction and the long reflux times. The palladium nanoparticles continue to be attached to the silica colloid surface as can be seen in the EDS spectrum in which the Pd peaks are present in addition to the Si peak.

Conclusions

We have designed a new type of intermediate nanocatalyst that we have termed colloidal supported metal nanoparticles (CSMNs) that we have characterized by using TEM and EDS. We have prepared the CSMNs by covalently attaching palladium nanoparticles to the MPTMS or APTES functionalized silica colloids. The CSMNs would serve as an attractive intermediate nanocatalyst in liquid-phase reactions. In the case of the CSMNs prepared with the MPTMS functionalized silica colloids, it is observed that there are additional deposits present between the individual MPTMS functionalized silica colloids. These additional deposits are formed due to a side-reaction which involves co-hydrolysis of TEOS with MPTMS in the presence of ammonium hydroxide base. The additional deposits are greatly diminished in the case of the APTES functionalized silica colloids and the CSMNs prepared with the APTES

functionalized silica colloids and this could be due to the co-hydrolysis side-reaction occurring at a much slower rate. After the full course of the Suzuki reaction, it is observed that there are structural changes in the silica colloids in which it becomes porous and the palladium nanoparticles are still bound to the silica colloids. Overall, both types of CSMNs have the potential to be used as intermediate types of nanocatalysts for liquid-phase reactions that require palladium based catalysts.

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Scheme 1. Four step process for the synthesis of colloidal supported metal nanoparticles (CSMNs).

Figure 2-1. TEM image of the silica colloids synthesized with the Stoeber method (a) and the size distribution histogram (b)

Figure 2-2. TEM image of the palladium nanoparticles (a) and the size distribution histogram (b)

Figure 2-3. TEM images and EDS spectrum of CSMNs prepared with silica colloids functionalized with 3-mercaptopropyl trimethoxysilane and palladium nanoparticles

Figure 2-4. TEM image of CSMNs prepared using APTES functionalized silica colloids (a) TEM image of the CSMNs at a higher magnification (b)

Figure 2-5. TEM images of the silica colloids before and after functionalization with 3-mercaptopropyl trimethoxysilane

Figure 2-6. TEM images of the silica colloids before and after functionalization with 3-aminopropyl triethoxysilane

Figure 2-7. Kinetics of the CSMNs prepared with palladium nanoparticles (NPs) bound to silica colloids (SC) functionalized with the amine linker

Figure 2-8. TEM images (a-b) and EDS spectrum (c) of the CSMNs after the Suzuki reaction.

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Colloidal Supported Metal Nanoparticles (CSMNs) as Effective Nanocatalysts for
Liquid-Phase Suzuki Cross-Coupling Reactions

Kalyani Gude and Radha Narayanan^{*}

Department of Chemistry, University of Rhode Island, Kingston, RI, USA, 02881

Chapter 3

Colloidal Supported Metal Nanoparticles (CSMNs) as Effective Nanocatalysts for Liquid-Phase Suzuki Cross-Coupling Reactions

Abstract

We investigate the catalytic activity obtained for three types of nanocatalysts: colloidal supported metal nanoparticles (CSMNs) prepared with silica colloids in solution that are air-dried, CSMNs prepared with dry silica colloids resuspended in doubly deionized water that are air-dried, and palladium nanoparticles loaded onto bulk silica dispersed in doubly deionized water that are air-dried. The three types of catalysts are prepared with and without the aminopropyltriethoxysilane (APTES) linker for a total of six different catalysts that are tested for the liquid-phase cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. TEM images and EDS spectra were obtained for the six different catalysts to see if the palladium nanoparticles are covalently attached to the functionalized silica colloids and functionalized bulk silica supports and to see if the palladium nanoparticles are adsorbed onto the unfunctionalized silica colloids and unfunctionalized bulk silica supports. The six different catalysts are tested for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs prepared using unfunctionalized wet silica colloids reacted with palladium nanoparticles that are air-dried resulted in the highest catalytic activity. In the case of the nanocatalysts prepared using the APTES linker for covalent attachment of the palladium nanoparticles to the wet silica colloids or bulk silica dispersed in doubly deionized

water that are air-dried, there is lower catalytic activity compared to their counterparts prepared without the use of the APTES linker. This suggests that the APTES could be acting as a catalyst poison resulting in lower catalytic activity for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl compared to unfunctionalized CSMNs.

Introduction

Transition metal nanoparticles are very attractive catalysts since they have a large surface-to-volume ratio which makes their surface atoms very active. Their large surface-to-volume ratio results in higher catalytic efficiency per gram than larger bulk catalytic materials. There have been numerous review articles that have focused on the use of homogeneous catalysts (transition metal nanoparticles in colloidal solution)¹⁻⁹, heterogeneous catalysts (transition metal nanoparticles adsorbed onto different supports)^{6, 9-20}, and lithographic arrays of nanoparticles²¹⁻²⁵ for many different organic and inorganic reactions. There also have been some studies involving the use of intermediate types of supports such as the use of carbon nanotubes²⁶⁻²⁹ and carbon nanofibers³⁰ as support materials.

Suzuki cross-coupling reactions involve reacting arylboronic acids with aryl halides to form biaryls. There have been many reports on the use of transition metal nanoparticles as catalysts for Suzuki reactions³¹⁻³⁶. Dendrimer supported palladium nanoparticles have been used as effective nanocatalysts for Suzuki cross-coupling reactions^{37, 38}. Shape dependent catalytic activity of copper oxide supported palladium nanoparticles have been tested as nanocatalysts for the Suzuki cross-coupling

reactions³⁶. Mesoporous silica supported palladium nanoparticles have been used as catalysts for Suzuki reactions³⁹. The catalytic activity for the Suzuki cross-coupling reactions have been compared for the use of palladium nanoparticles in solution and those adsorbed onto carbon nanotubes⁴⁰. Palladium nanoparticles have also been used as catalysts for the Suzuki reaction using water as the solvent⁴¹.

The CSMNs have a high surface area, highly active surface atoms of the nanoparticles, can be suspended in solution during catalysis, and can be easily separated from the reaction mixture. It can be seen that the colloidal supported metal nanoparticles (CSMNs) combine the advantages of heterogeneous catalysts in a near homogeneous format. Also, the ability to be suspended in solution is especially important for liquid-phase reactions. The CSMNs will have higher catalytic activity than homogeneous nanocatalysts (transition metal nanoparticles in colloidal solution) and heterogeneous nanocatalysts (transition metal nanoparticles adsorbed onto bulk supports). Previously we have reported the synthesis of colloidal supported metal nanoparticles (CSMNs) prepared using mercaptopropyl trimethoxysilane (MPTMS) and aminopropyl triethoxysilane (APTES) functionalized silica colloids⁴². MPTMS was chosen as the linker since it has a thiol group that the palladium nanoparticles can bind to and form Pd-S bond. APTES was chosen as a linker since it has a nitrogen group that the palladium nanoparticles can bind to and form the Pd-N bond. Palladium nanoparticles were covalently attached onto the MPTMS or APTES functionalized silica colloids. The preparation of the CSMNS involves four steps: synthesis of silica colloids, synthesis of palladium nanoparticles, functionalizing the silica colloids with MPTMS and APTES, and covalently attaching the palladium

nanoparticles to the functionalized silica colloids. In the case of the CSMNs prepared using MPTMS functionalized silica colloids, there is no catalytic activity during the entire reaction, which was run for 24 hours. MPTMS has a sulfur group which acts as a catalyst poison. The CSMNs prepared using APTES functionalized silica colloids exhibits catalytic activity during the first hour of the reaction.

In this paper, we report the use of different types of CSMNs as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs that we have investigated consist of metal nanoparticles covalently bound to functionalized silica colloids or adsorbed onto unfunctionalized silica colloids. Out of the six different nanocatalysts, the CSMNs prepared using palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids in solution that are air-dried results in the greatest catalytic activity. In the case of the CSMNs prepared by using palladium nanoparticles covalently attached to the APTES functionalized silica colloids in solution that are air-dried and palladium nanoparticles covalently attached to the APTES functionalized bulk silica dispersed in doubly deionized water that are air-dried, the catalytic activity is smaller than their unfunctionalized counterparts. This suggests that the APTES could be acting as a catalyst poison. Also, the CSMNs prepared by using palladium nanoparticles adsorbed onto unfunctionalized silica colloids in solution that are air-dried resulted in higher catalytic activity than the palladium nanoparticles in colloidal solution as nanocatalysts (containing the same number of grams of palladium).

Experimental

Synthesis of Silica Colloids

The silica colloids were synthesized by using the Stoeber synthesis method⁴³. First, 30 mL of ethanol and 2.4 mL of ammonium hydroxide was added to an Erlenmeyer flask and stirred for 5 minutes. Then, 1.2 mL of tetraethylorthosilicate (TEOS) was added to the solution containing ethanol and ammonium hydroxide and this solution was stirred overnight. The solution was initially clear and after 15-20 minutes, the solution starts to turn cloudy and the final solution is very turbid and consists of a suspension of the silica colloids.

Synthesis of PVP Stabilized Palladium Nanoparticles

The palladium nanoparticles were synthesized by using the ethanol reduction method similar to that described previously⁴⁴⁻⁴⁷. The palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887 g of PdCl_2 and 6 mL of 0.2 M HCl, and diluting to 250 mL with doubly deionized water. A solution containing 15 mL of 2 mM of H_2PdCl_4 , 21 mL of doubly deionized water, 0.0667 g of PVP, and 4 drops of 1 M HCl was heated. When the solution began to reflux, 14 mL of ethanol was added. The solution was then refluxed for 3 h, and this resulted in a dark brown suspension of Pd nanoparticles.

Functionalization of Silica Colloids

We have used 3-aminopropyl triethoxysilane (APTES) as the linker to functionalize the silica colloids. The functionalized silica colloids were prepared in

which 100 μ L of APTES is added to the silica colloid suspension and allowed to react for 6 hours. We have also prepared unfunctionalized silica colloids for direct adsorption of the metal nanoparticles onto the surface of the unfunctionalized silica colloids.

Synthesis of Colloidal Supported Palladium Nanoparticles (CSMNs) Using Functionalized and Unfunctionalized Silica Colloid Suspensions

In the case of the functionalized wet silica colloids, 100 mL of 3-aminopropyltriethoxysilane (APTES) was added and allowed to react for six hours. Two mL of the centrifuged functionalized or unfunctionalized silica colloids and four mL of the PVP capped palladium nanoparticles are placed into a scintillation vial and this suspension is mixed for 24 hours to allow the palladium nanoparticles to covalently bind to the functionalized silica colloids or adsorb onto the unfunctionalized silica colloids. The CSMNs prepared with palladium nanoparticles covalently attached to the functionalized silica colloids or adsorbed onto the unfunctionalized silica colloids were then centrifuged four times at 13,500 rpm for 3 minutes each time. During the first two centrifugation cycles, the CSMNs were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final centrifugation cycle, the supernatant is removed and the CSMNs prepared with functionalized and unfunctionalized silica colloids are allowed to air-dry, and 0.1 g of each type of CSMNs is used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene.

Synthesis of Colloidal Supported Metal Nanoparticles (CSMNs) Using Functionalized and Unfunctionalized Dry Silica Colloids Resuspended in Doubly Deionized Water

The silica colloid suspensions were synthesized by the Stoeber synthesis method⁴². The silica colloids were first centrifuged four times at 13,500 rpm for 3 minutes each time. During the first two centrifugation cycles, the functionalized and unfunctionalized silica colloids were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final cycle of centrifugation, the supernatant was removed and the silica colloids were allowed to air-dry overnight.

In the case of the functionalized silica colloids, 0.32 g of the dried silica colloids is mixed with 30 mL of doubly deionized water and stirred overnight. To this suspension of the initial dried colloids, 100 mL of APTES is added to the silica colloid suspension and allowed to react for 6 hours. In the case of the unfunctionalized silica colloids, 0.32 g of the dried silica colloids is mixed with 30 mL of doubly deionized water and stirred overnight. Two mL of the centrifuged functionalized or unfunctionalized silica colloids and four mL of the PVP capped palladium nanoparticles are placed into a scintillation vial and this suspension is mixed for 24 hours to allow the palladium nanoparticles to covalently bind to the functionalized silica colloids or adsorb onto the unfunctionalized silica colloids. The CSMNs were then centrifuged four times at 13,500 rpm for 3 minutes each time. During the first two centrifugation cycles, the CSMNs prepared using functionalized and unfunctionalized silica colloids were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final

centrifugation cycle, the CSMNs are allowed to air-dry overnight. Then, 0.1 gram of the two types of CSMNs is used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl.

Preparation of Palladium Nanoparticles Loaded onto Functionalized and Unfunctionalized Bulk Silica Dispersed in Doubly Deionized Water

In the case of the functionalized and unfunctionalized bulk silica, 0.32 g of the bulk dry silica and 30 mL of doubly deionized water were added to an Erlenmeyer flask and stirred overnight. In the case of the functionalized bulk silica, 100 mL of 3-aminopropyl triethoxysilane was added and reacted for 6 hours. Two mL of the centrifuged functionalized or unfunctionalized bulk silica and four mL of the PVP capped palladium nanoparticles are placed into a scintillation vial and this suspension is mixed for 24 hours to allow the palladium nanoparticles to bind to the functionalized bulk silica or adsorb onto the unfunctionalized bulk silica. The bulk silica was then centrifuged four times at 13,500 rpm for 3 minutes each time. During the first two centrifugation cycles, the functionalized and unfunctionalized bulk silica loaded with palladium nanoparticles were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final cycle of centrifugation, the supernatant is removed and the functionalized and unfunctionalized bulk silica loaded with palladium nanoparticles are allowed to air-dry overnight. Then, 0.1 g of palladium nanoparticles loaded onto functionalized and unfunctionalized bulk silica are used as the catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl.

Characterization Studies with TEM and EDS

One drop of dilute suspensions of colloidal supported palladium nanoparticles and palladium nanoparticles loaded onto bulk silica was placed on Formvar coated copper grids. The drop was allowed to air-dry for ~1 hour. The JEOL 2100EX TEM was used to obtain the TEM images of the colloidal supported metal nanoparticles (CSMNs) and palladium nanoparticles covalently attached or adsorbed onto silica nanoparticles. Energy dispersive spectroscopy (EDS) was used to determine what elements are present in the CSMNs.

Suzuki Cross-Coupling Reaction

The Suzuki reaction between phenylboronic acid and iodobenzene was catalyzed using the PVP-Pd nanoparticles as described previously^{44, 48, 49}. For this reaction, 0.49 g (6 mmol) of sodium acetate, 0.37 g (3 mmol) of phenylboronic acid, and 0.20 g (1 mmol) of iodobenzene was added to 150 mL of 3:1 acetonitrile:water solvent. The solution was heated to 100 °C and 0.1 gram of the CSMNs or palladium nanoparticles loaded onto bulk silica was added to start the reaction. The reaction mixture was refluxed for a total of 12 hours. Kinetic studies were conducted during the first hour of the reaction.

Results and Discussion

The CSMNs have a high surface area, highly active surface atoms of the nanoparticles, can be suspended in solution during catalysis, and can be easily separated from the reaction mixture. The colloidal supported metal nanoparticles

(CSMNs) combine the advantages of heterogeneous catalysts in a near homogeneous format. The ability of the CSMNs to be suspended in solution is especially important for liquid-phase reactions. The CSMNs will have higher catalytic activity than homogeneous nanocatalysts (transition metal nanoparticles in colloidal solution) and heterogeneous nanocatalysts (transition metal nanoparticles adsorbed onto bulk supports). We discuss the synthesis and characterization of different types of colloidal supported metal nanoparticles (CSMNs) and palladium nanoparticles loaded onto bulk silica as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. We also discuss the results of the kinetics experiments using HPLC for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl for the different types of nanocatalysts.

Synthesis of Different Types of CSMNs and Palladium Nanoparticles Loaded onto Bulk Silica

Six different types of nanocatalysts were synthesized as catalysts for the liquid-phase Suzuki cross-coupling reaction. The palladium nanoparticles have an average size of 2.9 nm as reported previously⁴². In all cases, the palladium nanoparticles are adsorbed or covalently attached to the surface of the silica colloids. The silica colloids are not hollow or porous so the palladium nanoparticles cannot be adsorbed or covalently attached inside the silica colloids. Two types of CSMNs involve the functionalized and unfunctionalized wet silica colloids reacting with the palladium nanoparticles to form CSMNs. In these two types of CSMNs, the term wet silica colloid refers to the silica colloids being in aqueous solution. Preparing the CSMNs

by adsorption of the palladium nanoparticles directly to the silica colloid suspensions involves fewer steps compared to covalently attaching the palladium nanoparticles to APTES functionalized silica colloid suspensions. Using the wet silica colloids involves adsorption or covalent attachment of the palladium nanoparticles to the silica colloids in its native form. Figure 1 shows a representative TEM image and EDS spectrum for the CSMNs prepared using aminopropyl triethoxysilane (APTES) functionalized suspended wet silica colloids. In this case, the palladium nanoparticles are covalently attached to the functionalized silica colloids. Figure 2 shows a representative TEM image and EDS spectrum for the CSMNs prepared using unfunctionalized suspended wet silica colloids. In this case, the palladium nanoparticles are adsorbed onto the unfunctionalized wet silica colloids. The black specks in the TEM images are the palladium nanoparticles covalently attached to the functionalized silica colloid or adsorbed onto unfunctionalized silica colloids. In the EDS spectra for both cases, the Pd and Si peaks are present confirming that the Pd nanoparticles are loaded onto the silica colloids. The copper peaks that are present are due to the copper TEM grids. These two CSMNs that are formed are allowed to air-dry and are used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene, which will be discussed later in the paper.

Another two types of CSMNs involve functionalized and unfunctionalized dried silica colloids resuspended in doubly deionized water and reacting with the palladium nanoparticles to form CSMNs. In these two cases, the silica colloids are air-dried and then resuspended in doubly deionized water. Preparing the CSMNs by adsorption of the palladium nanoparticles directly to the silica colloid suspensions

involves fewer steps compared to covalently attaching the palladium nanoparticles to APTES functionalized silica colloid suspensions. Using the dry silica colloids resuspended in doubly deionized water for adsorption or covalent attachment of the palladium nanoparticles is not in its native form, which is a disadvantage of this method compared to using the wet silica colloids in their native form. Figure 3 shows a representative TEM image and EDS spectrum for the CSMNs prepared using aminopropyl triethoxysilane (APTES) functionalized dried silica colloids resuspended in doubly deionized water. In this case, the palladium nanoparticles are covalently attached to the functionalized dried silica colloids resuspended in doubly deionized water. Figure 4 shows a representative TEM image and EDS spectrum for the CSMNs prepared using unfunctionalized dried silica colloids resuspended in doubly deionized water. In this case, the palladium nanoparticles adsorb onto the surface of the dried silica colloids resuspended in doubly deionized water. The black specks in the TEM images are the palladium nanoparticles covalently attached to the functionalized silica colloids in Figure 3 or adsorbed onto unfunctionalized silica colloids in Figure 4. In the EDS spectra for both cases, the Pd and Si peaks are present confirming that the Pd nanoparticles are loaded onto the Si colloids. The copper peaks that are present are due to the copper TEM grids. These two types of CSMNs are then air-dried and used as catalysts for the Suzuki cross-coupling reaction which is discussed later on in this paper.

In addition, two types of palladium nanoparticles covalently attached or adsorbed onto functionalized and unfunctionalized dry bulk silica dispersed in doubly deionized water were prepared. In these two cases, the bulk silica supports are

dispersed in doubly deionized water. Adsorption of the palladium nanoparticles directly to the bulk silica dispersed in water involves fewer steps compared to covalently attaching the palladium nanoparticles to APTES functionalized bulk silica dispersed in doubly deionized water. Figure 5 shows a representative TEM image and EDS spectrum for palladium nanoparticles supported on APTES functionalized dried bulk silica dispersed in doubly deionized water. In this case, the palladium nanoparticles are covalently attached onto the functionalized bulk silica. Figure 6 shows a representative TEM image and EDS spectrum for palladium nanoparticles supported on unfunctionalized dried bulk silica dispersed in water. In this case, the palladium nanoparticles are adsorbed onto the unfunctionalized bulk silica. In the EDS spectra for both cases, the Pd and Si peaks are present confirming that the Pd NPs are loaded onto the bulk silica. The palladium nanoparticles covalently attached or adsorbed onto bulk silica are air-dried and used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene as discussed later in the paper.

In the case of the nanocatalysts consisting of the palladium nanoparticles adsorbing onto the unfunctionalized silica colloids, the free sites on the palladium nanoparticles (sites not occupied by the PVP stabilizer) are accessible to act as a catalyst. Also, during the adsorption process, the PVP on the nanoparticle surface can be displaced and this results in more sites that can act as catalysts. In the case of the nanocatalysts consisting of the palladium nanoparticles covalently attached to the APTES functionalized silica colloids, the free sites on the palladium nanoparticles (sites not occupied by the PVP stabilizer) are accessible to act as a catalyst. In

addition, it is possible that during the process of the palladium nanoparticles covalently binding to the APTES functionalized silica colloids, some of the PVP could get displaced. This would result in more free sites available to act as catalysts.

Nanocatalysts for Liquid-Phase Suzuki Cross-Coupling Reactions

We have tested the use of the different types of nanocatalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The Pd content of all of the nanocatalysts is the same since we prepared them in the same way. We allowed the silica colloids and bulk silica to react with 5 mL of the palladium nanoparticles and centrifuged them. The supernatant is clear indicating that all of the palladium nanoparticles have been adsorbed or covalently bound to the silica colloids and bulk silica. We have also compared the catalytic activity of these catalysts to that of 5 mL of the colloidal palladium nanoparticles as catalysts. We have used reversed phase HPLC to follow the kinetics during the first hour of the Suzuki reaction for the different nanocatalysts we have prepared such as wet functionalized and unfunctionalized silica colloids in solution reacted with palladium nanoparticles, dried functionalized and unfunctionalized silica colloids resuspended in water reacted with palladium nanoparticles, dry functionalized and unfunctionalized bulk silica dispersed in doubly deionized water reacted with palladium nanoparticles, and palladium nanoparticles in colloidal solution. In the six cases involving CSMNs or palladium nanoparticles loaded onto bulk silica, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst were used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. We

have made comparisons of the catalytic activity for these different types of nanocatalysts.

We have compared the catalytic activity for CSMNs consisting of palladium nanoparticles covalently attached to APTES functionalized wet silica colloids to those of CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dry silica colloids resuspended in doubly deionized water, and palladium nanoparticles covalently attached to the APTES functionalized dry bulk silica dispersed in doubly deionized water. In all three cases, the nanocatalysts are allowed to air-dry and 0.1 gram of each catalyst were used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Figure 7 compares the catalytic activity of these three types of nanocatalysts based on the HPLC kinetics study during the first hour of the reaction. The catalytic activity of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried is the highest for the three types of nanocatalysts. The CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dry silica colloids resuspended in doubly deionized water that are air-dried results in an intermediate catalytic activity. The palladium nanoparticles covalently attached to the APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried results in the lowest catalytic activity out of the three types of nanocatalysts involving the palladium nanoparticles being covalently attached to the APTES functionalized silica colloids or bulk silica.

We have compared the catalytic activity of CSMNs consisting of palladium nanoparticles adsorbed onto wet silica colloids to those of CSMNs consisting of

palladium nanoparticles adsorbed onto the dry silica colloids resuspended in doubly deionized water, and palladium nanoparticles adsorbed onto the dry bulk silica dispersed in doubly deionized water. In all three cases, the nanocatalysts are allowed to air-dry and 0.1 gram of each catalyst were used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Figure 8 compares the catalytic activity of these three types of nanocatalysts based on the HPLC kinetics study during the first hour of the reaction. The CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried results in the highest catalytic activity. In this case, biphenyl is formed as soon as the nanocatalyst is added. In the case of the CSMNs consisting of palladium nanoparticles adsorbed onto the dry silica colloids resuspended in doubly deionized water that are air-dried and the palladium nanoparticles adsorbed onto the dry bulk silica redispersed in doubly deionized water that are air-dried, the catalytic activity is much lower than that of CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried.

The CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried as shown in Figure 8 results in higher catalytic activity compared to that of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried as shown in Figure 7. This result suggests that the APTES could be poisoning the catalytic activity for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Previously we have observed that if we use palladium nanoparticles covalently attached to mercaptopropyl trimethoxysilane (MPTMS) functionalized silica colloids,

there is no catalytic activity during the first hour of the reaction. In this case, the mercapto group in the linker results in poisoning of the catalyst. Nitrogen compounds result in poisoning of different catalysts⁵⁰⁻⁵². This supports the idea that in the case of the CSMNs consisting of palladium nanoparticles covalently attached to APTES functionalized silica colloids, there could be some poisoning of the catalyst due to APTES, which contain an amine group which results in the lower catalytic activity that is observed.

We have also compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids that are air-dried to that of palladium nanoparticles in colloidal solution. Both of these catalysts have the same number of grams of Pd. As can be seen in Figure 9, the CSMNs consisting of palladium nanoparticles adsorbed onto the unfunctionalized wet silica colloids that are air-dried results in larger catalytic activity compared to the palladium nanoparticles in colloidal solution. In addition to the higher catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids, these CSMNs have additional advantages such as having high surface area and being easily separated from the reaction mixture. This makes using the CSMNs consisting of palladium nanoparticles adsorbed onto the unfunctionalized wet silica colloids very attractive to use compared to the palladium nanoparticles in colloidal solution.

We have also compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed to the wet silica colloid surface that are air-dried to those of the CSMNs consisting of palladium nanoparticles covalently attached to the

APTES functionalized wet silica colloids that are air-dried as can be seen in Figure 10. In all three cases, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. The CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried results in higher catalytic activity compared to the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried. The TEM images of the two types of nanocatalysts are similar, yet there are differences in the catalytic activity. The lower catalytic activity for the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried could be due to APTES poisoning the catalyst resulting in lower catalytic activity. This poisoning effect could explain why there is lower catalytic activity in the case of the palladium nanoparticles being covalently attached to the APTES functionalized silica colloids in spite of the similar TEM images.

As can be seen in Figure 11, we have compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto dried silica colloids resuspended in doubly deionized water that are air-dried to that of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dried silica colloids resuspended in doubly deionized water that are air-dried. In both cases, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst were used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. There is very little difference in the catalytic activity for the two types of nanocatalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene

to form biphenyl. As shown in Figure 8, the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids that are air-dried have much higher catalytic activity than the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11 and CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11.

We have also compared the catalytic activity of the palladium nanoparticles adsorbed onto dry bulk silica dispersed in doubly deionized water that are air-dried to that of the palladium nanoparticles covalently attached onto APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried. In all three cases, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst was used for the Suzuki reaction between phenylboronic acid and iodobenzene. As shown in Figure 12, the palladium nanoparticles adsorbed onto dry bulk silica dispersed in doubly deionized water that are air-dried results in higher catalytic activity. It can also be seen that the palladium nanoparticles covalently attached onto APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried results in lower catalytic activity. The palladium nanoparticles covalently attached to bulk silica dispersed in doubly deionized water functionalized with 200 mL APTES that are air-dried resulted in lower catalytic activity than palladium nanoparticles covalently attached to bulk silica dispersed in doubly deionized water functionalized with 100 mL APTES that are air-dried. This trend supports the idea that the APTES acts as a catalyst poison resulting in lower catalytic activity.

Leaching Test

In the case of transition metal nanoparticles, there have been recent studies in which it has been found that heterogeneous catalysts are not truly heterogeneous in which the catalyst leaches into solution^{53, 54}. This raises the question about whether catalysis is homogeneous or heterogeneous. Our CSMNs combine the advantages of heterogeneous catalysts in a near homogeneous format. We have conducted experiments to determine if leaching of the palladium atoms into solution occurs. We have refluxed the CSMNs in 3:1 acetonitrile:water mixture for one hour. Then the solution is centrifuged to remove the CSMNs in which leached atoms would be in the supernatant solution. We used the supernatant solution as catalysts for the Suzuki reaction and compared the catalytic activity to that of the CSMNs catalyzing the Suzuki reaction. The results are shown in Figure 13 and it can be seen that while there is some catalytic activity in the case of the supernatant solution, there is a much greater amount of catalytic activity in the case of the CSMNs used as catalysts. Overall, while there is a small amount of leaching that occurs, the overall catalytic activity is much greater when the CSMNs are used as catalysts.

Conclusions

The catalytic activity is obtained for three types of nanocatalysts: colloidal supported metal nanoparticles (CSMNs) prepared with silica colloids in solution that are air-dried, CSMNs prepared with dry silica colloids that is resuspended in doubly deionized water that are air-dried, and palladium nanoparticles loaded onto bulk silica dispersed in doubly deionized water that are air-dried. These three types of catalysts

are prepared with and without the aminopropyl triethoxysilane (APTES) linker for a total of six different catalysts that are tested for the liquid-phase cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs prepared with the silica colloids in solution without the use of the APTES linker that are air-dried results in the highest catalytic activity for the Suzuki cross-coupling reaction. In the case of the CSMNs consisting of palladium nanoparticles covalently bound to APTES functionalized wet silica colloids that are air-dried and palladium nanoparticles covalently bound to the APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried, it is observed that there is lower catalytic activity than their counterparts prepared without the use of the APTES linker. This suggests that the APTES could be acting as a catalyst poison resulting in lower catalytic activity for the Suzuki reaction. Also, it was observed that the CSMNs prepared with the silica colloids in solution without the use of the APTES linker that are air-dried results in higher catalytic activity than the use of palladium nanoparticles in colloidal solution containing the same number of grams of palladium. Based on these results, it can be seen that the CSMNs prepared using the palladium nanoparticles adsorbed onto unfunctionalized silica colloids in solution that are air-dried result in the highest catalytic activity for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl.

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Figure 3-1— Example TEM image showing the palladium nanoparticles covalently bound to amine functionalized silica colloid suspensions (a) and EDS spectrum, which reflects the presence of both Pd and Si (b). The Cu peaks are due to the copper TEM grids.

Figure 3-2—Examples of TEM images showing palladium nanoparticles directly adsorbed onto the surface of the silica colloid suspensions (a) and EDS spectrum, which reflects the presence of both Pd and Si (b). The Cu peaks are due to Cu TEM grids.

Figure 3-3—A representative TEM image showing the palladium nanoparticles covalently bound to APTES functionalized dried silica colloid suspensions (a) and EDS spectrum, which reflects the presence of both Pd and Si (b). The Cu peaks are due to the copper TEM grids.

Figure 3-4—A representative TEM image showing the palladium nanoparticles adsorbed onto the unfunctionalized dried silica colloid suspensions (a) and EDS spectrum, which reflects the presence of both Pd and Si (b). The Cu peaks are due to the copper TEM grids.

Figure 3-5— Example of TEM image showing APTES functionalized bulk silica with palladium nanoparticles covalently attached to its surface (a) and EDS spectrum which reflects the presence of both Pd and Si (c). The Cu peaks are due to the copper TEM grids.

Figure 3-6— Example of TEM image showing unfunctionalized bulk silica with palladium nanoparticles adsorbed to its surface (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks that appear are due to copper TEM grids.

Figure 3-7—Comparisons of the catalytic activity with wet APTES functionalized Si colloids reacted with Pd nanoparticles that are air-dried, dry APTES functionalized Si colloids resuspended in doubly deionized water and reacted with Pd nanoparticles that are air-dried, and bulk dry APTES functionalized Si dispersed in doubly deionized water and reacted with Pd nanoparticles that are air-dried.

Figure 3-8— Comparisons of the catalytic activity with wet unfunctionalized Si colloids reacted with Pd NPs that are air-dried, dry unfunctionalized Si colloids resuspended in doubly deionized water and reacted with Pd NPs that are air-dried, and unfunctionalized bulk dry Si dispersed in doubly deionized water and reacted with Pd NPs that are air-dried.

Figure 3-9— Comparisons of the catalytic activity with wet Si colloids reacted with Pd NPs without linker that are air-dried and palladium nanoparticles in colloidal solution.

Figure 3-10— Comparisons of the catalytic activity with wet unfunctionalized Si colloids reacted with Pd nanoparticles that are air-dried, and two different wet APTES functionalized Si colloids reacted with Pd nanoparticles that are air-dried

Figure 3-11—Comparisons of the catalytic activity with unfunctionalized dried Si colloids resuspended in doubly deionized water that are air-dried and APTES functionalized dried Si colloids resuspended in doubly deionized water that are air-dried

Figure 3-12—Comparisons of the catalytic activity with unfunctionalized bulk dry Si dispersed in doubly deionized water that are air-dried and APTES functionalized bulk dry Si dispersed in doubly deionized water that are air-dried

Figure 3-13—Comparison of the catalytic activity of the supernatant solution after refluxing the CSMNs in 3:1 acetonitrile and centrifuging to that of the CSMNs used as catalysts for the Suzuki reaction.

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Functionalized Colloidal Supported Metal Nanoparticles (CSMNs) as Efficient
Recyclable Nanocatalysts for Liquid-Phase Heck Reaction

Kalyani Gude and Radha Narayanan^{*}

Department of Chemistry, University of Rhode Island, Kingston, RI, USA, 02881

Chapter 4

Functionalized Colloidal Supported Metal Nanoparticles (CSMNs) as Efficient Recyclable Nanocatalysts for Liquid-Phase Heck Reaction

Abstract

Transition metal nanoparticles show excellent catalytic activity because of their small size. We investigate the catalytic activity, stability and recycling potential of two different types of nanocatalysts. The two catalysts used are the palladium nanoparticles that are supported onto the surface of functionalized and unfunctionalized silica colloids. We used aminopropyltriethoxysilane (APTES) as the linker to functionalize silica colloids. Both the catalysts are used to catalyze Heck-reaction between styrene and iodobenzene that forms *trans*-stilbene. The fresh and recycled catalysts are characterized using TEM to observe any changes that might be taking place to the catalysts after its use in the reaction. Our studies showed that the palladium nanoparticles supported onto unfunctionalized silica colloid supports showed more catalytic activity than the palladium nanoparticles supported onto functionalized silica colloid supports during the first cycle of reaction. Our studies also showed that the palladium nanoparticles supported onto functionalized silica colloid supports showed more stability and recycling potential compared to palladium nanoparticles supported on unfunctionalized silica colloid supports.

Abbreviations

Transmission Electron Microscopy (TEM), (3-aminopropyl)triethoxysilane (APTES), Polyvinylpyrrolidone (PVP), Poly(N-vinylimidazole) (PVI), Colloidal Supported

Metal Nanoparticles (CSMNs), High Performance Liquid Chromatography (HPLC)
(3-mercaptopropyl)trimethoxysilane (MPTMS)

Introduction

Transition metal nanoparticles are attractive catalysts as they have large surface-to-volume ratio. The application of metal nanoparticles in catalysis is an important topic researchers have been working on in recent years because of their characteristic high surface to volume ratio. A greater number of surface atoms are exposed to reactant molecules that make them promising catalysts for some important industrial chemical reactions.¹⁻⁴ Traditionally available catalysts can be classified as homogeneous and heterogeneous catalysts. The homogeneous nanocatalysts include colloidal suspensions of transition metal nanoparticles⁵⁻¹² and the heterogeneous nanocatalysts include the colloidal suspensions of metal nanoparticles supported on supports such as polymers^{13,14} metal oxides,^{15,16} mesoporous silica,^{17,18} carbon materials¹⁹ and zeolites.²⁰ The direct use of metal nanoparticles (homogeneous) as catalysts is often difficult because of their high tendency to aggregate. Hence more research has been in progress to design a different kind of catalyst where the nanoparticles can be supported on solid matrix. The activity and selectivity of these catalysts depend on the nature and chemical structure of the support as well as the morphology of the supports. The presence of promoters and poisons and the interaction between the support and metal nanoparticles may also have an effect on catalysis by metal nanoparticles.^{21,22}

The palladium catalyzed reaction between an aryl halide and alkene was first

reported by Mizoroki²³ and Heck²⁴ in early 1970s. The Mizoroki-Heck reaction has been most widely used for the carbon-carbon bond formation reactions that allow alkylation, arylation, and vinylation of various alkenes through their reaction with alkyl, aryl and vinyl halides in the presence of palladium and base. This reaction is mostly carried out in the presence of palladium catalysts involving phosphine ligands. But, these ligands are air-sensitive, poisonous, and unrecoverable from the reaction medium. Later, researchers tried to test phosphine-free catalytic systems and were successful.^{25,26}

Beller and Reetz for the first time showed that the Heck and Suzuki reactions can also be catalyzed by preformed palladium nanoparticles that are stabilized by tetraalkyl ammonium halides or PVP^{27,28}. The problems with these homogeneous catalysts is extreme difficulty of separation, low recycling potential, loss of metal, or deactivation via aggregation of palladium nanoparticles formed in situ during Heck reaction. To overcome these problems, many chemists have tried designing heterogeneous catalytic systems. This system allows easy catalyst recovery, product separation, and inhibits loss of metal. In this regard, the homogeneous palladium nanoparticles are supported or immobilised on PVP-grafted silica,²⁹ PVI grafted silica³⁰ and amine functionalized mesoporous silica³¹ and are used as catalysts for Heck reaction. All the studies have shown leaching of palladium metal into the solution from the support.

The recycling potential is also an important factor to be considered while synthesizing the nanocatalysts because one wants to use it several times before losing its stability and catalytic activity. The recycling potential of both homogeneous and

heterogeneous catalysts is tested using Suzuki, Heck and many other kinds of reactions.^{32,33} The studies using colloidal palladium nanoparticles showed poor recycling potential for the Suzuki reaction and the studies using palladium nanoparticles supported on activated carbon showed better recycling potential for upto five consecutive cycles.^{34,35}

Here, we discuss the colloidal silica supported metal nanoparticles that are used as catalysts for Heck reaction. As far as we know, there is no report in the literature where the PVP-Pd nanoparticles is supported on silica colloids and used in cross-coupling reactions. From our previous work, the colloidal supported palladium nanoparticles showed better catalytic activity for Suzuki reaction between phenylboronic acid and iodobenzene compared to the bulk silica supported metal nanoparticles³⁶. The colloidal supported metal nanoparticles act as an intermediate kind of catalyst between homogeneous and heterogeneous catalytic systems. In this paper, we focused on testing the stability and recycling potential of colloidal supported metal nanoparticles.

The CSMNs have a high surface area and highly active surface atoms of the nanoparticles. They have the ability to be suspended in solution during catalysis and can be easily separated from the reaction mixture. They act as heterogeneous catalysts in a near homogeneous format. The palladium metal nanoparticles that are supported on functionalized silica colloids showed better stability and recycling potential compared to the palladium metal nanoparticles supported on unfunctionalized silica colloids. In the present study, APTES is chosen as a linker since it has a nitrogen group that the palladium nanoparticles can bind to and form the Pd-N bond. In the

case of unfunctionalized silica colloidal supports, palladium nanoparticles are adsorbed onto the surface of the support. In the case of APTES functionalized silica colloidal supports, palladium nanoparticles are covalently attached to the support. During the first cycle of Heck reaction, unfunctionalized colloidal supported metal nanoparticles showed higher catalytic activity compared to functionalized colloidal supported metal nanoparticles. The catalytic activity decreased drastically during the second and third cycles of Heck reaction for unfunctionalized CSMNs (Colloidal Supported Metal Nanoparticles). There is not much change in the catalytic activity exhibited by functionalized CSMNs during the second and third cycles of Heck reaction. The functionalised and unfunctionalised CSMNs before and after the reaction are characterized using TEM. TEM studies have shown that unfunctionalized CSMNs showed rapid aggregation of nanoparticles after their use for Heck reaction. The functionalized CSMNs showed an increase in the size of nanoparticles after their use in heck reaction and this increase can be attributed to the Ostwald ripening effect³⁷.

Experimental Procedure

Synthesis of Palladium Nanoparticles

The palladium nanoparticles were synthesized using ethanol reduction method.^{38,39} The palladium precursor solution is prepared by adding 0.0887g of PdCl_2 and 6ml of 0.2M HCl and then diluting to 250 mL of doubly deionized water. This mixture is sonicated for about an hour. A solution of 15ml of 2mM H_2PdCl_4 , 21 mL of doubly deionized water, 0.0667g of PVP and 4 drops of 1M HCl was heated to 100°C.

When the solution began to reflux, 14 mL of ethanol was added and refluxed for 3 hours. This resulted in a brown colored suspension of palladium nanoparticles.

Synthesis of Silica Colloids

The silica colloids were synthesized using Stoeber synthesis method.⁴⁰ At first, 30ml of ethanol and 2.4 mL of ammonium hydroxide were added to an Erlenmeyer flask and the solution was stirred for 5 min. Then, 1.2 mL of tetraethylorthosilicate (TEOS) was added to the solution containing ethanol and ammonium hydroxide and this solution was stirred overnight. The solution after the reaction consists of a suspension of silica colloids.

Functionalization of Silica Colloids

We used APTES as a linker to functionalize the silica colloids. To the suspension of silica colloids, 100 μ L of 3-aminopropyltriethoxysilane (APTES) linker was added and reacted for 6hrs. We have also prepared unfunctionalized silica colloids for direct adsorption of palladium nanoparticles onto the surface of silica colloids.

Synthesis of Colloidal Supported Palladium Nanoparticles using Functionalized and Unfunctionalised Silica Colloids

2 ml of functionalized and unfunctionalized silica colloids were added to 6ml of palladium nanoparticles in a scintillation vial and the suspension was stirred for 24 hrs. After 24 hrs, CSMNs, both functionalized and unfunctionalized, were centrifuged four times at 12,000 rpm for 3 minutes each time. During the first two centrifugation

cycles, they were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final cycle of centrifugation, the supernatant was removed and the colloidal silica supported palladium nanoparticles were allowed to air-dry. 0.1g of the functionalized and unfunctionalized CSMNs are used as catalysts for Heck reaction.

Heck Reaction

The Heck reaction between iodobenzene and styrene was catalyzed using the synthesized CSMNs. A mixture of iodobenzene (1.0 mmol), styrene (2.0 mmol), triethylamine (1.5 mmol), DMF (20 mL) and 0.1g of catalyst was stirred at 120° C under inert atmosphere. The reaction is allowed to proceed for 2 hours. To study the progress of the reaction, the aliquots of samples were collected at different time intervals and quantified by HPLC analysis.

Recycling of CSMNs for the Second and Third cycles of Heck Reaction

After the first cycle of reaction, the CSMNs, both functionalized and unfunctionalized, were centrifuged six times at 12,000 rpm for 3 minutes each time. During the first two cycles, they were redispersed in acetonitrile and during the next two cycles they were redispersed in ethanol and during the last two cycles they were redispersed in water. This whole process is done to remove any reactants and products that might be present on the surface of the catalyst. After the final cycle of centrifugation, the supernatant was removed and the CSMNs were allowed to air dry. The same procedure is followed to recycle the catalyst after the second cycle of

reaction.

Characterization Studies with TEM to assess the Stability of Catalysts

In order to observe the changes in the nanoparticles and also the support, the catalyst samples before and after their use in the reaction are spotted on Formvar-stabilized copper TEM grids. One drop of dilute suspensions of catalysts and recycled catalysts were used for spotting. The drop was allowed to air-dry for nearly 2 hours. JEOL 2100EX TEM was used to obtain the images of the spotted samples. The UTHSCSA ImageTool for Windows Version 3 image analysis software was used to determine the size distributions of the palladium nanoparticles supported on silica colloids.

Catalytic Activity Measurements using HPLC

HPLC measurements were conducted on Agilent 1120 Compact LC. A calibration curve for determining the concentration of *trans*-stilbene was constructed by plotting peak area versus concentration of *trans*-stilbene standards. The standards prepared were 1, 2.5, 5, 10, and 20 mM *trans*-stilbene in dimethylformamide. For HPLC measurements, all the samples were diluted to 1/4th or 1/8th or 1/12th of the original concentration, so that all the peak areas are within the range of the calibration curve. The actual concentration was determined by multiplying the concentration of the diluted sample with the dilution factor. The concentration of *trans*-stilbene formed during the first, second, and third cycles of the Heck reaction was investigated using HPLC.

Results and Discussion

The CSMNs have a high surface area and highly active surface atoms of the nanoparticles. They have the ability to be suspended in solution during catalysis and can be easily separated from the reaction mixture. The CSMNs act as heterogeneous catalysts in a near homogeneous format. A careful four-step procedure is applied to synthesize colloidal supported metal nanoparticles. These steps include, synthesis of palladium nanoparticles, synthesis of silica colloids, functionalization of silica colloids and supporting the palladium nanoparticles onto functionalized and unfunctionalized silica colloids. In our previous study, we have used mercaptopropyltrimethoxysilane (MPTMS) and aminopropyltriethoxysilane (APTES) as linkers to functionalize silica colloids. We tested the palladium nanoparticles supported on MPTMS and APTES functionalized silica colloids as catalysts for Suzuki reaction⁴¹. We found the palladium nanoparticles supported on MPTMS functionalized silica colloids showed no catalytic activity even after 24 hrs of running the reaction. But, the palladium nanoparticles supported on APTES functionalized silica colloids started showing the catalytic activity during the first hour of the reaction. Based on these results, we have chosen APTES as a linker to functionalize silica colloids and use them as catalysts for Heck reaction.

We discuss the synthesis and characterization of two different types of colloidal supported metal nanoparticles (CSMNs). We also discuss the separation of the catalyst from the reaction mixture after first, second and third cycles of Heck-reaction and their characterization using TEM. We also discuss the results of the catalytic activity obtained by the fresh and recycled catalysts. HPLC is used to monitor the kinetics of

the Heck reaction between styrene and iodobenzene that forms *trans*-stilbene.

Synthesis and Characterization of Unfunctionalized CSMNs

The PVP capped palladium nanoparticles having an average size of 4.3 ± 1.1 nm are adsorbed onto the surface of unfunctionalized silica colloids. Figure 1a shows the TEM image of PVP capped palladium nanoparticles and Figure 1b shows the size distribution histogram of PVP capped palladium nanoparticles obtained using the ethanol reduction method. It can be seen that the palladium nanoparticles have an average size of 4.3 ± 1.1 nm. The palladium nanoparticles cannot be adsorbed on the inside of silica colloids, as the silica colloids are not porous; instead they are adsorbed on the surface of silica spheres. The palladium nanoparticles supported on unfunctionalized silica colloids are characterized using TEM. Figure 2a shows the TEM image of palladium nanoparticles supported on the unfunctionalized silica colloids. Figure 2b shows the size distributions of the palladium nanoparticles supported on unfunctionalized silica colloids. The black specks in the TEM images are the palladium nanoparticles supported onto unfunctionalized silica colloids. It can be seen that the palladium nanoparticles supported onto unfunctionalized silica colloids have an average size of 4.3 ± 0.9 nm.

Recycled Catalyst Characterization

The unfunctionalized CSMNs are recycled after the first, second and third cycles of Heck reaction and are characterized using TEM. Figure 3a shows the TEM image of palladium nanoparticles supported on unfunctionalized silica colloids after the first

cycle of reaction. Figure 3b shows the size distribution of the palladium nanoparticles supported on unfunctionalized silica colloids after the first cycle of reaction. It can be seen that the average size of the palladium nanoparticles increased to 10.5 ± 2.9 nm. By comparing the average size of the palladium nanoparticles and the standard deviation of palladium nanoparticles before and after the first cycle in Figure 2b and Figure 3b, we can see that the size of the nanoparticles increased after the first cycle and also the standard deviation is increased too. The increase in the size of nanoparticles and also the increase in the standard deviation of the nanoparticles might be due to the Ostwald ripening process occurring under the reaction conditions. Ostwald ripening is a process of growth of metal clusters. This process involves the detachment of metal atoms from the less stable metal clusters and reattachment onto the most stable metal clusters that causes the growth of the nanoparticles. Figure 4a shows the TEM image of the palladium nanoparticles supported on unfunctionalized silica colloids after the second cycle of Heck reaction. Figure 4b shows the TEM image of palladium nanoparticles supported on unfunctionalized silica colloids after the third cycle of Heck reaction. It can be seen that in both Figure 4a and Figure 4b, the palladium nanoparticles aggregated and precipitated which shows the instability of the catalyst. These two observations make sense because the catalytic activity decreased drastically after the first cycle of Heck-reaction that will be explained later.

Synthesis and Characterization of Functionalised CSMNs

The palladium nanoparticles are covalently attached to the surface of functionalized silica colloids. The surface of the silica colloids is functionalized using

100 uL of aminopropyl triethoxysilane (APTES). Figure 5a shows the TEM image of palladium nanoparticles supported onto APTES functionalized silica colloids. Figure 5b shows the size distributions of the palladium nanoparticles supported on APTES functionalised silica colloids. It can be seen that the palladium nanoparticles attached onto functionalized silica colloids have an average size of 4.1 ± 0.8 nm.

Recycled Catalyst Characterisation

The functionalized CSMNs are recycled after the first, second and third cycles of Heck reaction and characterized using TEM. Figure 6a shows the TEM image of palladium nanoparticles supported on APTES functionalized silica colloids after the first cycle of reaction. Figure 6b shows the size distributions of the palladium nanoparticles supported on functionalized silica colloids after the first cycle of Heck reaction. It can be seen that the average size of the palladium nanoparticles increased slightly to 4.8 nm with a standard deviation of 1.2 nm. By comparing the average size of the palladium nanoparticles and the standard deviation of palladium nanoparticles before and after the first cycle in Figure 5b and Figure 6b, we can see that the size of the nanoparticles increased slightly after the first cycle and also the standard deviation is increased slightly too. By comparing the size distributions and standard deviations of palladium nanoparticles supported on unfunctionalized silica colloids (Figure 3b) and functionalized silica colloids (Figure 6b) after the first cycle of Heck-reaction, we can see that there is a drastic increase in the size of nanoparticles that are adsorbed onto unfunctionalized silica colloids. This can be due to large amount of detachment of metal atoms from the smaller metal clusters attached onto unfunctionalized silica

colloids and reattachment onto the larger metal clusters. This suggests that the palladium nanoparticles are weakly adsorbed on the unfunctionalized silica colloids and are less stable. This also explains why the nanoparticles attached onto functionalized silica colloids are more stable compared to the ones adsorbed on unfunctionalized silica colloids. Figure 7a shows the TEM image of palladium nanoparticles supported on APTES functionalized silica colloids after the second cycle of reaction. Figure 7b shows the size distributions of the palladium nanoparticles supported on functionalized silica colloids after the second cycle of Heck reaction. It can be seen that the average size of the palladium nanoparticles increased to 6.3 nm with a standard deviation of 2.2 nm. By comparing the average size of the palladium nanoparticles and the standard deviation of palladium nanoparticles after the first and second cycle of the heck reaction, in Figure 6b and Figure 7b, we can see an increase in the size and standard deviation. This could be attributed to the Ostwald ripening process as described earlier. Figure 8a shows TEM image of palladium nanoparticles supported on APTES functionalized silica colloids after the third cycle of Heck reaction. Figure 8b shows the size distribution of the palladium nanoparticles supported on functionalized silica colloids after the third cycle of Heck reaction. It can be seen that the average size of the palladium nanoparticles increased to 6.8 nm with a standard deviation of 2.5 nm. This could also be attributed to Ostwald ripening process described earlier. Figure 7b and 8b shows that there are smaller nanoparticles as well as larger nanoparticles supported on the functionalized silica colloids and hence wide distribution.

Catalytic Activity Studies

We have tested the use of two different catalysts for the Heck reaction between iodobenzene and styrene that forms *trans*-stilbene. The catalysts used were functionalized and unfunctionalized CSMNs. The palladium content was same on both the catalysts since we prepared them in the same way. We have used reversed phase HPLC to follow the kinetics of the Heck reaction for two hours. We will compare the catalytic activity of these two different catalysts during the first cycle of reaction. We will also compare the catalytic activity obtained by each individual catalyst for up to two reuses.

We have compared the catalytic activity of the palladium nanoparticles supported onto unfunctionalized silica colloids with that of palladium nanoparticles supported onto functionalized silica colloids. Figure 9 compares the catalytic activity of these two types of nanocatalysts based on the HPLC studies during the first cycle of the reaction. The catalytic activity of the palladium nanoparticles supported onto unfunctionalized silica colloids is a little higher than the palladium nanoparticles supported on functionalized silica colloids. In our previous report, where we used the same catalysts for Suzuki reaction between iodobenzene and phenylboronic acid, the same trend is observed. We reported that the lesser catalytic activity observed by the palladium nanoparticles that are supported onto APTES functionalized silica colloids could be due to the poisoning by the APTES linker. This could also be due to lower amount of detachment of metal atoms from the metal clusters that are covalently attached onto silica colloids. This also suggests that most of the catalytic activity exhibited by the functionalized CSMNs must be occurring heterogeneously. The

increased catalytic activity by the nanoparticles supported onto unfunctionalized silica colloids might be due to more detachment of metal atoms from the metal clusters that could participate in the catalytic cycle and attribute to the increase in catalytic activity. Figure 10 compares the catalytic activity obtained by the fresh and recycled catalysts for up to three cycles of the reaction done with palladium nanoparticles supported onto unfunctionalized silica colloids. The first cycle of the reaction is done with the fresh catalyst, the second and third cycles of the reaction is done with reused catalysts. There is a drastic decrease in the catalytic activity after the first cycle of the reaction. The decrease in catalytic activity after the first cycle can be attributed to the increase in the average size of the nanoparticles after the first cycle of reaction that can be seen in figures 3a and 3b. Also there is a decrease in the catalytic activity from 2nd cycle to 3rd cycle. This can be explained based on the fact that the nanoparticles aggregated after the second cycle of the reaction that can be seen from figure 4a. Figure 11 compares the catalytic activity obtained by the fresh and recycled catalysts for up to three cycles of the reaction done with palladium nanoparticles supported onto APTES functionalized silica colloids. The first cycle of the reaction is done with the fresh catalyst, the second and third cycles of the reaction is done with reused catalysts. There is not much decrease in the yield of *trans*-stilbene after the first and second cycles of the reaction that can be attributed to the stability of the nanoparticles covalently attached onto APTES functionalized silica colloids. This also can be explained based on the fact that there is not much increase in the size of the nanoparticles after the first cycle of the reaction. This suggests that the palladium

nanoparticles covalently attached onto functionalized silica colloids are more stable compared to the ones adsorbed on unfunctionalized silica colloids.

Conclusions

The palladium nanoparticles supported on unfunctionalized silica colloids showed a greater increase in size compared to the ones supported on functionalized silica colloids after the first cycle of Heck reaction. There is greater aggregate formation of palladium nanoparticles that are supported on unfunctionalized silica colloids after the second and third cycles of Heck-reaction. Also, the palladium nanoparticles supported on unfunctionalized silica colloids showed a decrease in catalytic activity during the second and third cycles of Heck reaction. The palladium nanoparticles supported on functionalized silica colloids showed an increase in size after the first, second and third cycles of Heck-reaction, but there is no aggregation of nanoparticles even after the third cycle of Heck-reaction. There is not much decrease in the catalytic activity exhibited by the functionalized CSMNs after the first and second cycles of Heck-reaction. The catalytic activity exhibited by the palladium nanoparticles supported onto unfunctionalized silica colloids is higher than the catalytic activity exhibited by the ones supported on APTES functionalized silica colloids during the first cycle of Heck reaction. But, the stability and recycling potential of the palladium nanoparticles supported on functionalized silica colloids is better than the ones supported on unfunctionalized silica colloids. Based on the results obtained, it can be seen that palladium nanoparticles supported on functionalized

colloidal silica supports are better catalysts for Heck reaction between iodobenzene and styrene compared to the ones supported on unfunctionalized colloidal silica.

Figure 4-1. TEM image of the palladium nanoparticles (1a) Size distribution of palladium nanoparticles (1b)

Figure 4-2. TEM image showing the palladium nanoparticles supported onto unfunctionalized silica colloid suspensions (a) Size distribution of palladium nanoparticles supported on unfunctionalised silica colloids (b)

Figure 4-3. TEM image showing the palladium nanoparticles supported onto unfunctionalized silica colloid suspensions after the first cycle of heck reaction (a) Size distribution of palladium nanoparticles supported on unfunctionalised silica colloids after the first cycle of heck reaction (b)

Figure 4-4. TEM image showing the palladium nanoparticles supported onto unfunctionalized silica colloid suspensions after the second cycle of heck reaction (a) TEM image showing the palladium nanoparticles supported onto unfunctionalized silica colloid suspensions after the third cycle of heck reaction (b)

Figure 4-5. TEM image showing the palladium nanoparticles supported onto APTES functionalized silica colloid suspensions (a) Size distribution of palladium nanoparticles supported onto APTES functionalized silica colloids (b)

Figure 4-6. TEM image showing the palladium nanoparticles supported onto APTES functionalized silica colloid suspensions after the first cycle of Heck reaction (a) Size distribution of palladium nanoparticles supported onto APTES functionalized silica colloids after the first cycle of Heck reaction (b)

Figure 4-7. TEM image showing the palladium nanoparticles supported onto APTES functionalized silica colloid suspensions after the second cycle of heck reaction (a) Size distribution of palladium nanoparticles supported onto APTES functionalized silica colloids after the second cycle of heck reaction (b)

Figure 4-8. TEM image showing the palladium nanoparticles supported onto APTES functionalized silica colloid suspensions after the third cycle of heck reaction (a) Size distribution of palladium nanoparticles supported onto APTES functionalized silica colloids after the third cycle of heck reaction (b)

Figure 4-9. Comparisons of the catalytic activity obtained with functionalized and unfunctionalized CSMNs

Figure 4-10. Comparisons of the catalytic activity with fresh and reused catalysts of palladium nanoparticles supported onto unfunctionalized silica colloids

Figure 4-11. Comparisons of the catalytic activity with fresh and reused catalysts of palladium nanoparticles supported onto functionalized silica colloids

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