

MAGNETIC NANOPARTICLES SUPPORTED BIO-STABILISED PALLADIUM
CATALYST FOR THE COPPER-FREE SONOGASHIRA REACTION

NURAFIQAH BINTI NORDIN

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*In the name of Allah, the Beneficent and the Most Merciful,
and peace be upon Muhammad, His messenger.*

*To my dearest family for the immense love and support,
and to my beloved cats Mimo, Puteh and Mimi for the great companions.*

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ABSTRACT

Palladium mediated catalysis has achieved an impressive place in numerous commercial chemical processes. In particular, due to its high surface area to volume ratio, palladium nanoparticles (PdNPs) show high reactivity that makes them a powerful catalyst for many organic transformations. Green synthesis of PdNPs employing plant extract has been suggested as eco-friendly alternatives to chemical and physical methods. In this research, the synthesis of PdNPs using *Artocarpus altilis* aqueous leaf extract was investigated. The biomolecules present in the *Artocarpus altilis* leaf extract are believed to act as reducing and as capping agent for the formation of PdNPs. Effect of reaction time, metal ion concentration, volume of leaf extract and pH of the extract on the formation of PdNPs were investigated and monitored using UV-vis spectroscopic analysis. The optimised conditions were used in the synthesis of PdNPs supported on the amine functionalised silica-coated magnetite nanoparticles. The use of magnetite as catalyst support is attractive since magnetic separation has emerged as a robust, highly efficient, and rapid catalyst separation tool. Meanwhile, ligand assisted method employing 3-(2-aminoethylamino)propyl trimethoxysilane (AEAPTS) covalently anchored the PdNPs thus controlled the PdNPs size and prevented agglomeration. The bio-stabilised PdNPs supported on the amine functionalised silica-coated magnetite (Fe₃O₄-SiO₂-AEAPTS-PdNPs) catalyst was characterised using Fourier transform infrared spectroscopy (FTIR), CHN analysis, X-ray diffraction (XRD), flame atomic absorption spectrophotometry (FAAS), high resolution transmission electron microscopy-energy dispersive X-ray spectroscopy (HRTEM-EDX), vibrating-sample magnetometer (VSM), zeta potential and X-ray photoelectron spectroscopy (XPS) analyses. The Fe₃O₄-SiO₂-AEAPTS-PdNPs catalyst was then tested in the copper-free Sonogashira reaction under aerobic condition in water. Effect of base, catalyst amount, and temperature on the reaction conversion was investigated and monitored using gas chromatography-flame ionisation detection (GC-FID). The optimisation reaction between phenylacetylene and iodobenzene to yield diphenylacetylene successfully gave 90% conversion using 0.2 mol% of Fe₃O₄-SiO₂-AEAPTS-PdNPs catalyst with triethylamine as base at 60°C for 24 h. Fe₃O₄-SiO₂-AEAPTS-PdNPs showed an impressive catalytic performance with turnover number of 450 and turnover frequency of 18.8 h⁻¹. In addition, the recycle test result showed that the catalyst can be used up to four cycles without significant loss of catalytic activity. Fe₃O₄-SiO₂-AEAPTS-PdNPs catalyst was further examined in the reaction between phenylacetylene and less reactive aryl halides which reacted well at 80°C and gave desired products with good yields. The coupling of bromobenzene and phenylacetylene gave good conversion of 49% while activated bromobenzene such as 4-bromoacetophenone and 1-bromo-4-nitrobenzene, bearing electron-withdrawing group at their *para*-positions gave better conversion of 53% and 56%, respectively. All crude products were isolated and purified using column chromatography and were characterised using gas chromatography-mass spectrometry (GC-MS) and FTIR, ¹H nuclear magnetic resonance (¹H-NMR) and ¹³C nuclear magnetic resonance (¹³C-NMR) spectroscopic analyses.

ABSTRAK

Pemangkinan pengantara palladium telah mencapai status yang mengagumkan dalam pelbagai proses kimia komersial. Khususnya, disebabkan nisbah luas permukaan kepada isipadunya yang tinggi, nanopartikel palladium (PdNPs) menunjukkan kereaktifan yang tinggi yang menjadikannya sebagai mangkin yang berkuasa bagi kebanyakan transformasi organik. Sintesis hijau PdNPs yang menggunakan ekstrak tumbuhan telah dicadangkan sebagai alternatif yang mesra alam berbanding kaedah kimia dan fizikal. Dalam penyelidikan ini, sintesis PdNPs menggunakan ekstrak akueus daun *Artocarpus altilis* telah dikaji. Biomolekul yang terdapat di dalam ekstrak daun *Artocarpus altilis* dipercayai berfungsi sebagai agen penurun dan penutup untuk pembentukan PdNPs. Kesan masa tindak balas, kepekatan ion logam, isipadu ekstrak daun dan pH ekstrak terhadap pembentukan PdNPs telah disiasat dan dipantau menggunakan teknik spektroskopi ultra lembayung-nampak (UV-vis). Keadaan optimum telah diguna dalam sintesis PdNPs yang disokong pada nanopartikel magnetit bersalut silika berkefungsian amina. Penggunaan magnetit sebagai penyokong mangkin adalah menarik kerana pengasingan magnetik telah muncul sebagai alat pengasingan mangkin yang teguh, sangat cekap dan cepat. Sementara itu, kaedah berbantuan ligan menggunakan 3-(2-aminaetilamina)propil trimetoksisilan (AEAPTS) telah memegang PdNPs secara kovalen, dengan itu dapat mengawal saiz PdNPs dan menghalang aglomerasi. Mangkin bio-stabil PdNPs yang disokong pada magnetit bersalut silika berkefungsian amina (Fe₃O₄-SiO₂-AEAPTS-PdNPs) telah dicirikan menggunakan analisis spektroskopi inframerah transformasi Fourier (FTIR), analisis CHN, pembelauan sinar-X (XRD), spektrofotometri penyerapan atom nyala (FAAS), mikroskopi elektron penghantaran resolusi tinggi spektroskopi serakan tenaga sinar-X (HRTEM-EDX), magnetometer sampel bergetar (VSM), potensi zeta dan spektroskopi fotoelektron sinar-X (XPS). Mangkin Fe₃O₄-SiO₂-AEAPTS-PdNPs kemudian telah diuji dalam tindak balas Sonogashira bebas-tembaga di bawah keadaan aerobik di dalam air. Kesan bes, jumlah mangkin, dan suhu terhadap penukaran tindak balas telah dikaji dan dipantau menggunakan kromatografi gas-pengesanan pengionan nyala (GC-FID). Pengoptimuman tindak balas antara fenilasetilena dan iodobenzena untuk menghasilkan difenilasetilena telah berjaya memberikan 90% penukaran menggunakan 0.2 mol% mangkin Fe₃O₄-SiO₂-AEAPTS-PdNPs dengan trietilamina sebagai bes pada 60°C selama 24 jam. Fe₃O₄-SiO₂-AEAPTS-PdNPs menunjukkan prestasi mengagumkan dengan jumlah perolehan 450 dan kekerapan perolehan 18.8 h⁻¹. Tambahan lagi, hasil ujian kitar semula menunjukkan bahawa mangkin itu boleh digunakan sehingga empat kitaran tanpa kehilangan aktiviti pemangkinan yang ketara. Mangkin Fe₃O₄-SiO₂-AEAPTS-PdNPs selanjutnya diuji dalam tindak balas antara fenilasetilena dan aril halida yang kurang reaktif bertindak balas pada 80°C dan memberikan produk dikehendaki dengan hasil yang baik. Gabungan bromobenzena dan fenilasetilena memberikan penukaran yang baik iaitu 49% sementara bromobenzena diaktifkan misalnya 4-bromoasetofenon dan 1-bromo-4-nitrobenzena, yang mengandungi kumpulan penarik elektron pada kedudukan-*para* memberikan penukaran yang lebih baik, iaitu masing-masing 53% dan 56%. Semua produk mentah telah diasingkan dan dituliskan menggunakan kromatografi turus dan dicirikan menggunakan analisis kromatografi gas-spektrometri jisim (GC-MS) dan spektroskopi FTIR, resonans magnet nucleus ¹H (¹H-NMR) dan resonans magnet nucleus ¹³C (¹³C-NMR).

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LIST OF ABBREVIATIONS

AAS	- atomic absorption spectrometry
AEAPTS	- amino ethyl amino propyl trimethoxy silane
CDCl_3	- deuterated chloroform
CHNS	- carbon, hydrogen, nitrogen, sulphur analysis
Cu	- Copper
DIPEA	- N, N-Diisopropylethylamine
EDX	- energy dispersed X-ray
Fcc	- face-centred cubic
Fe	- Iron
FeO	- wustite
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	- Ferrous chloride tetrahydrate
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	- Ferric chloride hexahydrate
FRAP	- Ferric reducing antioxidant power
FeSO_4	- Ferrous sulphate
FTIR	- fourier transform infrared spectra
Fe_2O_3	- Ferric oxides
Fe_3O_4	- magnetite
$\text{Fe}_3\text{O}_4\text{-SiO}_2$	- silica-coated magnetite
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AEAPTS}$	- AEAPTS functionalised $\text{Fe}_3\text{O}_4\text{-SiO}_2$
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AEAPTS-Pd(II)}$	- Pd(II) ions immobilised on $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AEAPTS}$
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AEAPTS-PdNPs}$	- $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AEAPTS}$ supported PdNPs
GC	- gas chromatography
GC-FID	- gas chromatography-flame ionisation detector
GC-MS	- gas chromatography mass spectrometry
H_c	- coercivity
HCl	- hydrochloric acid

HRTEM	- high-resolution transmission electron microscopy
KBr	- potassium bromide
KBSI	- Korea Basic Science Institute
K ₂ CO ₃	- potassium carbonate
MCM-41-S-Pd(0)	- MCM-41-supported thioether palladium(0) complex
<i>Mr</i>	- remanence
MRI	- magnetic resonance imaging
<i>Ms</i>	- saturation magnetisation
NaOH	- sodium hydroxide
Na ₂ CO ₃	- sodium carbonate
NHC	- N-heterocyclic carbene
NH ₄ OH	- ammonium hydroxide
Ni	- Nickel
N ₂	- nitrogen gas
Pd	- Palladium
PdCl ₂	- Palladium chloride
PdNPs	- Palladium nanoparticles
<i>pK_a</i>	- acid dissociation constant
PNP-SSS	- Palladium nanoparticles on a silica-starch substrate
PS-PEG-terpyridine-Pd(II)	- polystyrene-poly(ethylene glycol) resin-supported terpyridine-palladium complex
SiO ₂	- silica
TEOS	- tetraethyl orthosilicate
TOF	- turnover frequency
TON	- turnover number
TPTZ	- 2,4,6-tris(2-pyridyl)-5-triazine
UTM	- Universiti Teknologi Malaysia
UKM	- Universiti Kebangsaan Malaysia
UV-Vis	- ultraviolet-visible spectroscopy
VSM	- vibrating sample magnetometer

- XPS - X-ray photoelectron spectroscopy
- XRD - X-ray powder diffraction analysis
- ^1H -NMR - ^1H nuclear magnetic resonance
- ^{13}C -NMR - ^{13}C nuclear magnetic resonance

LIST OF SYMBOLS

%	-	percent
λ	-	wavelength
°	-	degree angle
°C	-	degree Celsius
°C min ⁻¹	-	degree Celsius per minute
μ L	-	microlitre
2 θ	-	Bragg angle
Å	-	Angstrom
cm	-	centimetre
cm ⁻¹	-	frequency
Cu K α	-	X-ray diffraction from copper energy levels
emu/g	-	magnetic moment per gram
eV	-	electron volt
g	-	gram
g mL ⁻¹	-	density
g mol ⁻¹	-	gram per mole
h	-	hour
h ⁻¹	-	per hour
Hz	-	Hertz
kV	-	kilovolt
M	-	Molarity
m	-	metre
mA	-	milliampere
mg	-	milligram
MHz	-	Mega Hertz
min	-	minute(s)
mL	-	millilitre
mm	-	millimetre
mM	-	milliMolar

mmol	- millimole
mmol g ⁻¹	- millimole per gram
mol g ⁻¹	- mole per gram
mol%	- mole percent
mV	- millivolt
nm	- nanometre
Oe	- Oersted
ppm	- part per million
rpm	- revolutions per minute
R ²	- coefficient of determination

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G6	¹³ C-NMR spectrum of substrate (2c)	100
G7	FTIR spectrum of substrate (2d)	101
G8	¹ H-NMR spectrum of substrate (2d)	102
G9	¹³ C-NMR spectrum of substrate (2d)	103
H1	GC-MS spectrum of compound (3a)	104
H2	FTIR spectrum of product (3a)	105
H3	¹ H-NMR spectrum of compound (3a)	106
H4	¹³ C-NMR spectrum of compound (3a)	107
I1	GC-MS spectrum of compound (3b)	108
I2	FTIR spectrum of compound (3b)	109
I3	¹ H-NMR spectrum of compound (3b)	110
I4	¹³ C-NMR spectrum of compound (3b)	111
J1	GC-MS spectrum of compound (3c)	112
J2	FTIR spectrum of compound (3c)	113

J3	^1H -NMR spectrum of compound (3c)	114
J4	^{13}C -NMR spectrum of compound (3c)	115

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Sonogashira cross-coupling reaction is one of the earliest discovery of organic synthesis to form carbon-carbon bonds (**Figure 1.1**) (Sonogashira, Tohda, & Hagihara, 1975). Due to its mild reaction conditions, Sonogashira cross-coupling reaction become highly useful in the synthesis of various compounds (Chinchilla & Najera, 2011; Kniess & Wust, 2003), including heterocycles (Aronica, Albano, Giannotti, & Meucci, 2017) and pharmaceuticals (Biajoli, Schwalm, Limberger, Claudino, & Monteiro, 2014; Leyva-pe, Cabrero-antonino, Rubio-marque, & Al-resayes, 2014). Since it was first reported in the year 1975, a tremendous development has taken place especially in terms of reaction conditions (Liang, Dai, Chen, & Yang, 2005; Strappaveccia et al., 2015; Zhong, Wang, Li, & Wang, 2014). Traditional reaction condition for Sonogashira reaction requires copper as co-catalyst to the palladium catalyst. Today, the reaction can even be carried out without copper as co-catalyst. This copper-free sonogashira reaction is the result of wise modification as copper can cause unwanted side products from the copper acetylide homocoupling.

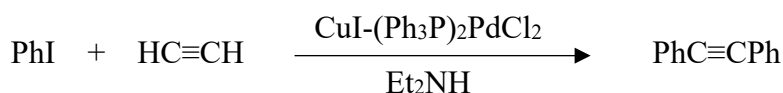


Figure 1.1 Original reaction scheme of Sonogashira cross-coupling reaction (Sonogashira et al., 1975)

In earlier development of Sonogashira cross-coupling reaction, variety of Palladium (Pd) complexes have been used as catalyst (Chinchilla & Najera, 2007). Example of such Pd catalyst include, most commonly used Pd-phosphorus complexes, Pd-nitrogen complexes, N-heterocyclic carbene (NHC) Pd complexes as well as palladacycle. However, these catalysts have some drawbacks especially in terms of reaction conditions, catalyst separation and environmental concerns. To overcome these issues, many attempts have been done to modify and enhance the catalyst to afford wide range of potentials for the best catalytic performance. One of the major works was the immobilisation of homogenous palladium catalyst onto various solid supports such as silica (Polshettiwar, Len, & Fihri, 2009), polymers (Qi, Longfeng, Zhenhua, Xiangju, & Feng-shou, 2012), and magnetic iron oxides (Sydnes, 2017). On the other hand, interest on the development of Pd nanoparticles (PdNPs) as catalyst was also growing (Cuenya, 2010; Mandali & Chand, 2014). These two efforts received significant attentions which lead to the evolution of much better and versatile catalyst for cross-coupling reactions such as Sonogashira.

In recent years, the use of magnetic supported metal nanoparticles to replace the conventional metal complexes as catalyst in any C-C coupling reaction has becomes prominent (Salemi, Kaboudin, Kazemi, & Yokomatsu, 2016; Sydnes, 2017). This type of catalyst system exhibits unique properties as it can bridge the gap between homogenous and heterogenous system. Metal nanoparticles provide larger surface area to volume ratio compared to bulk metal. Since the catalyst particles are in the nano-sized scale, more exposed surface area of the active components become readily and easily available to come into contact with the reactants, resulting in higher selectivity and catalytic activity. While the magnetic support such as well-known magnetite (Fe_3O_4) behave as a robust, highly efficient, and rapid catalyst separation tool. Energy such as heat is not required throughout the separation process while the mass of catalyst loss can be prevented, and operation time will also be reduced. By using magnetite (Fe_3O_4) as the main support, the catalyst can be separated from reaction mixture easily with the aid of an external magnet. As compared to other conventional separation techniques such as filtration and centrifugation, magnetic separation is often the best choice in terms of high efficiency and specificity.

Among all type of available iron oxides, magnetite (Fe_3O_4) is much favorable as magnetic support for catalysts due to its superparamagnetic properties which is strongly attracted to an applied magnetic field and instantaneously become non-magnetic material in the absence of an applied magnetic field. This is one of the important features that a support must have for efficient handling and application. The synthesis of Fe_3O_4 is also relatively easy as compared to other magnetic iron oxides. In addition, Fe_3O_4 is stable under most reaction condition such as temperature, pressure, solvents, reagents, substrates, and products. Fe_3O_4 can also be surface coated with silica which then can be functionalised with suitable ligands such as aminosilanes or alkoxysilanes. Moreover, coating with silica will stabilised Fe_3O_4 from attack by strong acids and protects Fe_3O_4 from oxidation to form maghemite.

1.2 Problem Statement

Conventionally, most synthesis of PdNPs is achieved via chemical reduction of Pd(II) ions by phosphine compounds. Phosphine has strong reducing properties and it can also be used as one of efficient activators and stabilisers especially for palladium species. However, despite all these great advantages, this toxicant gas is worrisome to handle. On the other hand, it is not only toxic and highly flammable, but also much expensive than palladium metal. Hence, synthesis of PdNPs in a greener procedure is highly desirable. Plant extract with high antioxidant content such as *Artocarpus altilis* leaf extract promises a safer, environmental friendly and cheaper procedure for the reduction of Pd(II) to synthesis PdNPs.

One of the major challenges in synthesising transition-metal nanoparticles is to make sure that they are kinetically stabilised to avoid agglomeration as well as regeneration. This is typically achieved by using a protective stabiliser such as surfactants, dendrimers, polymers, and organic ligands. Sulfur-based ligand is frequently used as stabiliser for PdNPs. However, the poisoning effect of sulfur may somehow restrict the catalytic potential of PdNPs. Hence, nitrogen-based ligand such as 3-(2-aminoethylamino)propyl trimethoxysilane (AEAPTS) is much more

advantageous. The nitrogen lone pair from the two amines group will chemically adsorb onto the surface of the metal and the alkyl group preventing agglomeration via steric stabilisation.

Homogenous catalyst such as Pd complexes has known to perform a very excellent job in many catalytic reactions. However, no matter how effective homogenous catalyst can be, major problem arises when it comes to the recovery part. Not only products or catalyst itself are difficult to be collected and separated from the reaction mixture, but homogenous catalyst also seems impossible to be recycled and reused for several times. Thus, PdNPs immobilised onto magnetic support would be the best alternative solution since recovery of the catalyst can be simply done by using external magnetic field. In addition, PdNPs has very high surface area to volume ratio, hence it provides good catalytic activity mimicking the homogenous catalyst.

1.3 Objectives

The objectives of this study are:

1. To synthesise and characterise silica-coated magnetite functionalised with aminosilane derivatives.
2. To immobilise Pd(II) ions onto the modified surface of the silica-coated magnetite nanoparticles.
3. To reduce the supported Pd(II) ions to Pd(0) nanoparticles (PdNPs) via green approach using *Artocarpus altilis* aqueous leaf extract as the reducing and stabilising agent.
4. To evaluate the catalytic performance of the supported PdNPs catalyst in the copper-free Sonogashira cross-coupling reaction.

1.4 Scope of Research

This research focused on the synthesis of magnetic supported PdNPs which is useful for the catalytic application. Fe_3O_4 was first synthesised and used as the main support for the catalyst. The synthesised Fe_3O_4 was coated with a layer of silica using tetraethyl orthosilicate (TEOS). The silica surface was then modified with an aminosilane ligand of 3-(2-aminoethylamino)propyl trimethoxysilane (AEAPTS) which contained two amines group per molecule. The supported Pd(II) ions was then reduced to form PdNPs via biosynthetic method employing aqueous leaf extract of *Artocarpus altilis*. Effect of reaction time, metal ion concentration, the volume of leaf extract and pH of the extract on the formation of PdNPs were investigated and monitored by using UV-vis spectroscopic analysis. Bio-reduction approach was chosen because it is safe, environmentally friendly and cheaper as compared to chemically toxic approach. The synthesised supported PdNPs catalyst was then tested in the copper-free Sonogashira cross-coupling reaction between phenylacetylene and aryl halide derivatives with triethylamine base in water for 24 h.

1.5 Significance of Research

The supported palladium nanoparticles (PdNPs) prepared in this research could be a promising catalyst in providing excellent and impressive catalytic efficiency for C-C cross-coupling reaction such as Sonogashira reaction. Thus, it has the potential to supersede other catalysts which were conventionally used in the chemical industry. Also, supported PdNPs provide magnetic nanocatalyst recovery method which can be simply done with the aid of an external magnet. Hence, this ideal method will take off the tedious separation method such as distillation and crystallisation which require high temperature and cause the catalyst to be decomposed. In addition, Supported PdNPs can be recycled for several times and the preparation employing plant extract instead of toxic and hazardous chemicals open the new path toward more sustainable and green technology.

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