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SIZE EFFECT INVESTIGATION OF PALLADIUM
NANOPARTICLES SUPPORTED INTO SILICA
COLLOIDS AS THE CATALYST FOR SUZUKI CROSS
COUPLING REACTION

BY

MARSHA SINTARA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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MASTER OF SCIENCE THESIS
OF
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2013

ABSTRACT

Palladium nanoparticles (Pd NPs) provide high activity in catalyzing Suzuki cross coupling reaction, which is the most versatile reaction for forming carbon-carbon bond, due to its high surface to area ratio. Silica colloids are used as the support for Pd NPs to provide heterogeneous catalysis for the reaction. Size factor is very important in the activity of the catalyst.

Four different sizes of Pd NPs stabilized by Polyvinylpyrrolidone (PVP) are synthesized using seed-mediated growth method and supported onto silica colloids. Besides that, four different sizes of silica colloids were synthesized as the support of seed Pd NPs. All of the catalysts were used for Suzuki reaction of phenylboronic acid and iodobenzene. The size effect of the PdNPs supported by silica colloids was compared by comparing the activity of each of the catalysts. We found out that the smaller the size of the Pd NPs, the higher the activity of the catalyst. In addition, the smaller the size of the silica colloids, the higher the activity of the catalysts.

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TABLE OF CONTENTS

| | |
|--|------------|
| ABSTRACT | ii |
| ACKNOWLEDGMENTS | iii |
| TABLE OF CONTENTS..... | iv |
| LIST OF SCHEMES | vi |
| LIST OF FIGURES | vii |
| CHAPTER 1 | 1 |
| REVIEW OF LITERATURE | 1 |
| 1. Palladium Nanoparticles as Catalyst in Suzuki Reactions..... | 1 |
| 1.1. Suzuki Reaction and Classic Catalyst used in Suzuki Reaction | 1 |
| 1.2. Palladium Nanoparticles as Catalyst for Suzuki Reaction | 5 |
| 2. Effect of Nanoparticles Size in Catalysis..... | 9 |
| 2.1. Nanoparticle Size Effect on Tsuji-Trost Reaction..... | 9 |
| 2.2. Nanoparticle Size Effect on Hydrogenation Reaction | 11 |
| 2.3. Nanoparticle Size Effect on Suzuki Reaction | 12 |
| 3. Types of Intermediate Nanocatalysts | 14 |
| 3.1. Nanocatalysts Supported on Metal Oxides | 15 |
| 3.2. Nanocatalysts Supported on Carbon Nanotubes | 17 |
| 3.3. Nanocatalysts Supported on Silica | 18 |
| Bibliography | 22 |

| | |
|---|-----------|
| CHAPTER 2 | 28 |
| SIZE EFFECT INVESTIGATION OF PALLADIUM NANOPARTICLES SUPPORTED INTO SILICA COLLOIDS AS THE CATALYST FOR SUZUKI CROSS COUPLING REACTION | 28 |
| Introduction | 28 |
| Experimental | 29 |
| Synthesis of Different Sizes Palladium Nanoparticles | 29 |
| Synthesis of Different Sizes of Silica Colloids..... | 30 |
| Synthesis of Colloidal-Supported Palladium Nanoparticles | 30 |
| Characterization by Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) | 31 |
| Size Distribution Analysis | 31 |
| Suzuki Cross-Coupling Reaction | 31 |
| Results and Discussion..... | 31 |
| Synthesis of Different Sizes of Palladium Nanoparticles and Silica Colloids | 32 |
| Suzuki Cross-Coupling Reaction Catalyzed by Pd Nanoparticles Loaded onto Silica Colloids..... | 42 |
| Conclusions | 47 |
| Bibliography | 49 |

LIST OF SCHEMES

| | |
|--|----|
| 1.1..... | 1 |
| Generic scheme of Suzuki cross-coupling reaction | |
| 1.2..... | 2 |
| General catalytic cycle of Suzuki reaction | |
| 1.3..... | 3 |
| Palladacycle example | |
| 1.4..... | 8 |
| Proposed mechanism of Palladium nanoparticles as a catalyst for Suzuki reaction | |
| 1.5..... | 9 |
| Tsuji Trost reaction catalyzed by Palladium nanoparticles | |
| 1.6..... | 13 |
| Suzuki reaction of phenylboronic acid and iodobenzene | |
| 1.7..... | 16 |
| Suzuki reaction of aryl halides and aryl boronic acids using PdNPs/LDH | |

LIST OF FIGURES

| | |
|--|----|
| 1.1..... | 3 |
| Cis and trans phosphine ligand | |
| 1.2..... | 4 |
| Example of carbene complex | |
| 1.3..... | 5 |
| Stabilization of Palladium nanoparticles | |
| 1.4..... | 7 |
| XAS analysis of Pd nanoparticles during Suzuki reaction | |
| 1.5..... | 10 |
| Kinetic curves of the catalytic activity of different size Palladium nanoparticles | |
| 1.6..... | 11 |
| Plot of the rate of hydrogen consumption as a function of particle | |
| 1.7..... | 12 |
| Plots of the normalized TOF as a function of nanoparticles diameter | |
| 1.8..... | 13 |
| Plot of TOF as a function of particles size on the basis of (a) total number of surface atoms and (b) total number of vertex and edge | |
| 1.9..... | 17 |
| TEM images of Pd nanoparticles supported onto MWCNT after | |

hydrogen reduction of (a) 10 mg, (b) 20 mg, (c) 30 mg, and (d) 50 mg

$\text{Pd}(\text{hfa})_2$

| | |
|--|----|
| 1.10..... | 19 |
| Synthesis of nanoreactor | |
| 1.11..... | 20 |
| Synthesis of Palladium nanoparticles capped with DT and MPMS | |
| 2.1..... | 32 |
| TEM image of Pd nanoparticles seed (a) and size distribution histogram of the nanoparticles (b) | |
| 2.2..... | 33 |
| TEM image of second growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b) | |
| 2.3..... | 34 |
| TEM image of third growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b) | |
| 2.4..... | 34 |
| TEM image of fourth growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b) | |
| 2.5..... | 35 |
| TEM image of Pd seed nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b) | |
| 2.6..... | 36 |

| | | |
|------------------|--|-----------|
| | TEM image of second growth of Pd nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b) | |
| 2.7..... | | 37 |
| | TEM image of third growth of Pd nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b) | |
| 2.8..... | | 38 |
| | TEM image of fourth growth of Pd nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b) | |
| 2.9..... | | 39 |
| | TEM image of Pd seed loaded into 2.0 mL base (a) and size distribution histogram of the nanoparticles (b) | |
| 2.10..... | | 39 |
| | TEM image of Pd seed loaded into 2.6 mL base (a) and size distribution histogram of the nanoparticles (b) | |
| 2.11..... | | 40 |
| | TEM image of Pd seed loaded into 3.0 mL base (a) and size distribution histogram of the nanoparticles (b) | |
| 2.12..... | | 41 |
| | EDS spectrum of Pd nanoparticles loaded into silica colloids | |
| 2.13..... | | 42 |
| | Chromatograph of Suzuki reaction using HPLC | |
| 2.14..... | | 43 |
| | Calibration curve of biphenyl concentration | |

| | |
|---|----|
| 2.15..... | 44 |
| Graph of Suzuki reaction of different sizes Pd nanoparticles loaded into silica colloids for 1 hour reaction | |
| 2.16..... | 45 |
| Graph of Suzuki reaction of different sizes Pd nanoparticles loaded into silica colloids for 12 hours reaction | |
| 2.17..... | 46 |
| Graph of Suzuki reaction of Pd seed nanoparticles loaded into different sizes of silica colloids for 1 hour reaction | |
| 2.18..... | 47 |
| Graph of Suzuki reaction of Pd seed nanoparticles loaded into different sizes of silica colloids for 12 hours reaction | |

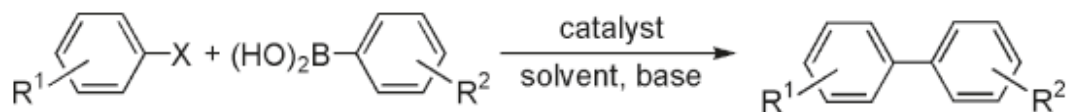
CHAPTER 1

REVIEW OF LITERATURE

1. Palladium Nanoparticles as Catalysts in Suzuki Reactions

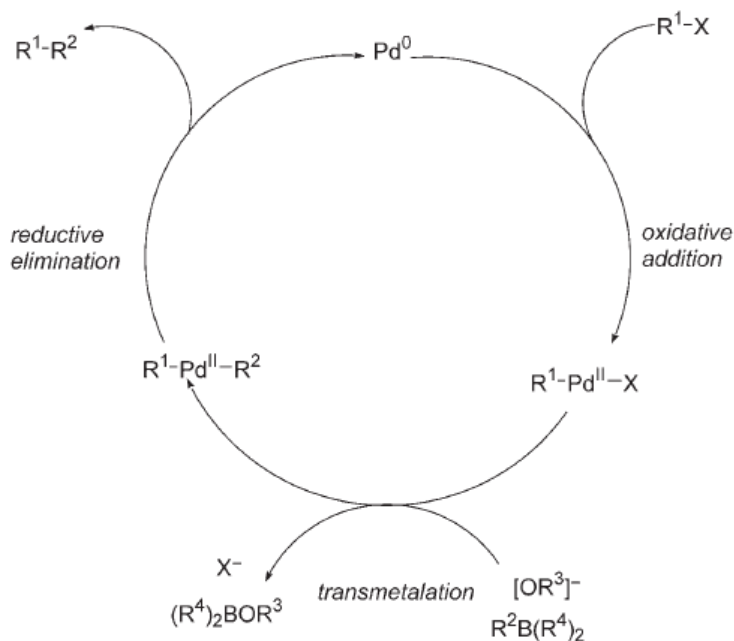
1.1 Suzuki Reaction and Classic Catalyst used in Suzuki Reaction

First published in 1979, Suzuki reaction is one of the most important carbon-carbon bond formation reaction.¹ **Scheme 1.1** shows an example of the Suzuki reaction, which is the cross-coupling reaction between arylboronic acids with aryl halides to form biaryls in the presence of a base. The reaction has been used widely to construct complex carbon-carbon bonds as intermediates in the synthesis of polymers, agrochemicals, pharmaceutical intermediates, and advanced materials.^{2,3}



Scheme 1.1. Generic scheme of Suzuki cross-coupling reaction

The popularity of Suzuki reaction is due to its versatility and efficiency in the synthesis of biaryl compounds.⁴ A variety of substrates and functional groups can be used under the reaction conditions, which is ideal to synthesize many intermediates in constructing the complex drug molecules. Besides that, boronic acid, which is a starting material needed for the reaction is stable, has high selectivity for cross-coupling reactions, is nontoxic, and also is tolerable of the various functional groups.



Scheme 1.2. General catalytic cycle of Suzuki Reaction

The general mechanism of the Suzuki reaction can be seen on **Scheme 1.2**. The first step of the catalytic cycle is attachment of palladium (Pd) catalyst to the halides by oxidative addition, which increases the oxidation state of Pd catalyst from 0 to 2. This step is the rate determining step of the reaction. After oxidative addition, the boronic acid is activated by the base present in the solution which enhances the polarization of the ligand and facilitates transmetalation. The base has been suggested to have a role of increasing the nucleophilicity of the organic group of boron atom and forming alkoxy palladate from aryl palladium halide.⁵⁻⁷ The last step of the cycle is reductive elimination, releasing the biaryl product and regenerating Pd catalyst back to its original oxidation state so that it can participate in the catalytic cycle again.

One of the classic catalysts for Suzuki reaction is Pd⁰ metal coordinated with ligands as the precursor, mainly phosphine ligands.⁸ Early Suzuki reactions used

triphenylphosphine as the ligand for Pd metal to support catalysis.⁹ The phosphine ligand was widely used because it is an electron-rich ligand,

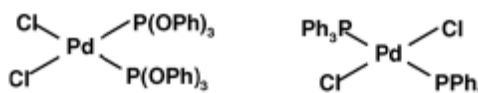
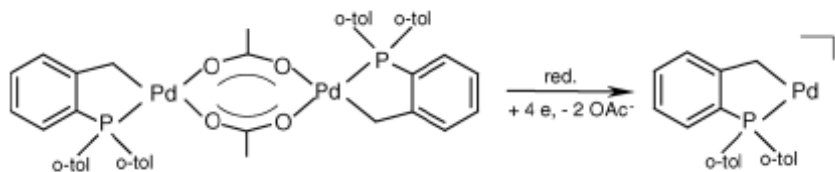


Figure 1.1. Cis and trans phosphine ligand

which could facilitate the oxidative addition step in the catalytic cycle.¹⁰ Besides that, phosphine ligands could bind strongly to Pd⁰ intermediate to prevent aggregation and precipitation which is the contributing factor in the stabilization of Pd⁰ intermediate by forming π interactions with the aryl ring.^{11,12} Phosphine ligand as the precursor of Pd catalyst for Suzuki reaction is one example of homogeneous catalysis. Homogeneous catalysis is a catalysis process where the catalyst is the same phase as the reaction. Because of the same phase, it is hard to separate the catalyst from the product, which makes this one of the disadvantages of phosphine ligand. The other disadvantage of this type of catalyst is that often the phosphine ligands poisons the product, lowering the yield of the reaction.



Scheme 1.3. Palladacycle example

Another precursor for Pd catalysts is using chelating ligands, better known as palladacycles.¹³ Palladacycles was proven to have better activity than phosphine ligands, therefore it could result in better yields. The catalytic mechanism of palladacycles is still unclear. The proposed mechanism includes different oxidation states of Pd involved in the cycle. The first one is Pd(II) and Pd(IV) system which

involves oxidative addition of aryl halides to Pd(II) and then followed by reductive elimination of Pd(IV) species.^{14,15} However in Pd(0)/Pd(II) cycle, transient complex of Pd(0) with Pd-C and Pd-P bonds were proposed instead of terminally bonded phosphine complex.¹⁵ Palladacycles provide an efficient way to catalyze Suzuki reaction. However, it is complicated to synthesize Palladacycles complex, which results in a lot of work and time.

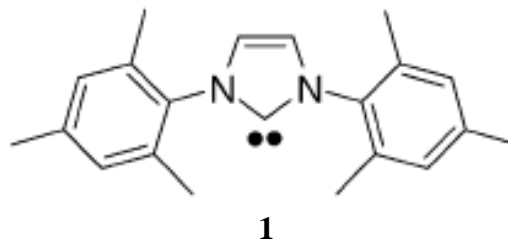


Figure 1.2. Example of carbene complex

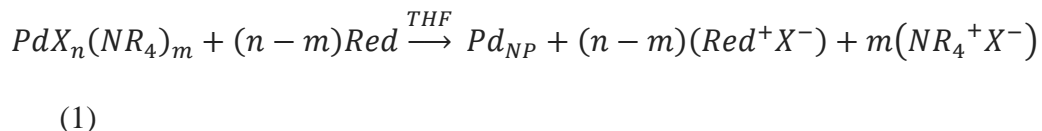
Another type of catalyst for Suzuki reaction is phosphine-free catalyst.¹⁶ Phosphine free catalysts are most useful in the coupling reaction of aryl iodides. The addition of tertiary ammonium salts make the catalyst more reactive and hence the coupling reaction of aryl bromides could be done.^{17,18} The family of phosphine-free catalysts includes carbene complex coordinated with palladium. Carbene has similar electron configuration as trialkylphosphine, which has high σ -basicity and π -acidity.¹⁹ The size of substituents' of carbene ligands affects the activity of the catalyst. Compound **1** (**Figure 1.2**) was shown to be an effective catalyst due to the large size of the substituent and being more electron-donating compared to the classic PCy₃ ligand.²⁰ However, it takes a lot of steps to synthesize larger substituents of carbene complex.

The overall disadvantages of the catalysts above are the high cost to make the metal coordinated with the ligands, and high concentration of catalyst that is needed to produce a good yield of product, which leads to the high cost of cleanup.²¹

1.2 Palladium Nanoparticles as Catalyst for Suzuki Reaction

Nanoparticles as catalyst has increased in popularity due to its high surface to volume ratio and high activity of surface atoms compared to bulk catalysts.²² Due to its high activity as catalyst, no ligands are needed as the precatalyst. Low concentration of metal nanoparticles in solution could produce high Turnover Number (TON) of the product. Therefore, the use of palladium nanoparticles as catalysts of Suzuki reaction provides simpler synthesis methods that leads to reduced production cost.²³

Metal nanoparticles have been synthesized since 1980s. Bonnemann's method is the one that is generally used in synthesizing metal nanoparticles in the presence of stabilizer.²⁴⁻²⁶ The reaction of nanoparticles synthesis is:



With X = Cl or Br, R = C4-12 alkyl, and Red = M'H (M' = H, Li, LiBEt₃, NaBEt₃, KBEt₃).

The surface of the nanoparticles holds some positive charge. In this reaction, a layer of anions surround palladium nanoparticles and stabilize them.^{27, 28} A layer of bulky cations also surrounds the anion, which further stabilizes the nanoparticles.²⁹ (**Figure 1.3**)

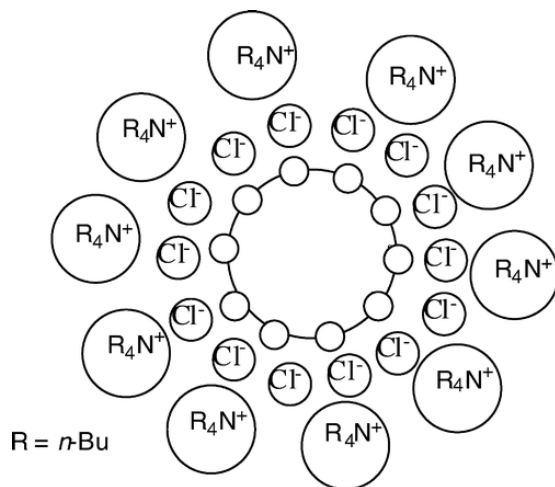


Figure 1.3. Stabilization of Palladium nanoparticles

Another way to synthesize nanoparticles is by thermal decomposition of metal (0) precursors in the presence of stabilizer.³⁰ Stabilizers are used to prevent agglomeration of Pd atoms in the solution so that Pd black precipitate can be avoided. Many organic and inorganic stabilizers in the form of micelles, microemulsions, surfactants, polymers, and dendrimers have been used to synthesize Pd nanoparticles. The function of stabilizers are not only preventing the agglomeration but also making access to the nanoparticle surface for substrate activation and transformation.³¹⁻⁴²

Inverse micelles containing palladium nanoparticles is synthesized using KBH_4 as the reducing agent.³¹ The nanoparticles is synthesized with the help of surfactants. One common surfactant used is fluoro surfactant. It assists the stabilization for palladium nanoparticles in water-in-supercritical CO_2 microemulsions in the form of micelles.³⁵ Polymers are widely used as stabilizers. **Figure 1.4** shows poly-(N-vinyl-2-pyrrolidone) (PVP), a polymer that is widely used for nanoparticles stabilization and catalysis. Palladium nanoparticles are synthesized in reflux conditions by ethanol reduction of the palladium halide.⁴³ Other examples of polymers that can be used as stabilizers for palladium nanoparticles are poly(2,5-dimethylphenylene oxide), polyuria,⁴⁴ polyacrylonitrile and/or poly-(acrylic acid),⁴⁵ multilayer polyelectrolyte films,⁴⁶ polysilane shell-cross-linked micelles,⁴⁷ polysiloxane,⁴⁸ oligosaccharides,⁴⁹ copolymers synthesized by aqueous reversible addition-fragmentation chain-transfer polymerization,⁵⁰ pi-conjugated conduction polypyrrole,⁵¹ poly(4-vinylpyridine),⁵¹ poly(N,N-dialkylcarbodiimide),⁵² poly(ethylene glycol) (PEG),⁵³ chitosan,⁵⁴ and hyperbranched aromatic polyamides (aramids),⁵⁵ and common surfactants such as sodium dodecylsulfate.⁵⁶

Dendrimer is another example of stabilizer for nanoparticles. It encapsulates the nanoparticles with single dendrimer or it can also surround the nanoparticles with several dendrimers. PAMAM is the most common type of dendrimer that is used as stabilizer. Nanoparticles are encapsulated inside the dendrimer and stabilized. PAMAM G4-OH-terminated dendrimers had been used as catalyst for Suzuki reaction.⁴³ The stability and activity of the dendrimer stabilized nanoparticles was compared to PVP stabilized nanoparticles. The nanoparticles encapsulated inside the dendrimer are more stable but also had lower activity compared to PVP stabilized nanoparticles.

Scientists have not reached an agreement yet about the mechanism of Suzuki reaction catalyzed by palladium nanoparticles.²³ Some authors reported that Pd nanoparticles underwent homogeneous catalysis, the soluble Pd species is the one that

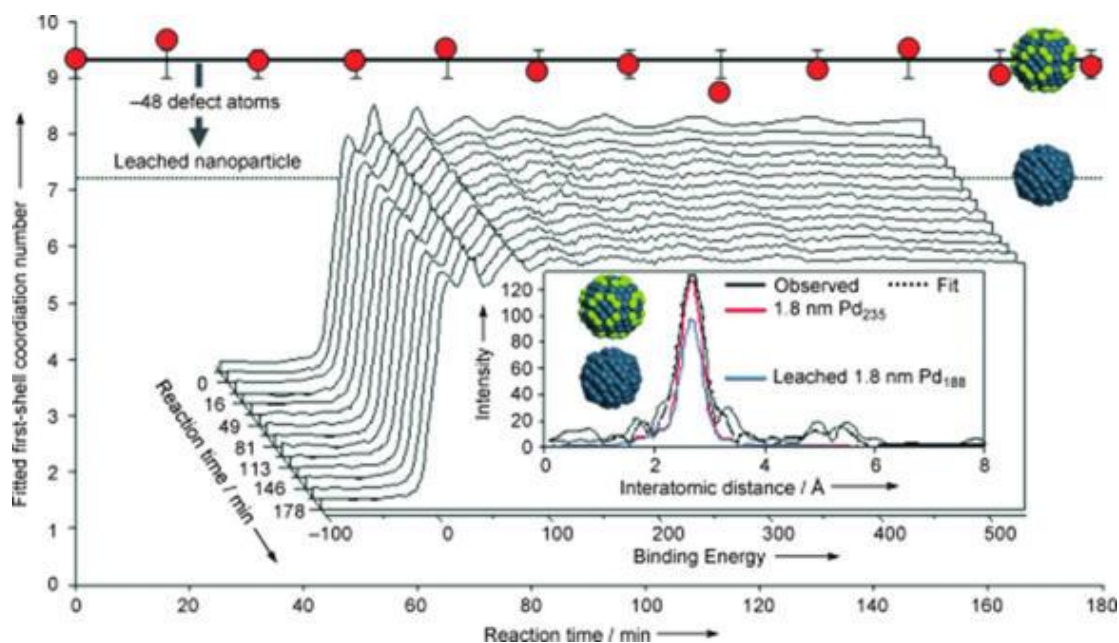
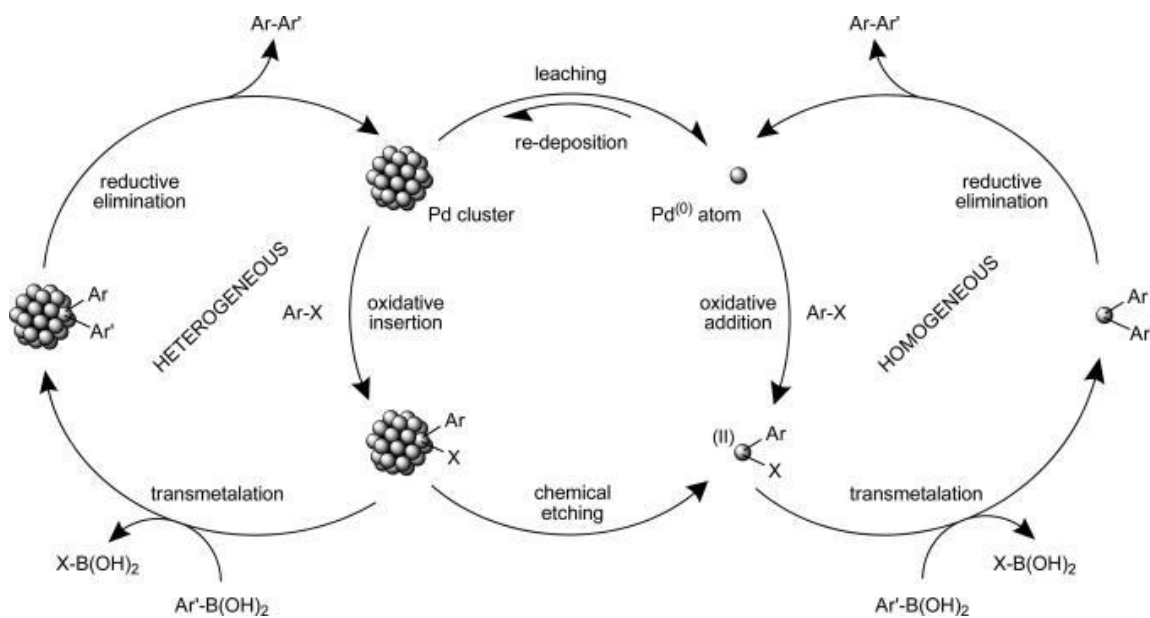


Figure 1.4. XAS analysis of Pd nanoparticles during Suzuki reaction

catalyzes the reaction. Some other authors also point at the heterogeneous nature of the catalysis; both aryl halide and boronic acid are reacting by coming into contact and colliding on the nanoparticle surface, which is not within the solution.

To confirm the nature of the Suzuki reaction mechanism by Pd nanoparticles, metal leaching test was done. The test confirms that the dissolved molecular palladium is catalytically active.⁵⁷⁻⁵⁹ This finding indicates that the Suzuki reaction catalyzed by palladium nanoparticles occurs via homogeneous catalysis. The study using X-ray absorption spectroscopy (XAS), which was used to quantitatively monitor the structure of palladium nanoparticles during the reaction, indicates that Pd-Pd coordination number stays constant during the reaction (**Figure 1.4**). The stability of the atoms indicate the stability of the surface during catalysis, which points to the heterogeneous nature catalysis of Suzuki reaction by palladium nanoparticles.^{60, 61}

The two contradicting pieces of evidence of the catalysis nature by nanoparticles



Scheme 1.4. Proposed mechanism of Palladium nanoparticles as a catalyst for Suzuki Reaction.

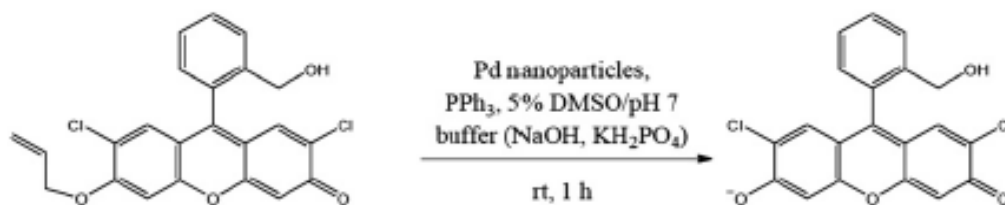
lead to the catalysis mechanism described in **Scheme 1.4**. Many have proposed that the nanoparticles catalyze the Suzuki reaction both homogeneously and heterogeneously. Pd(0) atom will leach into the solution and catalyze the reaction homogeneously. It can also be deposited back to the Pd cluster and catalyze the reaction heterogeneously. However, depending on the reaction conditions, the leached Pd could also agglomerate and Pd black could be formed.

2. Effect of Nanoparticles Size in Catalysis

One reason for the popularity of nanoparticles as catalyst for various reactions is due to its high surface area to volume ratio, which makes it catalyze the reaction faster than the other ligand bound catalysts. The ratio of surface area to volume determines the activity of nanoparticle catalyst. As a result, the size of nanoparticles itself determines the activity of the catalyst. Size dependence of nanocatalysts has been proven on different type of nanoparticles and different reactions.

2.1. Nanoparticle Size Effect on Tsuji-Trost Reaction

The first example of the size effect of the nanoparticles was observed in the Tsuji Trost reaction, an allylic substitution reaction catalyzed by palladium nanoparticles. Yang, *et al.*, 2011 investigated the activity of different sizes of nanoparticles in catalyzing Tsuji Trost reaction in **Scheme 1.5**.⁶² They monitored the reaction by



Scheme 1.5. Tsuji Trost reaction catalyzed by Palladium nanoparticles

fluorimeter since the product is fluorescent while the starting material is not. They synthesized different sizes of spherical palladium nanoparticles using stepwise growth reaction and the Pd seed was synthesized using ethanol reduction method with PVP as the stabilizer. They also synthesized larger sizes of cubic palladium nanoparticles using Cetyltrimethylammonium Bromide (CTAB) as the stabilizer in the presence of ascorbic acid. The diameter of Pd seed was 2.4 nm, the larger Pd nanoparticles was 3.8 nm, and the size of Pd nanocubes was 18 nm. The nanocubes were tested because the catalytic activity is also related to the amount of defect (edge and vertex) atoms on the nanoparticle surface.

The result on **Figure 1.5** showed that 2.4nm spherical nanoparticles had the highest catalytic activity compared to the larger size of nanoparticles and the largest size had the lowest catalytic activity. This indicates even though the catalytic activity

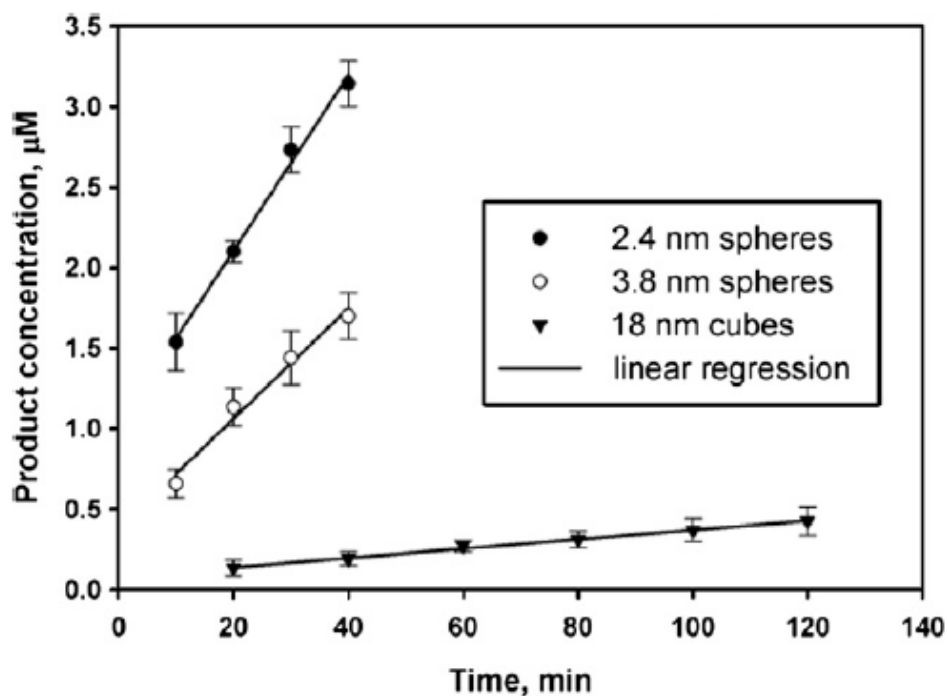


Figure 1.5. Kinetic curves of the catalytic activity of different size Palladium nanoparticles

depends on the amount of defect, the size of nanoparticles is more important in the activity of the catalyst. The importance of nanoparticles size is because Tsuji-Trost reaction occurs via atomic dissolution and oxidative addition of the ether to make the product.

2.2. Nanoparticles Size Effect on Hydrogenation Reaction

Wilson, *et al.*, 2006 studied the effect of nanoparticle size on the hydrogenation of allyl alcohol.⁶³ They used dendrimer as the stabilizer as well as template to control nanoparticle size. The Horiuti-Polanyi mechanism of alkene hydrogenation showed that H₂ is adsorbed onto the catalyst surface and hydrogenation of C=C double bond occurs.⁶⁴ They measured the rate of allyl alcohol hydrogenation by measuring hydrogen uptake of the reaction.

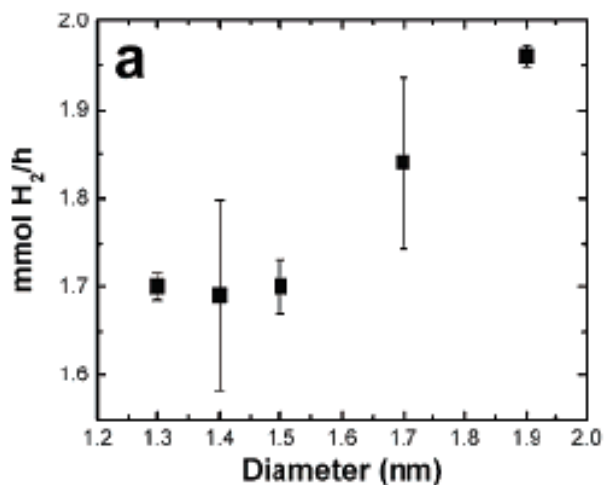


Figure 1.6. Plot of the rate of hydrogen consumption as a function of particle

From the result on **Figure 1.6**, it could be seen that as the size of nanoparticles increased, the activity also increased. They continued the study to determine the origin of size effect from the above result. They calculated the number of moles of surface, defect, and face atoms.

Three of the plots in **Figure 1.7** indicate that the TOF increased as the size of nanoparticles increased but the TOF stayed constant at nanoparticle size between 1.5 nm and 1.9 nm for face atoms. The plots indicated that the hydrogenation of allyl alcohol occurs preferentially at the surface atom at the particles size between 1.5 nm and 1.9 nm (geometric effect). However, at the particle size below 1.5 nm, the catalytic activity is dominated by the electronic effect.

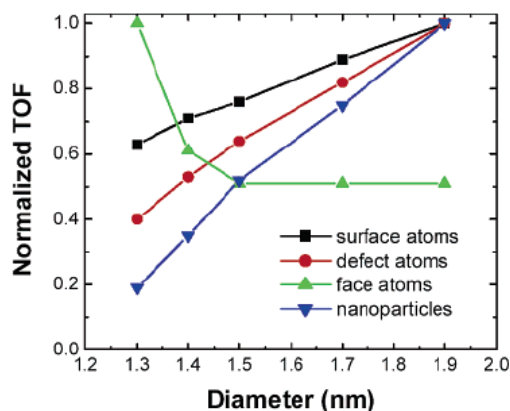
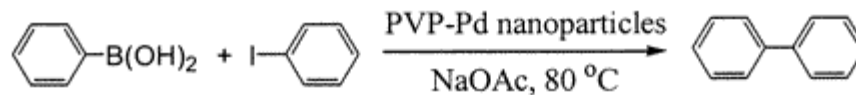


Figure 1.7. Plots of the normalized TOF as a function of nanoparticles diameter

2.3. Nanoparticle Size Effect on Suzuki Reaction

Li, *et al.*, 2000 studied the effect of different sizes of nanoparticles on Suzuki reaction between phenyl boronic acid and iodobenzene (**Scheme 1.6**).⁶⁵ The reaction was monitored using HPLC with L4500A diode array detector (254 nm wavelength). A reverse-phase packed column (Rainin Microsorb-MV C18, 300Å, diameter 4.6 x 250 mm) was used with acetonitrile-water mixture as the solvent for the separation. They used the stepwise growth reaction to prepare palladium nanoparticles with PVP as the stabilizer. Palladium seeds had a size of 3 nm. The three larger nanoparticles had the size of 3.9 nm, 5.2 nm, and 6.6 nm, respectively.



Scheme 1.6. Suzuki reaction of phenylboronic acid and iodobenzene

The initial rate of the reaction using different size of nanoparticles indicated that the activity of the catalyst decreases as the size increases, with the exception of the smallest size (3 nm), which has less activity than the 3.9 nm catalyst. They also calculated the Turnover Frequency (TOF) on the basis of total number of surface atoms and total number of vertex and edge and plotted them as a function of particle size.

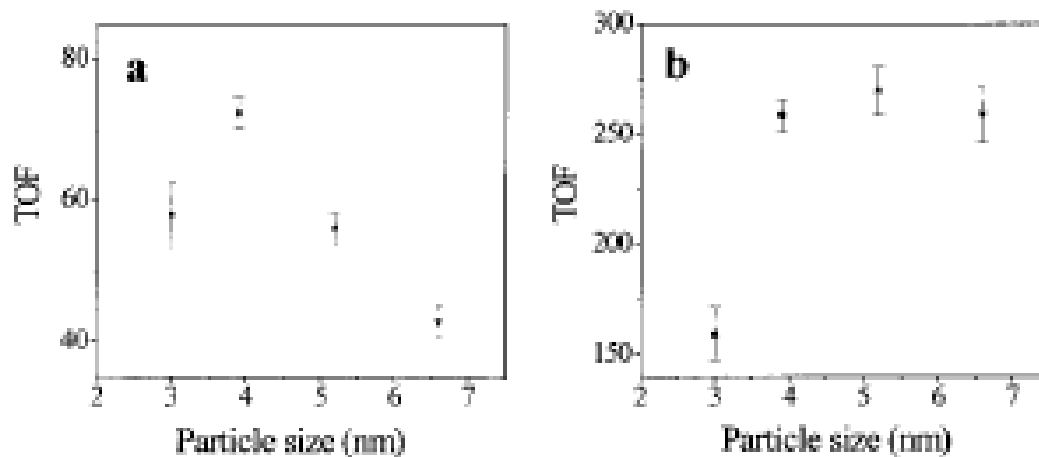


Figure 1.8. Plot of TOF as a function of particles size on the basis of (a) total number of surface atoms and (b) total number of vertex and edge

The plot on **Figure 1.8b** shows that the TOF does not depend on the particle size except for the smallest particle size when only the vertex and edge are considered. That happens because the particle surface is poisoned by strongly bound species. The reaction intermediates adsorb strongly to the particle surface, and then cover the surface of the catalyst, which leads to catalyst poisoning. On **Figure 1.8a**, it is shown that the catalytic activity has the same trend as the initial rate when all of the surface atoms are considered. From both of the plots, it can be concluded that the active sites of catalysis are on the vertex and edge of the particles.

From all of the examples above, it could be seen that as the particles size decrease, the total surface area increases; therefore the activity will also increase. However if the size of the nanoparticles is too small, catalyst poisoning could occur. As a result, the activity of very small catalyst will decrease. For the Suzuki reaction, the catalysis site is located on the vertex and edge of the nanoparticles.

3. Types of Intermediate Nanocatalysts

Homogeneous palladium nanoparticles provide excellent methods for catalyzing C-C coupling reaction, especially Suzuki reaction because of the high activity and selectivity. However, it is hard to separate the catalyst from the product and recycle it because it has the same phase as the product. The disadvantage of homogeneous catalyst includes the loss of expensive metal and product contamination.

In dealing with this problem, heterogeneous catalysts have been synthesized by many people. A lot of materials, organic and inorganic, have been synthesized to

support the palladium nanoparticles. However, heterogeneous catalysts do not have as high activity as the homogeneous catalysts. As the result, a lot of studies nowadays are dedicated to find the support materials that could maximize the activity of catalysts and have high recycling capacity.

3.1. Nanocatalysts Supported on Metal Oxides

Some examples of metal oxides that are used for nanoparticle support are MgO, KF/Al₂O₃, Al₂O₃, MgLa, ZrO₂, and LDH (double-layered hydroxide).⁶⁶ MgO supported palladium nanoparticles are made by counter ion stabilization of PdCl₄²⁻ with MgO and followed by reduction.⁶⁷ Suzuki reaction of aryl bromides and iodides with arylboronic acids was done with this catalyst. The catalyst was found to be an effective one for Suzuki reaction, and 0.5 mol% of the catalyst could lead the reaction to completion in 5-6 hours. Recycling the catalyst is also proven to be simple. It is recovered by simple filtration and it could be reused for four cycles with comparable activity to the first cycle. The high activity of this catalyst is due to the high surface area and strong basicity.

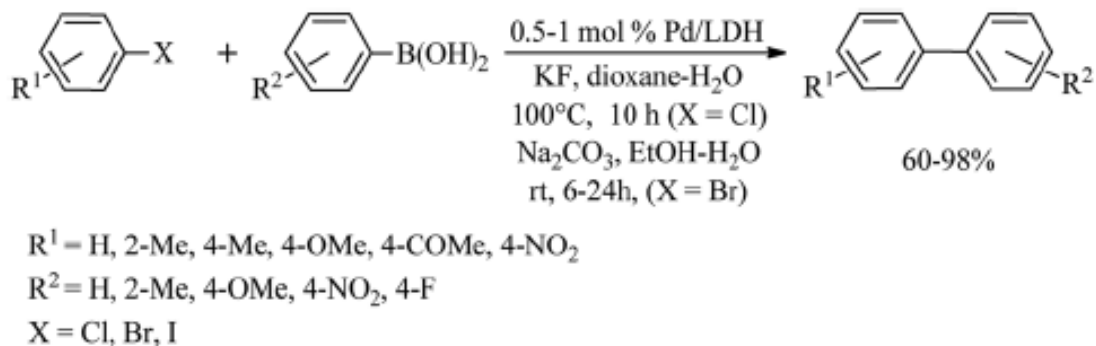
Copper oxides can also be used as the support for Palladium nanoparticles. It could be prepared by reacting Cu(NO)₃ and Pd(OAc)₂ in polyethylene glycol (PEF-6000).⁶⁸ In this case, the amount of PEG determines the shape of the composite. For Suzuki reaction, oval CuO/Pd is the best catalyst among other shapes. The catalyst could be recycled up to five times without notable loss of activity.

Another example of metal oxide is zirconium oxide (ZrO₂). It was used to catalyze Suzuki reaction between aryl bromides and iodides with phenylboronic acid using tetrabutylammonium hydroxide.⁶⁹ (TBAOH) as the base. TBAOH was proven to

catalyze the reaction better than inorganic bases such as KOH, NaHCO₃, and K₂CO₃. This occurs because TBAOH could serve as a base and a phase transfer agent. It is also an efficient catalyst, which could be recycled up to ten times while maintaining its activity.

Alumina based oxides (Al₂O₃, Al₂O₃-ZrO₂ and Al₂O₃-ZrO₂-Eu₂O₃) could be synthesized using sol-gel method and used as support for palladium nanoparticles and then used as the catalyst for the Suzuki reaction.⁶⁶ This catalyst has been proven to be effective in catalyzing Suzuki reaction of 2-bromotoluene with phenylboronic acid. Very high yield was observed when the Pd²⁺ was not reduced before supporting it to the oxides.

Beside metal oxides, layered double hydroxides (LDH) could also be used as nanoparticle support. LDH is also referred to as anionic clays or hydrotalcite-like materials. It is a class of ionic lamellar solids with positively charged layers with two kinds of metallic cations and exchangeable hydrated gallery anions. It gains interest because of its potential as the support for carbon-carbon coupling reactions.⁷⁰ It has been reported that Pd supported by LDH could effectively catalyze Suzuki reaction of activated aryl chlorides with arylboronic acids (**Scheme 1.7**). The catalyst could be recycled up to five times without notable loss of activity.



Scheme 1.7. Suzuki reaction of aryl halides and aryl boronic acids using PdNPs/LDH

3.2. Nanocatalysts Supported on Carbon Nanotubes

Carbon nanotubes are popular support materials for nanoparticles because of its small size so that it can be dispersed uniformly into solution. One simple way to attach metal to carbon nanotubes is by depositing metal nanoparticles onto the surface of multiwalled carbon nanotubes (MWCNT) by hydrogen reduction of Pd(II)- β -diketone precursor in a supercritical carbon dioxide medium.⁷¹ The method resulted well dispersed and spherical Palladium nanoparticles attached to the outside wall of MWCNT (**Figure 1.9**). The size of Palladium nanoparticles is between 5-10 nm.

Palladium nanoparticles supported onto MWCNTs was then used as a catalyst for the Suzuki reaction of phenylboronic acid and 1-iodo-4-nitrobenzene in methanol.⁷² With TOF of 709 h⁻¹, the catalyst performed 24 times better than commercially available Pd/C catalysts under the same conditions. Aryl halides substituted with electron-withdrawing groups were proven to be more reactive with this catalyst compared to non-substituted aryl halides. The recycling study was done with the Suzuki reaction of 4-iodobenzene and phenylboronic acid with this catalyst resulted in six cycles of

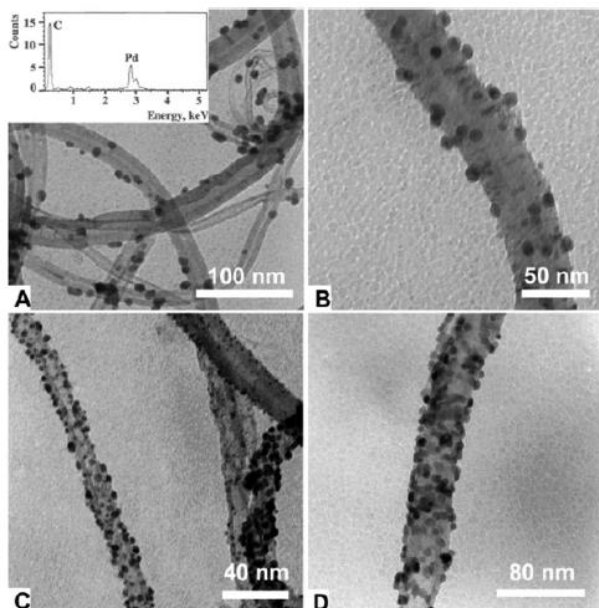


Figure 1.9. TEM images of Pd nanoparticles supported onto MWCNT after hydrogen reduction of (a) 10 mg, (b) 20 mg, (c) 30 mg, and (d) 50 mg Pd(hfa)₂

catalysis without notable decrease in activity.

Attaching palladium nanoparticles onto single-walled carbon nanotubes (SWNT) had also been studied. A three step method to deposit palladium nanoparticles to the SWNT involved the electrochemical activation of SWNT by Na₂SO₄ for 10 minutes followed by the formation of Pd(IV) complex on the activated site of SWNT and then palladium nanoparticles attached to SWNT were formed by the reduction of Pd(IV) complex.⁷³ Pd/SWNT was then used as the catalyst for Suzuki reaction of 4-iodoacetophene and phenylboronic acid. The conversion of the product reached 98% in 40 minutes, suggesting that this catalyst has much higher activity compared to hollow palladium spheres under the same reaction conditions.⁷⁴ This catalyst could also be recycled up to five times without notable loss of activity.

3.3. Nanocatalysts supported on Silica

Silica is widely used as solid support of nanoparticles because it is widely accessible, stable, and provides an inert environment for the immobilization of the nanoparticles. Some methods to deposit palladium nanoparticles to mesoporous silica include ion exchange, wetness impregnation, chemical vapor infiltration, and in situ reduction.

There are many types of mesoporous silica. One example is SBA-15, which is Santa Barbara amorphous type silica. It has a highly ordered pore structure and has pore size between 5-10 nm, which makes it have a large surface area. Palladium nanoparticles could be loaded to SBA-15 and the loading amount is adjusted using different amount of palladium salts.⁷⁵ The catalyst was proven to have good activity in

catalyzing the Suzuki reaction of activated aryl bromides. It can be recycled for five times without notable loss of activity.

Another type of silica is MCM-41 (Mobil Composition of Matter). It can be used as a support to synthesize highly dispersed palladium nanoparticles with narrow size distributions inside the pores.⁷⁶ The pores are used as the template to synthesize nanoparticles, and produced controlled size of the nanoparticles. This catalyst was found to have good activity to catalyze Suzuki reaction of aryl bromides and iodides with phenylboronic acid. It could be recycled for three times without notable loss of activity.

Silica could also be modified using organic compounds such as mercaptopropyl and aminopropyl.⁷⁷ Palladium nanoparticles were loaded into the functionalized silica by treating the surface with Palladium acetate as the precursor and then reducing the precursor to form Palladium nanoparticles. The choice of organic modifiers has an important role for the activity and recyclability of the catalyst. The catalyst had a good activity for Suzuki reaction of phenylboronic acid and 4-bromoanisole when chelators such as diamines or triamines were used as the modifiers.

Nanoreactors could be synthesized using palladium nanoparticles that are anchored to the surface of hollow spheres of mesoporous silica by hydroxyl group.⁷⁸ A thin layer of mesoporous silica is coated onto the Pd/C spheres using tetraethoxysilane as silica source and CTAB as the stabilizer (**Figure 1.10**). C and CTAB are then removed by calcination, producing only nanoparticles inside the hollow spheres. This catalyst has been proven to have a good activity in catalyzing Suzuki reaction between aryl iodides and phenylboronic acids.

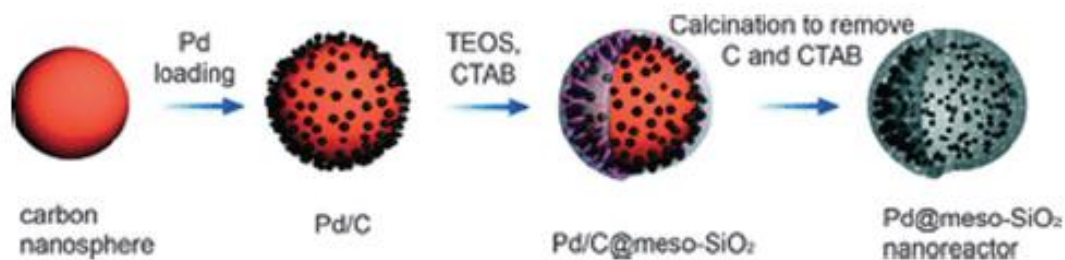


Figure 1.10. Synthesis of nanoreactor.

Another way to support Palladium nanoparticles into silica is capping by dodecanethiol (DT) and 3-mercaptopropyltrimetoxysilane (MPMS).⁷⁹ First, palladium nanoparticles are made by reducing PdCl_2 with hydrazine in an inverse micelle microemulsion. The compound then stabilized with DT and MPMS, which co-condensed with TEOS (**Figure 1.11**). This catalyst has been proven to actively catalyze the Suzuki reaction between 4-bromoanisole and phenylboronic acid. Unfortunately, this catalyst could not be recycled efficiently because of the leaching of palladium into the solution, which reduced the activity significantly.

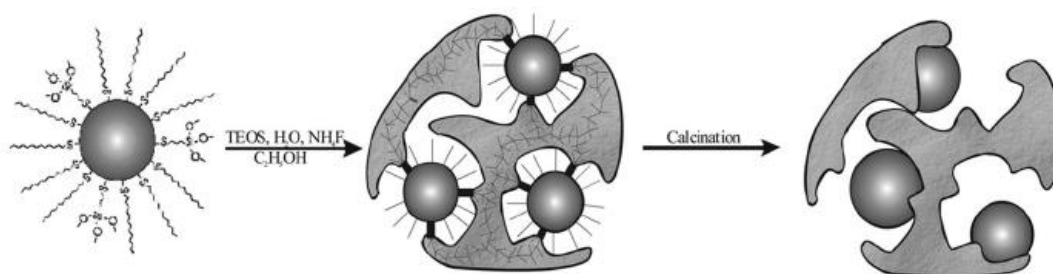


Figure 1.11. Synthesis of Palladium nanoparticles capped with DT and MPMS

In conclusion, there are many ways to synthesize the support materials for nanoparticles, from organic to inorganic materials. The research nowadays are focusing on the most effective and easy way to synthesize the support materials for the nanoparticles so it could be used as an efficient and highly active catalyst with high recycling capacity.

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CHAPTER 2

SIZE EFFECT INVESTIGATION OF PALLADIUM NANOPARTICLES SUPPORTED INTO SILICA COLLOIDS AS THE CATALYST FOR SUZUKI CROSS COUPLING REACTION

Introduction

Published in 1979, Suzuki reaction is a cross coupling reaction between arylboronic acid with aryl halides to form biaryls in the presence of base and catalyst.¹ This versatile and efficient reaction is used to construct complex carbon-carbon bonds as the intermediates in many types of industries. The common catalyst that is used for this reaction is palladium metal.

Nanoparticles are often used as catalyst due to its high surface to volume ratio and high activity of surface atoms compared to bulk catalysts.² It means that low concentration of metal nanoparticles in solution could produce high TON of the product.³ Palladium nanoparticles provide a good catalyst for Suzuki reaction because of its high activity and selectivity.

The ratio of surface area to volume determines the activity of nanoparticle catalyst. As a result, the size of nanoparticles itself determines the activity of the catalyst. Size dependence of homogeneous nanocatalysts has been proven on Suzuki reaction. In 200, Li, *et al.* studied the effect of different sizes of nanoparticles on Suzuki reaction between phenylboronic acid and iodobenzene.⁴ They used the stepwise growth reaction to prepare palladium nanoparticles with PVP as the stabilizer. Palladium

seeds had a size of 3 nm. The three larger nanoparticles had the size of 3.9 nm, 5.2 nm, and 6.6 nm, respectively. Their results showed that the activity of nanoparticles increased as the size decreased except for the smallest nanoparticles. The smallest size nanoparticles showed less catalytic activity because of the surface poisoning by strongly bound species by reaction intermediates.

The problem with homogeneous nanoparticles lies in its recyclability.⁵⁻⁸ It has the same phase as the product, which makes it hard to separate the catalyst and the product. Therefore, heterogeneous nanoparticles are often used as the catalyst for the reaction. In this experiment, silica colloids are used as the support for palladium nanoparticles to catalyze Suzuki reaction. Silica is used because it is widely accessible, stable, easy to synthesize, and provides an inert environment for the immobilization of the nanoparticles.^{9,10} The size of silica colloids can also be modified.

In this experiment, the effect of different sizes of nanoparticles and different sizes of silica colloids was investigated. Different sizes of nanoparticles were synthesized and loaded into the silica colloids. Different sizes of silica colloids were also synthesized and the smallest size of palladium nanoparticles was loaded into the silica colloids. The activity was measured by measuring the amount of product formed over time using HPLC.

Experimental

Synthesis of Different Sizes Palladium Nanoparticles. The different sizes of nanoparticles were synthesized using seed mediated growth method.⁴ The palladium

nanoparticle seeds was synthesized using 0.0667 g of PVP as the stabilizer which was dissolved in 15 mL of 2 mM H_2PdCl_4 added to 21 mL of deionized water and 14 mL of ethanol.^{11,12} The solution was then refluxed for 3 hours at 100°C. The seed was aged for at least a day. The second growth was synthesized by adding 25 mL of the seed to 25 mL of 0.6 mM H_2PdCl_4 in 2:3 ethanol:water (v/v). It was refluxed at 100°C for 3 hours. For the third and fourth growth of palladium nanoparticles, 25 mL of the previous growth was added to 0.3 mM and 0.15 mM H_2PdCl_4 in 2:3 ethanol:water (v/v), respectively. The solution is also refluxed at 100°C for 3 hours.

Synthesis of Different Sizes of Silica Colloids. Silica colloids were synthesized using Stoeber synthesis method.¹³ The smallest silica colloids were synthesized by stirring 30 mL of ethanol and 2.4 mL of ammonium hydroxide for 5 minutes. Then, 1.2 mL of tetraethylorthosilicate was added to the solution and stirred overnight. For the other sizes of silica colloids, the amount of ammonium hydroxide was varied and the volume of ethanol was adjusted so that the total volume became 33.6 mL. For the different sizes of silica colloids, the amounts of ammonium hydroxide used were 2.0 mL, 2.6 mL, and 3.0 mL.

Synthesis of Colloidal-Supported Palladium Nanoparticles. Palladium nanoparticles was added to the silica colloid suspension in 2:1 ratio of nanoparticles:silica colloid and stirred for 24 hours. After that, the solution was centrifuged at 13,500 rpm for 3 minutes. After the first centrifugation, silica colloids were dispersed in ethanol for two times and deionized water for another two times for a total of four times of centrifugation. For the last centrifugation, the supernatant was poured off and the pellet was air-dried overnight.

Characterization by Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS). The pellet from the step above was dispersed in deionized water and diluted 10-fold. One drop of the solution was spotted on copper grids and air-dried overnight. TEM images and EDS spectra were obtained using JEOL 2100EX TEM.

Size Distribution Analysis. The UTHSCSA ImageTool for Windows Version 3 image analysis software was used to determine the size distribution of palladium nanoparticles and silica colloids. The number of pixels in the scale bar of the TEM image was measured using distance tool in the Analysis pull-down menu. Based on the number of pixels for the fixed size associated with the scale bar and measuring the number of pixels for nanoparticles and silica colloids from several TEM images, the size can be calculated by dividing the number of pixels of nanoparticles and silica colloids by the number of pixels of the scale bar and multiplying by the fixed size associated with the scale bar of the TEM image. The histogram was plotted based on the size of the nanoparticles and silica colloids and percent of nanoparticles. Gaussian fit for the histogram was obtained to determine the average size and standard deviation of the nanoparticles and silica colloids.

Suzuki Cross-Coupling Reaction. Suzuki reaction of phenylboronic acid and iodobenzene to form biphenyl was used in this experiment. Six mmol of sodium acetate, 3 mmol of phenylboronic acid, and 1 mmol of iodobenzene were added of 150 mL of 3:1 acetonitrile:water (v/v). The solution was heated to 100°C and 0.1 g of dried catalyst synthesized before was added. The mixture was refluxed for 24 hours and samples were taken at certain times to be analyzed using HPLC. The column used was

Zorbax Eclipse Plus C18 (4.6 x 150 mm, 5 micron) and the solvent used for the separation was 70% acetonitrile and 30% water. The flow rate was set at 1 mL/min, isocratic elution, and the wavelength of the detector used was 230 nm.

Results and Discussion

Synthesis of Different Sizes of Palladium Nanoparticles and Silica Colloids.

Figure 2.1 showed the representative TEM image of palladium nanoparticle seeds and their size distribution histogram with the average size of the nanoparticles. The size distributions that were determined by using ImageTool software were plotted into a size distribution histogram. Gaussian fit of the histogram showed an average size of (2.03 ± 0.46) nm. The small standard deviation showed that the nanoparticles were monodisperse in the solution.

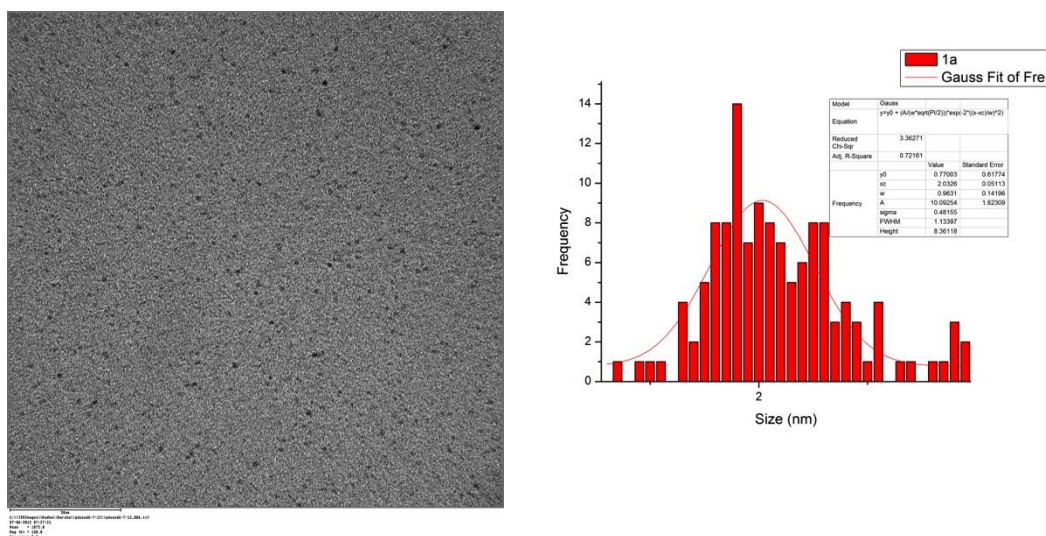


Figure 2.1. TEM image of Pd nanoparticles seed (a) and size distribution histogram of the nanoparticles (b)

Figure 2.2 showed the representative TEM image of the second growth of palladium nanoparticles and their histogram. The Gaussian fit of the histogram showed the average size of (4.80 ± 1.04) nm. The standard deviation also showed that the nanoparticles are relatively monodisperse in the solution.

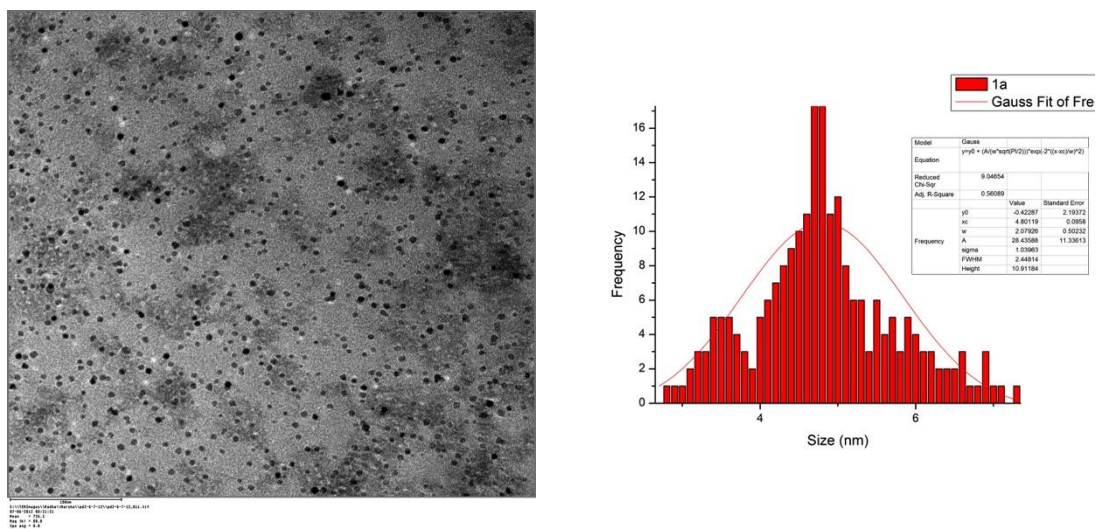


Figure 2.2. TEM image of second growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b)

Figure 2.3 showed the TEM representative image of the third growth of Palladium nanoparticles and their histogram. The Gaussian fit of the histogram showed the average size of (5.01 ± 1.08) nm. The standard deviation also showed that the nanoparticles are relatively monodisperse in the solution

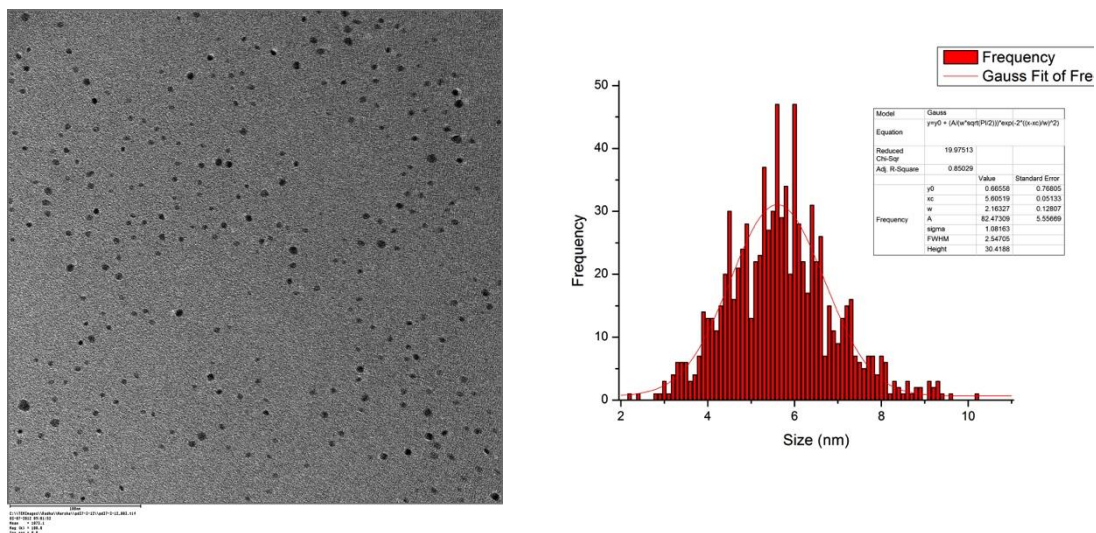


Figure 2.3. TEM image of third growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b)

Figure 2.4 showed the TEM representative image of the fourth growth of Palladium nanoparticles and their histogram. The Gaussian fit of the histogram showed the average size of (6.01 ± 0.93) nm. The standard deviation also showed that the nanoparticles are relatively monodispersed in the solution

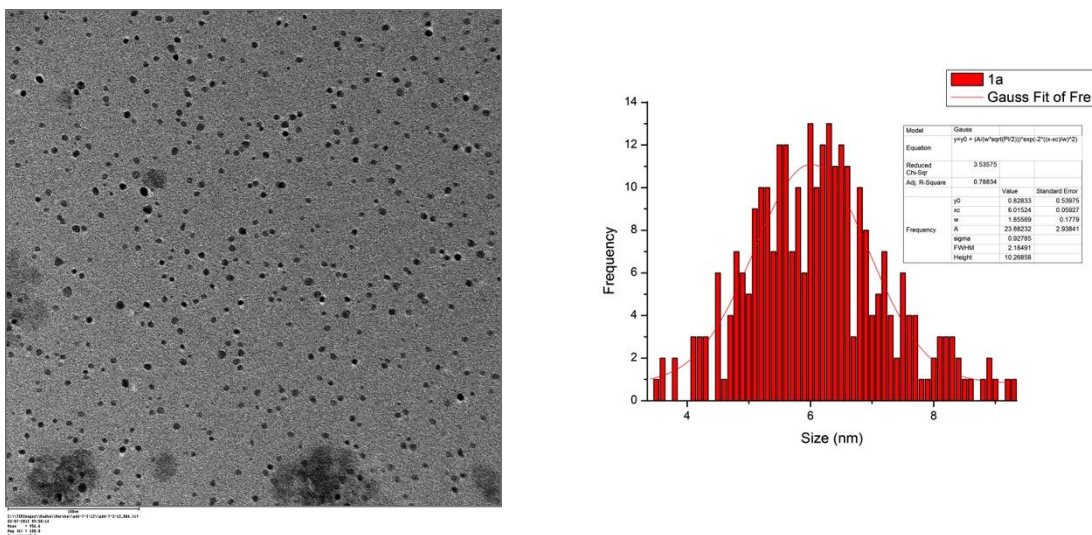


Figure 2.4. TEM image of fourth growth of Pd nanoparticles (a) and size distribution histogram of the nanoparticles (b)

The representative TEM images and size distribution histograms above showed that the seed-mediated growth method to synthesize different size nanoparticles worked well as it provides larger size of nanoparticles on each growth and small standard deviations which meant that the nanoparticles produced are uniform in size and monodisperse in the solution well.

Different sizes of palladium nanoparticles above were then loaded into the same size silica colloid (2.4 mL ammonium hydroxide). **Figure 2.5** showed the representative TEM image of Pd seed loaded into the silica colloids and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (120 ± 1.84) nm. The small standard deviation showed the size uniformity of silica colloids.

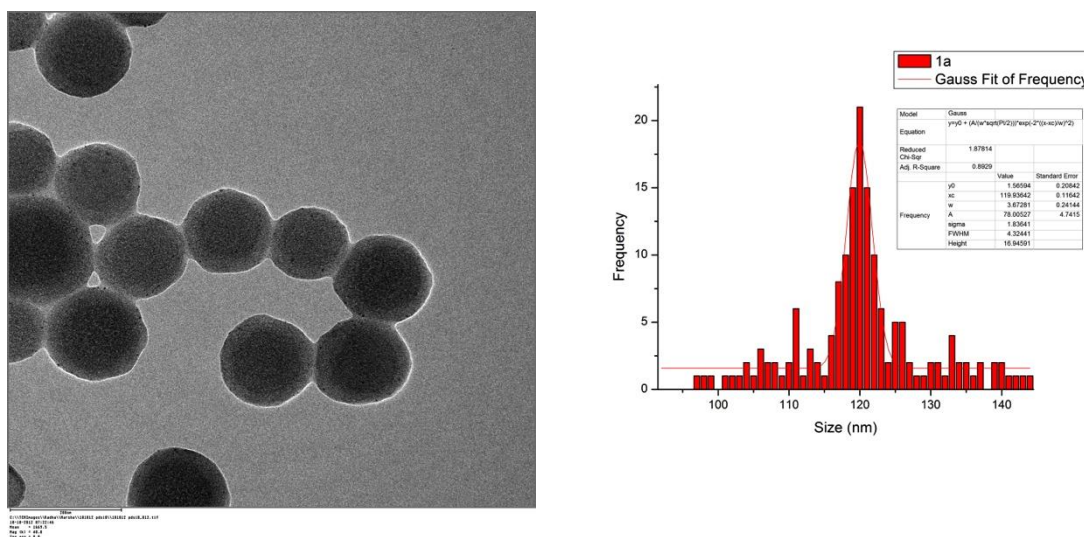


Figure 2.5. TEM image of Pd seed nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b)

Figure 2.6 showed the representative TEM image of second growth nanoparticles loaded into the silica colloids and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (120 ± 8.67) nm. The small standard deviation showed the size uniformity of the silica colloids.

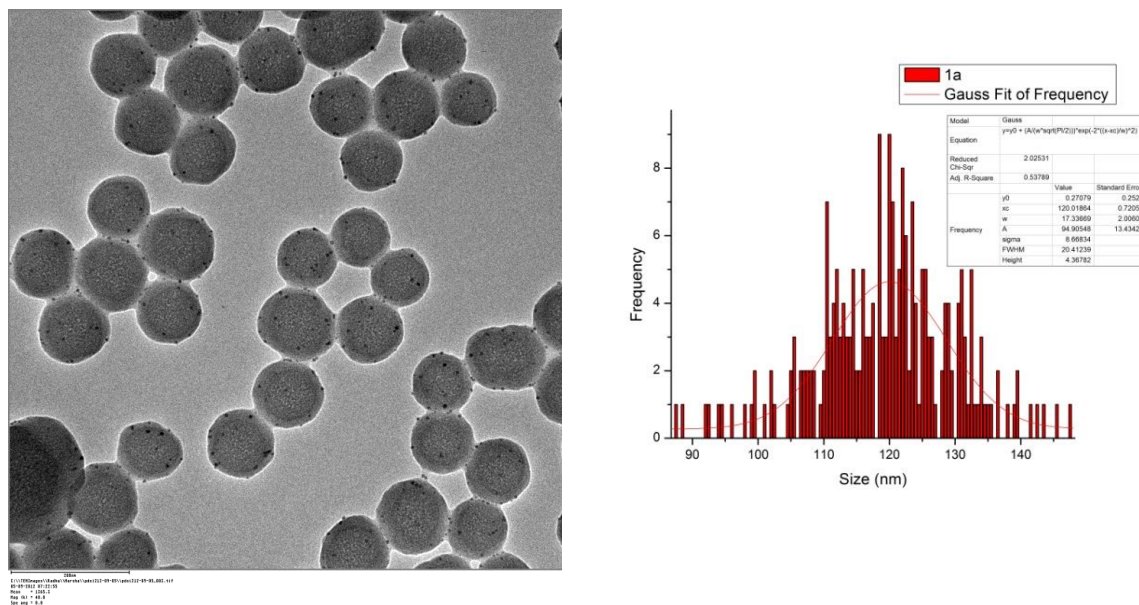


Figure 2.6. TEM image of second growth of Pd nanoparticles loaded into silica colloids(a) and size distribution histogram of the nanoparticles (b)

Figure 2.7 showed the representative TEM image of third growth of Pd nanoparticles loaded into the silica colloids and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (120 ± 6.32) nm. The small standard deviation showed the size uniformity of the silica colloids.

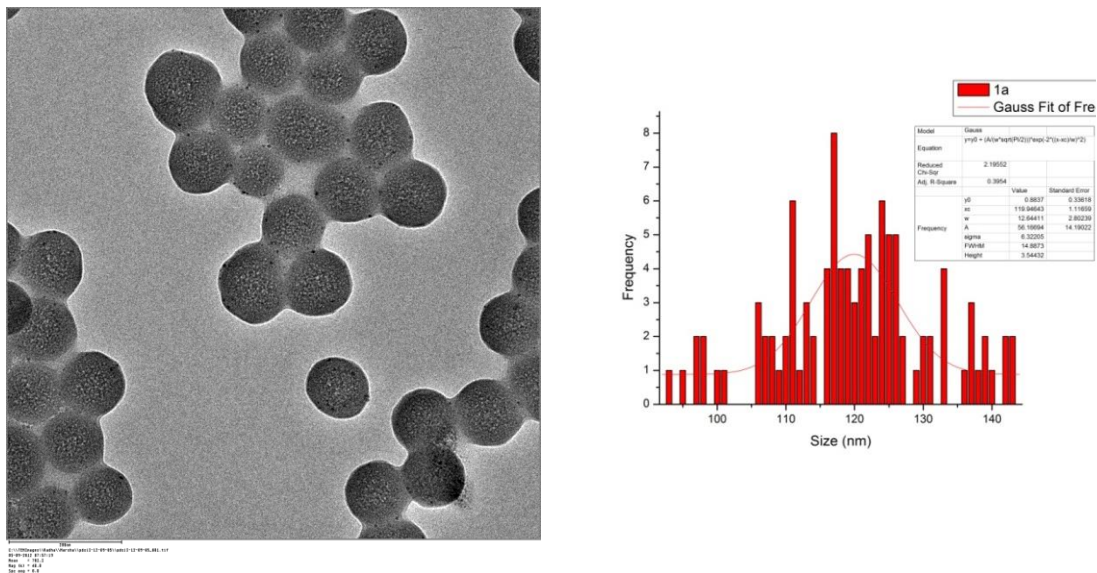


Figure 2.7. TEM image of third growth of Pd nanoparticles loaded into silica colloids(a) and size distribution histogram of the nanoparticles (b)

Figure 2.8 showed the representative TEM image of the fourth growth of Pd nanoparticles loaded into the silica colloids and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (120 ± 2.57) nm. The small standard deviation showed the size uniformity of the silica colloids.

The representative images and size distribution histograms above showed that the same size silica colloids had been synthesized. Furthermore, different size of nanoparticles had also been successfully loaded into the silica colloids as the nanoparticles could be seen attached to the silica colloid.

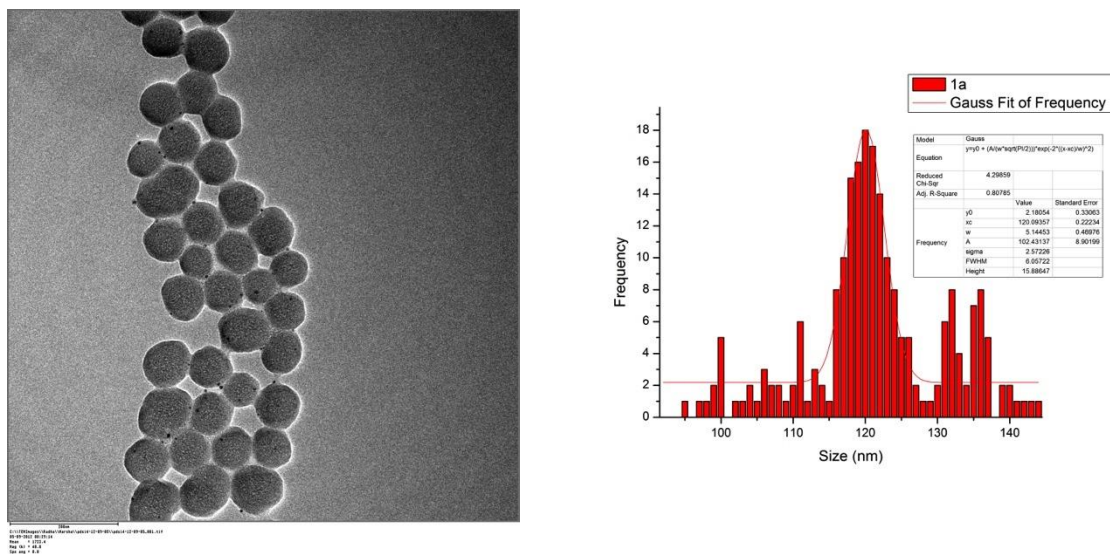


Figure 2.8. TEM image of fourth growth of Palladium nanoparticles loaded into silica colloids (a) and size distribution histogram of the nanoparticles (b)

The next experiment was to synthesize different size of silica colloids and loaded Pd seeds into them. The base in the Stober method synthesis acted as catalyst to form the silica colloid. So, adding different amount of base could produce different size of silica colloids. Smaller amount of ammonium hydroxide produced the smaller size of silica colloids and larger amount of ammonium hydroxide produced larger size of silica colloids. However, there is also limitation in the smallest and largest size of the silica colloids obtained by varying the amount of base. Too little base would not catalyze the reaction to form the silica colloids and too much base would not be able to control the size of silica colloids, which made the size distributions not uniform. The amount of ammonium hydroxide had been optimized in this experiment to produce different size of silica colloid with uniform size distribution.

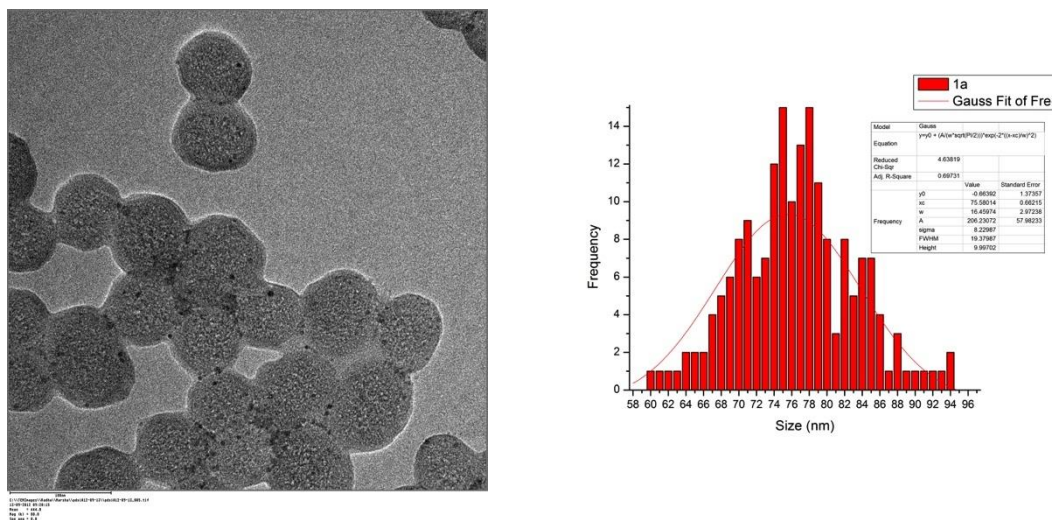


Figure 2.9. TEM image of Pd seed loaded into 2.0 mL base (a) and size distribution histogram of the nanoparticles (b)

Figure 2.9 showed the representative image of Pd seed loaded into the 2.0 mL ammonium hydroxide added silica colloid and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (75.58 ± 8.23) nm.

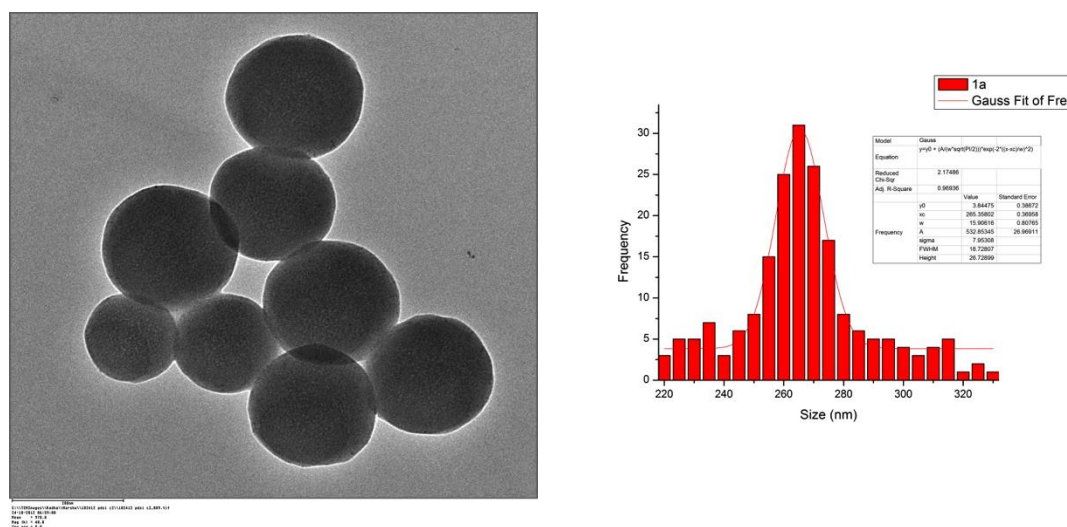


Figure 2.10. TEM image of Pd seed loaded into 2.6 mL base (a) and size distribution histogram of the nanoparticles (b)

Figure 2.10 showed the representative image of Pd seed loaded into the 2.0 mL ammonium hydroxide added silica colloid and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (265 ± 7.95) nm.

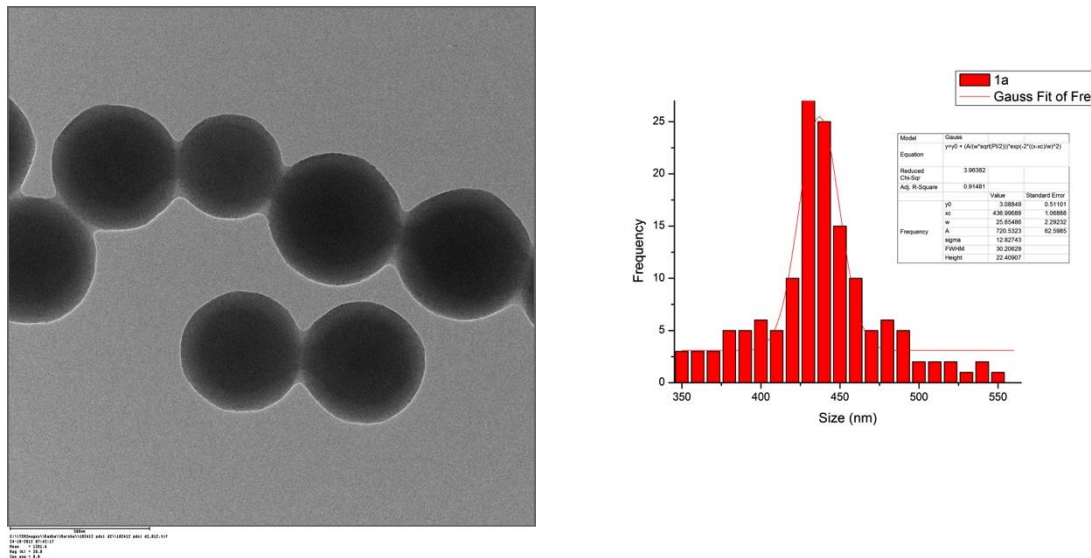


Figure 2.11. TEM image of Pd seed loaded into 3.0 mL base (a) and size distribution histogram of the nanoparticles (b)

Figure 2.11 showed the representative image of Pd seed loaded into the 2.0 mL ammonium hydroxide added silica colloid and its size distribution histogram. The Gaussian fit of the histogram showed the average size of silica colloids to be (437 ± 12.8) nm.

The representative TEM images and size distribution histograms of the Pd seed loaded into the different size of silica colloids showed that changing the amount of base was also changing the size of silica colloids. The relatively low standard deviation showed that the method produced uniform size of silica colloids which

ensured that most of the silica colloids used for the catalysis had similar size. The Pd nanoparticles could also be seen in the picture, which ensured that the Pd nanoparticles is loaded into the silica colloids.

Beside TEM images and size distribution histograms, Energy Dispersive X-Ray Spectroscopy (EDS) spectra were also obtained to ensure that the metal nanoparticles formed were Palladium. **Figure 2.12** showed representative of EDS spectra of palladium nanoparticles loaded into the silica colloids. On the spectrum, it could be seen that the samples contained silicon and palladium. The presence of Si and Pd confirmed that the catalyst that are used contained palladium metal loaded to the silica colloids.

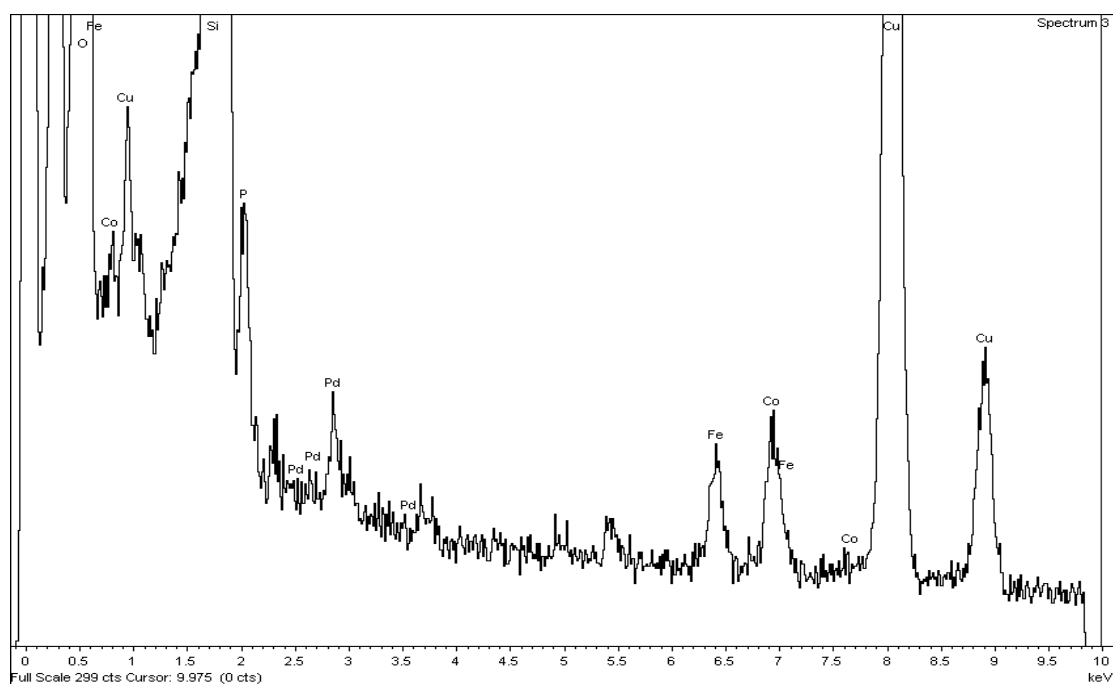


Figure 2.12. EDS spectrum of Pd nanoparticles loaded into silica colloids

Suzuki Cross-Coupling Reaction Catalyzed by Pd Nanoparticles Loaded onto Silica Colloids. Suzuki reaction was done for 24 hours. Samples were taken at 0 mins, 5 mins, 10 mins, 20 mins, 30 mins, 45 mins, 1 hr, 3 hr, 6 hr, 9 hr, and 12 hours. The concentration of biphenyl was determined using HPLC. The experiments were done for four times and the reading of HPLC was done in triplicates.

Figure 2.13 showed the representative of chromatograph for the Suzuki reaction obtained by HPLC. The retention time of phenylboronic acid, iodobenzene, and biphenyl were found to be around 1.8 mins, 7.0 mins, and 9.6 mins, respectively.

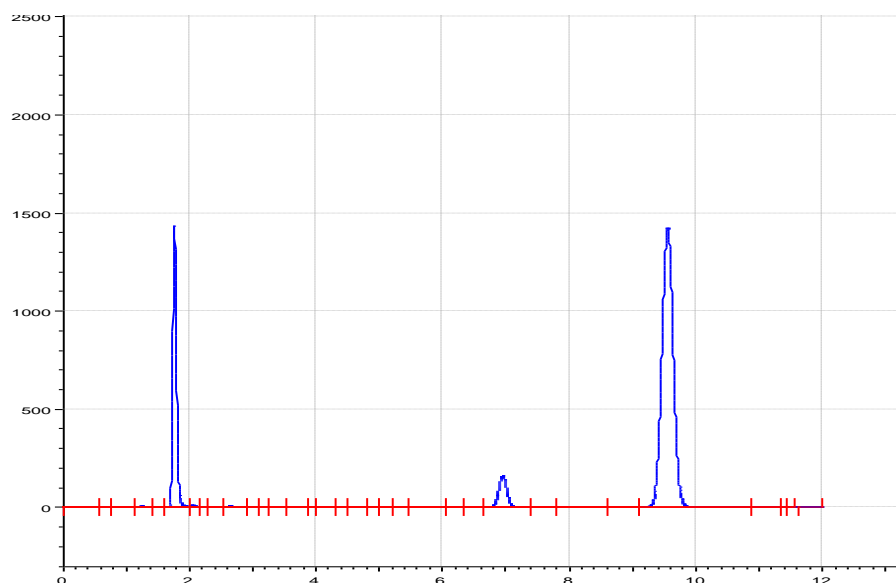


Figure 2.13. Chromatograph of Suzuki reaction using HPLC

Figure 2.14 showed the calibration curve of the area versus biphenyl concentration. The high R^2 showed that the area could be confidently used as to determine the concentration of the product.

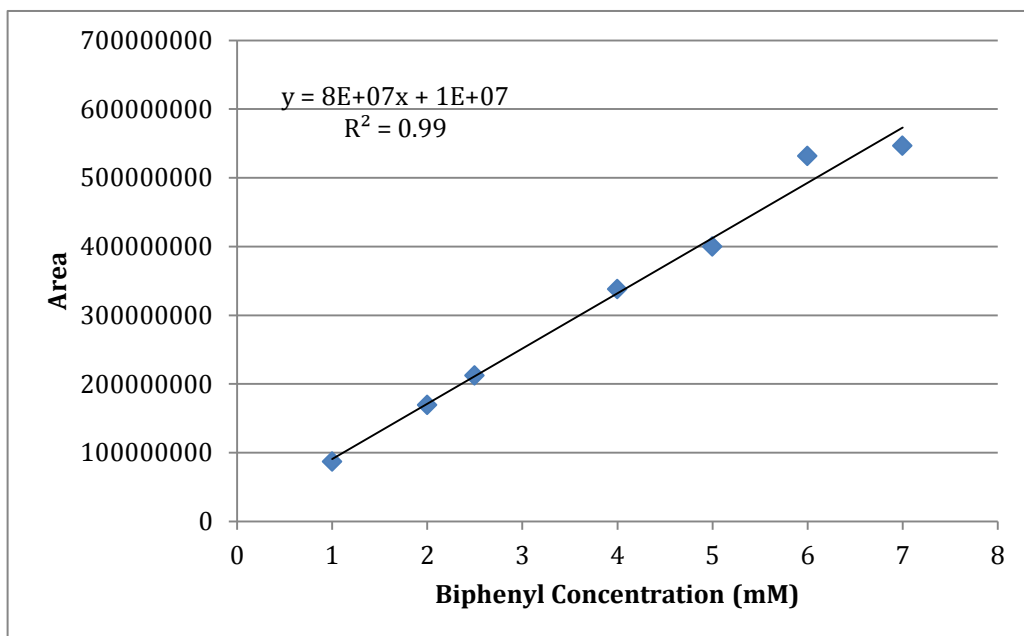


Figure 2.14. Calibration curve of biphenyl concentration

Figure 2.15 showed the biphenyl concentration versus time up to one hour of the Suzuki reaction with different sizes of Pd nanoparticles loaded into the same size of silica colloids. Overall it showed that the smaller the size of nanoparticle was, the higher activity it had. The higher catalytic activity was indicated by the higher biphenyl concentration over time. However, the seed showed less activity than the second growth but still higher than the third and fourth growth for the first 10 minutes. It could happen because the leeching of nanoparticles from the silica colloid into the solution. The leached nanoparticles catalyzed the reaction homogeneously. It has been proven that the smaller size of nanoparticles has stronger adsorption to the reaction

intermediate, which leads to catalytic poisoning.¹⁴⁻¹⁸ The result of catalytic poisoning is decreased activity in the smaller sized nanoparticles. The same thing happened with the leached nanoparticles in here. It also underwent catalytic poisoning in the homogeneous phase. However, most of the nanoparticles were loaded into the silica colloids. The heterogeneous phase of the catalyst did not undergo catalytic poisoning, so it had higher activity after 10 minutes compared to the others.

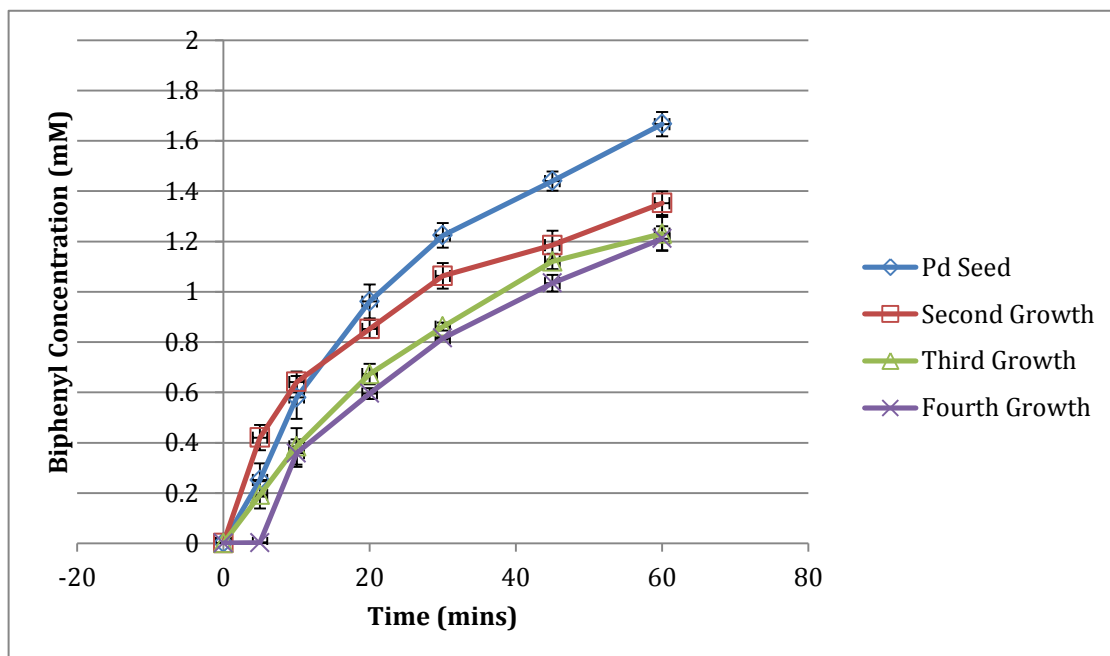


Figure 2.15. Graph of Suzuki reaction of different sizes Pd nanoparticles loaded into silica colloids for 1 hour reaction

Figure 2.16 showed the biphenyl concentration versus time up to 12 hours of the Suzuki reaction with different sizes of Pd nanoparticles loaded into the same size of silica colloids. Overall, it also showed that the smaller size of nanoparticles provided higher catalytic activity to the reaction. It could also be seen that the reaction

was completely done after around nine hours. The final concentration of biphenyl was found to be around 3 mM.

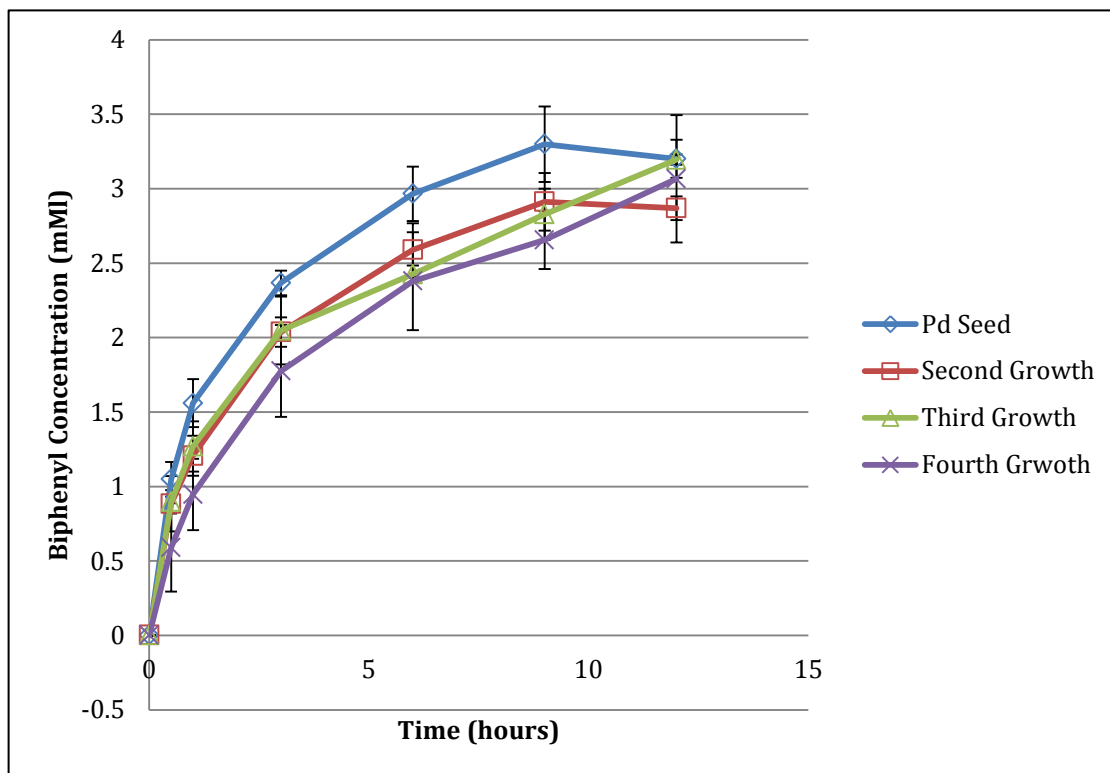


Figure 2.16. Graph of Suzuki reaction of different sizes Pd nanoparticles loaded into silica colloids for 12 hours reaction

Figure 2.17 showed the biphenyl concentration versus time up to 1 hour of the Suzuki reaction with different sizes of Pd seed nanoparticles loaded into the different sizes of silica colloids. The graph showed that the smaller size of silica colloids provided higher catalytic activity compared to the larger size silica colloids. The 76 nm silica colloids showed significantly higher activity compared to the 120 nm silica colloids. However, the 265 nm and 437 nm silica colloids showed similar catalytic activity. This trend could also be observed up to 12 hours of reaction (**Figure 2.18**).

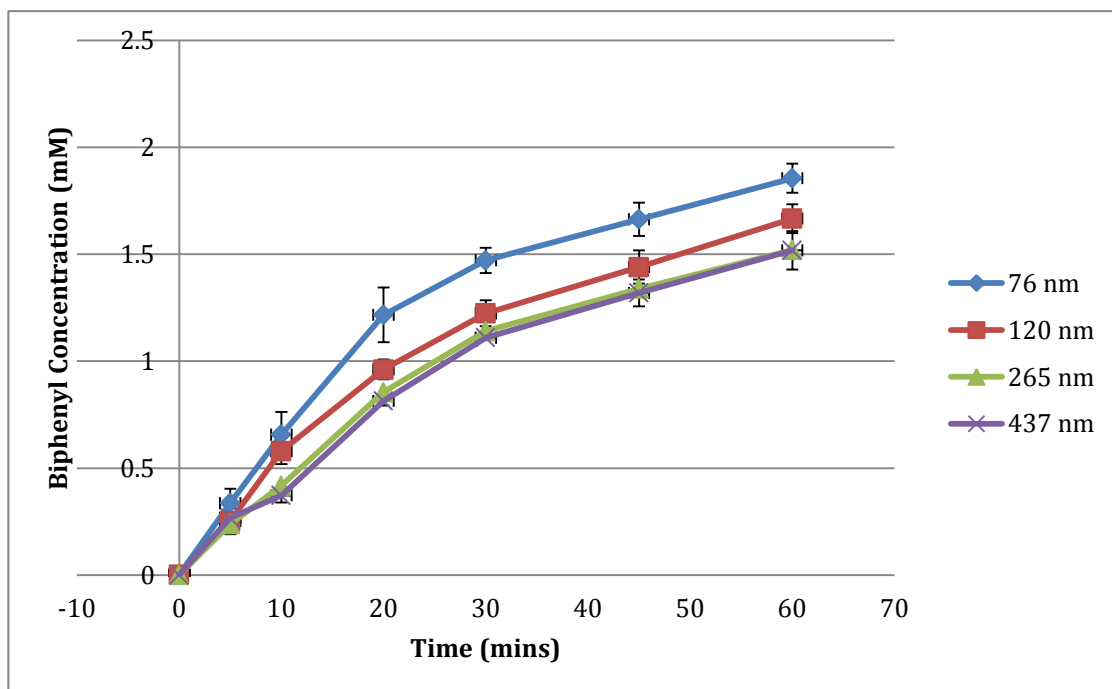


Figure 2.17. Graph of Suzuki reaction of Pd seed nanoparticles loaded into different sizes of silica colloids for 1 hour reaction

The smaller size of silica colloids has larger surface area to volume ratio, therefore many nanoparticles are more readily available to the substrate. Therefore, it could produce higher concentration of product in shorter time. As for the larger size of the silica colloids, similar activity could happen because of saturation of nanoparticles that could be loaded into the silica colloids. Because the volume was too big compared to the available surface area, the silica colloids touched each other and therefore reducing the surface area of the sphere for Pd nanoparticles to attach themselves.

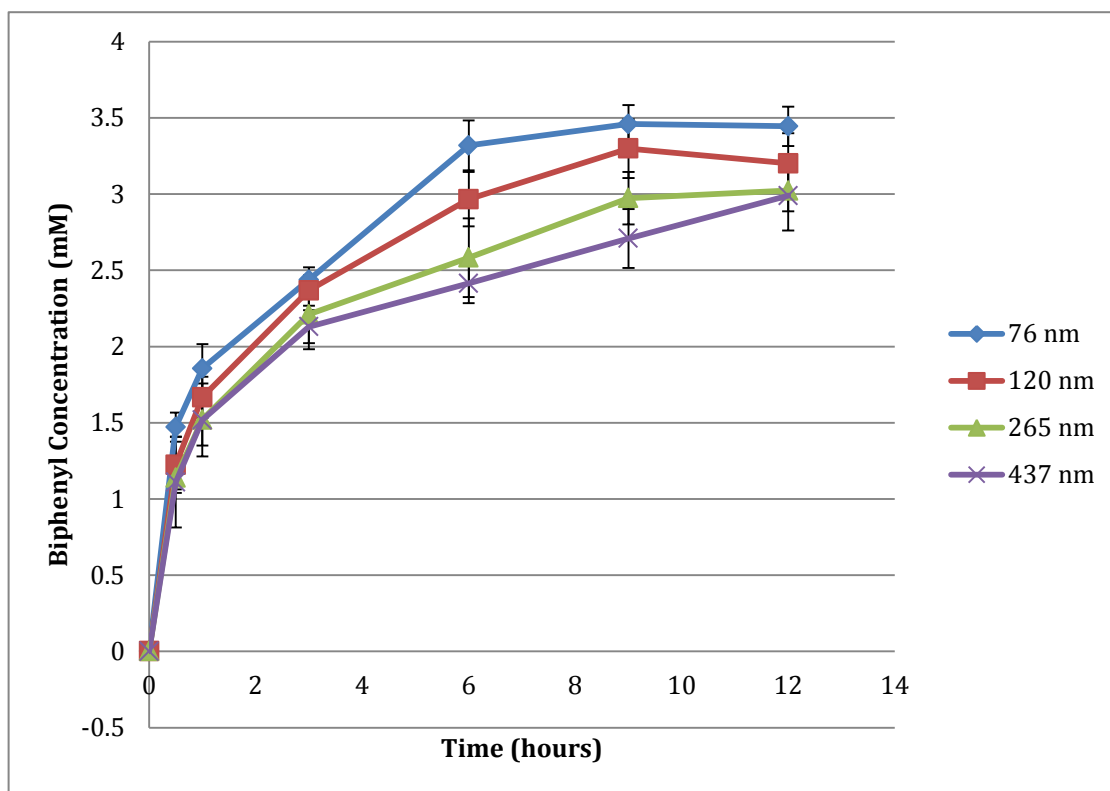


Figure 2.18. Graph of Suzuki reaction of Pd seed nanoparticles loaded into different sizes of silica colloids for 12 hours reaction

Conclusions

Different sizes of Palladium nanoparticles were successfully synthesized using seed-mediated growth method. The sizes of nanoparticles obtained from this method were 2.0 nm, 4.8 nm, 5.0 nm, and 6 nm from the seed to the fourth growth, respectively. TEM images and size distribution histogram showed that the different sizes of Pd nanoparticles loaded into the silica colloids were relatively uniform in size. These different sizes of nanoparticles were loaded into 120 nm silica colloids that

were then used as the catalyst for Suzuki reaction. Overall, the result showed that smaller size of nanoparticles produced higher catalytic activity of the reaction.

Different sizes of silica colloids were also successfully synthesized using different amount of ammonium hydroxide. Lower amount of ammonium hydroxide produced smaller size of silica colloids. The sizes of silica colloids produced were 76 nm, 120 nm, 265 nm, and 437 nm. TEM images and size distribution histogram showed that the Pd nanoparticles loaded into the different sizes of silica colloids were relatively uniform in size. Palladium nanoparticles with the size of 2.0 nm (seed) were loaded into these different sizes of silica colloids. The smaller size of silica colloids produced higher catalytic activity than the larger ones. However, the two largest of silica colloids showed similar catalytic activity.

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