

SYNTHESIS AND CHARACTERIZATION OF COBALT-BASED
CATALYSTS FOR SELECTIVE OXIDATION OF STYRENE AND
PHOTODEGRADATION OF METHYLENE BLUE

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In the name of Allah, the Most Beneficent and the Most Merciful.

This thesis is dedicated to my beloved parents, Siti Rohani bte Abd Kadir, Ayob bin Ismail and my siblings Azizah, Hafiz, Ashikin, Hakim, Nuraizan, Hatta, Aifa, Baharuddin and Bahiyah

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ABSTRACT

Cobalt is one of the transition metals that has been widely used in various fields of modern research, especially as a catalyst and photocatalyst for various types of reactions. In this work, two types of cobalt-based catalyst, *i.e.* cobalt oxide and cobalt Schiff base complex, each supported on silica and silica-coated magnetite, have been investigated. Silica-coated magnetite ($\text{SiO}_2@\text{Fe}_3\text{O}_4$) has been widely used as a catalyst support because it can be easily separated from the reaction mixture by applying only an external magnetic field. Herein, magnetite was synthesized by using the co-precipitation method before being coated with the silica via the sol-gel method in order to stabilize and reduce toxicity. Cobalt complex/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$ was synthesized by the condensation between cobalt(II) salicylaldehyde and 3-aminopropyltrimethoxysilane (APTMS) on the surface of $\text{SiO}_2@\text{Fe}_3\text{O}_4$. Cobalt oxide ($\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$) was later produced after calcination of its complex at the temperature 550 °C. The same method was used to synthesize cobalt complex/ SiO_2 and cobalt oxide/ SiO_2 . These cobalt-based catalysts were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), adsorption-desorption nitrogen analysis, photoluminescence (PL) and diffuse reflectance ultraviolet visible (DRUV-Vis) spectroscopy. The performance of the cobalt-based catalysts was tested in the oxidation of styrene at room temperature (27 °C) and 50 °C for 24 h. The results revealed that the cobalt complex catalyst has the highest turnover number (TON) compared to the cobalt oxide catalyst. This is because the amount of Co^{2+} ions in the complex system which act as the active sites in the reaction is higher than in the oxides. Moreover, all of the active sites in the complexes are more accessible by the substrate, unlike those of the the oxide system, in which the active sites are confined inside the particles. The photocatalytic activity of the synthesized $\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$ and $\text{Co}_3\text{O}_4/\text{SiO}_2$ were also tested and showed positive results. The $\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$ catalyst showed the highest percentage of methylene blue (MB) photodegradation under UV and visible light irradiations. This can be explained by the relationship between the PL spectra and photocatalytic activity. Hence, the photocatalytic activity is expected to be higher when PL with stronger intensity is used. This difference is due to the larger amount of oxygen vacancies and defects in the sample. It can be concluded that the amount of Co^{2+} ion plays an important role in the oxidation of styrene, while the oxygen vacancies and defects are crucial for the photodegradation of MB.

ABSTRAK

Kobalt merupakan salah satu logam peralihan yang digunakan secara meluas dalam pelbagai bidang penyelidikan moden, khususnya sebagai mangkin dan fotomangkin untuk pelbagai jenis tindak balas. Dalam penyelidikan ini, dua jenis mangkin berasaskan kobalt, iaitu kobalt oksida dan kompleks bes Schiff kobalt yang setiap satunya tersokong pada silika dan magnetit bersalut silika, telah dikaji. Magnetit bersalut silika ($\text{SiO}_2@\text{Fe}_3\text{O}_4$) telah digunakan secara meluas sebagai penyokong mangkin kerana ia mudah dipisahkan daripada campuran tindak balas dengan hanya menggunakan medan magnet luar. Di sini, magnetit telah disintesis menggunakan kaedah ko-pemendakan sebelum disalutkan dengan silika melalui kaedah sol-gel untuk menstabilkan dan mengurangkan ketoksikan. Kompleks kobalt/ $\text{SiO}_2@\text{Fe}_3\text{O}_4$ telah disintesis secara kondensasi antara kobalt(II) salisilaldehid dan 3-aminopropiltrimetoksilana (APTMS) pada permukaan $\text{SiO}_2@\text{Fe}_3\text{O}_4$. Kobalt oksida ($\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$) seterusnya dihasilkan selepas pengkalsinan kompleks pada suhu 550 °C. Kaedah yang sama telah digunakan untuk mensintesis kompleks kobalt/ SiO_2 dan kobalt oksida/ SiO_2 . Mangkin berasaskan kobalt ini dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi pengimbasan elektron pelepasan medan (FESEM), mikroskopi elektron penghantaran (TEM), analisis termogravimetri (TGA), spektroskopi fotoelektron sinar-X (XPS), analisis penjerapan-nyahjerapan nitrogen, fotopendarcahaya (PL) dan spektroskopi pantulan serakan ultralembayung-cahaya nampak (DRUV-Vis). Prestasi mangkin berasaskan kobalt telah diuji dalam pengoksidaan stirena pada suhu bilik (27 °C) dan 50 °C selama 24 jam. Hasil kajian mendedahkan bahawa mangkin kompleks kobalt mempunyai nombor perolehan (TON) tertinggi berbanding dengan mangkin kobalt oksida. Ini adalah kerana jumlah ion Co^{2+} dalam sistem kompleks yang bertindak sebagai tapak aktif dalam tindak balas, adalah lebih tinggi daripada yang terdapat dalam oksida. Selain itu, kesemua tapak aktif di dalam kompleks lebih mudah didatangi oleh substrat, tidak seperti sistem oksida, di mana tapak aktif adalah terbatas di dalam zarah. Aktiviti fotopemangkinan $\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$ dan $\text{Co}_3\text{O}_4/\text{SiO}_2$ yang telah disintesis juga diuji dan menunjukkan hasil yang positif. Mangkin $\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$ menunjukkan peratusan fotodegradasi metilena biru (MB) tertinggi di bawah penyinaran UV dan cahaya nampak. Ini dapat dijelaskan dengan hubungan antara spektrum PL dan aktiviti fotopemangkinan. Dengan demikian, aktiviti fotopemangkinan dijangkakan menjadi semakin tinggi apabila PL dengan keamatan yang lebih kuat digunakan. Perbezaan ini adalah disebabkan oleh jumlah kekosongan oksigen dan kecacatan yang lebih banyak dalam sampel. Dapat disimpulkan bahawa jumlah ion Co^{2+} memainkan peranan penting dalam pengoksidaan stirena, manakala kekurangan oksigen dan kecacatan pula adalah sangat penting bagi fotodegradasi MB.

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LIST OF ABBREVIATIONS

Co ₃ O ₄	-	Cobalt oxide
SiO ₂	-	Silica
SiO ₂ @Fe ₃ O ₄	-	Silica-coated magnetite
Fe ₃ O ₄	-	Magnetite
APTMS	-	3-Aminopropyl trimethoxysilane
a.u.	-	Arbitrary unit
Cps	-	Counts Per Second
XRD	-	X-ray Diffraction
TEM	-	Transmission Electron Microscopy
BJH	-	Barret-Joyner-Teller
FESEM	-	Field Emission Scanning Electron Microscopy
EDX	-	Energy Dispersive X-ray
GC-FID	-	Gas Chromatography-Flame Ionization Detector
eV	-	Electronvolt
TGA	-	Thermal Gravimetric Analysis
DRUV-vis	-	Diffuse Reflectance Ultraviolet visible
MB	-	Methylene Blue
PL	-	Photoluminescence
UV-vis	-	Ultraviolet visible
TON	-	Turnover Number
Ca.	-	Around, about or approximately (Latin: <i>circa</i>)
i.e	-	That is (Latin: <i>id est</i>)
MNP	-	Magnetite Nanoparticles
nm	-	Nanometre

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Schiff base transition metal complexes have been widely used as either homogeneous or heterogeneous catalysts in various organic transformations (Malumbazo and Mapolie, 2009). Between these two types of catalyst, homogeneous catalyst is preferred due to its high catalytic activity and selectivity in many organic reactions. However, this system has several weaknesses, such as the difficulty in separating the homogeneous catalyst from the reaction mixture and its recoverability after use in the reaction (Malumbazo and Mapolie, 2009). The heterogenization of homogeneous catalysts on a solid support is one of the methods taken to overcome these weaknesses. The heterogenization process is favourable as it leads to easy recovery and recycling of the catalyst (Malumbazo and Mapolie, 2009).

Currently, the development of the nanosized catalysts offers enhancement in activity and selectivity of heterogeneous catalysts due to large surface area and surface to volume ratio provided (Masteri and Tayebbi, 2011). Several insoluble solid materials, such as silica, have been applied as the supporting material for Schiff base complexes (Malumbazo and Mapolie, 2009). One of the examples is the immobilization of Schiff base complex on MCM-41-type hybrid mesoporous silica. This catalyst shows high catalytic activity in the oxidation of styrene with hydrogen peroxide as the oxidant (Luo and Lin, 2005). However, handling nanosized material

poses some difficulties, such as the separation after reaction due to their small size. This problem might be solved by impregnating a magnetite material on the solid catalyst. The introductions of magnetic material on the catalyst support open the possibility to the catalyst being easily separated from the reaction mixture by applying an external magnetic field. Magnetite nanoparticles have super paramagnetic property, in which the particles are attracted to a magnetic field but retain no residual magnetism after removing the applied magnetic field (Masteri and Kashef, 2012; Masteri and Tayebbi, 2011). Thus, suspended super paramagnetic nanoparticles may be easily removed from the reaction mixture simply by using an external magnetic field without modifying the physical and chemical properties of the particle (Masteri and Kashef, 2012; Masteri and Tayebbi, 2011). In this research, the magnetic supporting material used to make the materials can be easily separated from the reaction mixture by applying external magnetic field.

Apart from cobalt Schiff base complex, cobalt oxide also shows good catalytic activity in oxidation reactions. It was reported that cobalt oxide supported on hydroxyapatite-encapsulated γ -hematite (Fe_2O_3) nanocrystallites are highly efficient for olefin oxidation with hydrogen peroxide (H_2O_2) as the oxidant (Zhang *et al.*, 2008). However, synthesis of cobalt oxide involves tedious techniques. One previous study prepared cobalt oxide from corresponding alkoxide using the sonochemical technique (Srivastava *et al.*, 2003). Another technique utilized is the precipitation–oxidation method, where hydrogen peroxide acted as the oxidant (Lin *et al.*, 2003). Syntheses of cobalt oxide can also be carried out through thermal decomposition (Ahmed *et al.*, 2008; Shao *et al.*, 2006). Microemulsion–based process is also one of the methods that has been used to synthesize cobalt oxide (Ahmed *et al.*, 2008). In this research, a simple synthesis method has been employed in order to obtain cobalt oxide, which is by calcination of the complex.

This research proposed the immobilization of cobalt Schiff base complex on silica and silica–coated magnetite ($\text{SiO}_2@\text{Fe}_3\text{O}_4$) nanoparticles. These materials may function as good catalysts for the oxidation of alkene, as previously reported for their homogeneous counterpart (Kooti and Afshari, 2012). Figure 1.1 shows the immobilization steps of cobalt Schiff base complex on silica-coated magnetite. In

this process, hydrophilic magnetite material was covered by silica via sol-gel process. The next step involves the attachment of alkyl amine on the surface of silica using alkoxyamine as the precursor. Condensation of amine with salicylaldehyde will produce cobalt Schiff base complex functionalized silica-coated magnetite nanoparticles. Meanwhile, the same preparation method was employed for the synthesis of cobalt Schiff base complex on silica but without the preparation of magnetite, silica-coated magnetite and functionalization of alkyl amine.

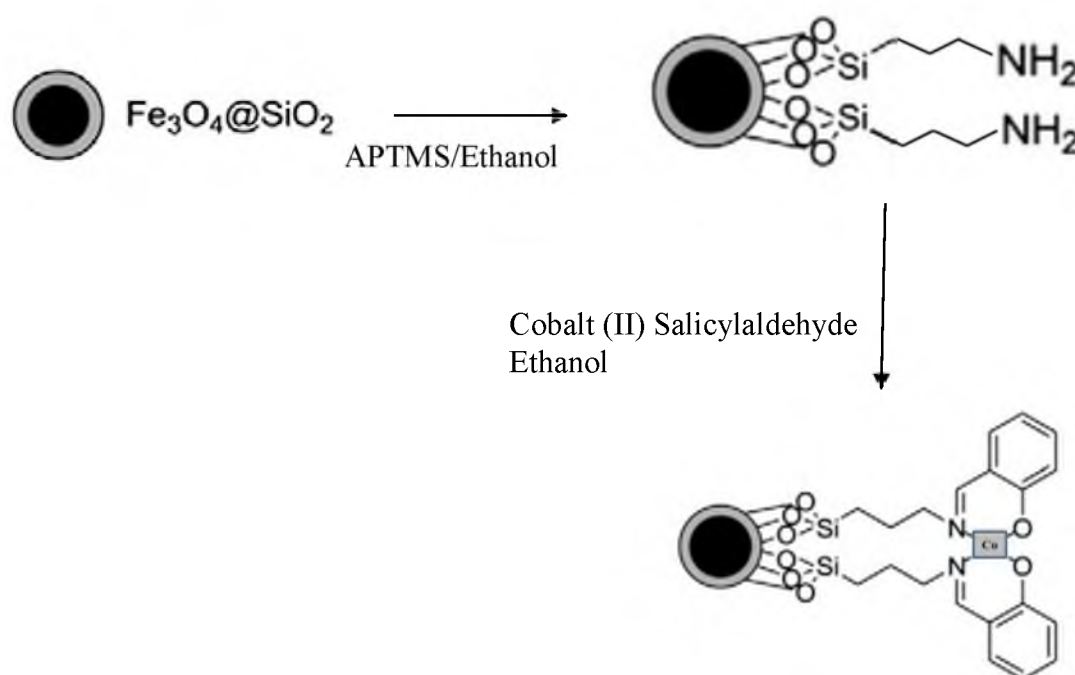


Figure 1.1 The strategy to synthesis cobalt Schiff base complex / $\text{SiO}_2@ \text{Fe}_3\text{O}_4$

Further treatment of cobalt Schiff base complex functionalized on silica-coated was then carried out. Calcination of cobalt Schiff base complex / $\text{SiO}_2@ \text{Fe}_3\text{O}_4$ resulted in the attachment of cobalt oxide on the silica's surface that has been coated by the nanosized magnetite, as illustrated in Fig 1.2. Meanwhile, the calcination of cobalt Schiff base complex/ SiO_2 resulted in the attachment of cobalt oxide on the silica's surface. The calcination process removed the organic part of the complex and

oxidizes the cobalt into cobalt oxide. By using the calcination technique, cobalt oxide can be uniformly distributed on the surface of the silica.

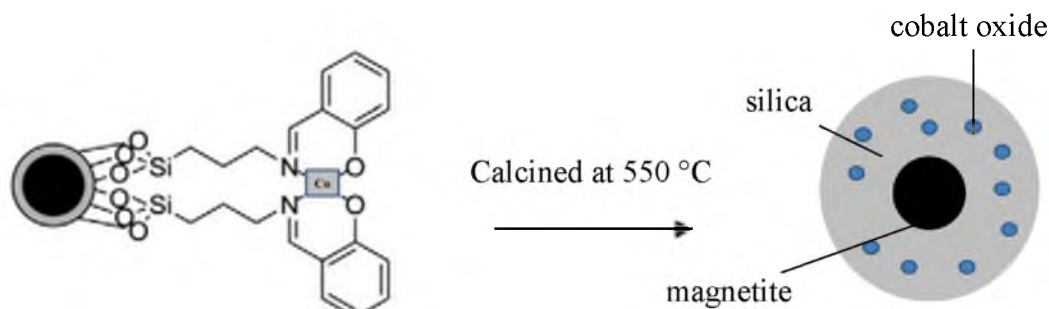


Figure 1.2 The strategy to synthesis $\text{Co}_3\text{O}_4/\text{SiO}_2@\text{Fe}_3\text{O}_4$

1.2 Problem Statement

Schiff base complex has been widely used as a homogeneous catalyst due to its ability to exhibit high catalytic activity. However, this material has several drawbacks and one of them is the separation difficulties after the reaction (Kooti and Afshari, 2012). Therefore, some modification had been made in order to heterogenize the catalyst by supporting it on inorganic materials such as silica. Many studies have been carried out on Schiff base complex supported on silica. However, using silica (non-magnetic supporting material) also has some drawbacks. Among of them is the difficulty in separating them from the reaction mixture. This can be overcome by using solid catalyst supported on the magnetic supporting material such as magnetite since it can be easily separated by simply applying an external magnetic field. The presence of magnetite in the catalyst can lead to easy separation of the silica based catalysts. Apart of that, cobalt oxide also shows good properties that can be utilized as catalysts in many reactions. However, a simple method can also be applied to synthesis cobalt oxide, which is by calcination of the cobalt complex (thermal decomposition).

Hence, in this research, two types of supporting material were used in the preparation of cobalt-based catalysts. The first one is a magnetic material (silica-coated magnetite) while the other is a non-magnetic material (silica alone). The comparison between the catalytic activity and ease of separation after the reaction was then made. As mentioned previously, cobalt oxide catalysts can be easily obtained by thermal decomposition of the cobalt complex catalyst. Numerous catalysts have been developed for oxidation and photodegradation reactions but not many on the usage of cobalt-based catalyst. Hence, in the present approach, the design of cobalt-based catalysts, with the aim of improvising selectivity and catalytic activity, has been carried out. The research question is as follows: **Will the synthesized material be a good catalyst in the oxidation of styrene, and photodegradation of methylene blue?**

1.3 Objectives

The research described in this thesis proposed a fundamental study of heterogeneous catalysis and photocatalysis for oxidation of styrene and photodegradation of methylene blue. This research embarks on the following objectives:

- To prepare and design cobalt-based catalysts functionalized on non-magnetic (silica) and magnetic (silica coated magnetite) supporting materials
- To investigate the physicochemical properties of cobalt-based catalysts
- To testing catalytic activity on the oxidation of styrene and the photodegradation of methylene blue.
- To study the structure-catalytic activity relationship of the cobalt-based catalysts on the oxidation of 1-octene and styrene and photodegradation of methylene blue

In addition, the thesis outlines of the each chapter are described as the following:

Chapter 1 describes the introduction of the research consist of research background followed by the research problem statement, objectives, scope and the significance of the present study. Chapter 2 is comprised of literature reviews that are related to this study. In Chapter 3, the preparation of the magnetite, silica coated magnetite and cobalt-based catalyst were described. It also includes instrumentation methods and catalytic activity testing. Chapter 4 discusses the result obtained from the characterization and catalytic activity. This chapter also discussed the structure-catalytic activity relationship of the cobalt-based catalysts. Lastly, Chapter 5 represents concluding remarks based on the research findings.

1.4 Significance of the Research

The cobalt-based catalyst that has been prepared in this research could be a promising catalyst in the production of fine chemicals, especially for organic synthesis and treatment of dyes (oxidation and photodegradation reaction purpose). This is due to the high catalytic activity and selectivity as reported by many researchers. Furthermore, the method of synthesis proposed is simple and environmentally friendly. Besides that, the magnetic separation technology offers many advantages over conventional filtration and other purification methods. The cobalt-based catalysts could be easily and efficiently recovered from the reaction media, simply by applying an external magnetic field.

1.5 Scope of Research

This study was devoted to selective oxidation of styrene and photodegradation of methylene blue by cobalt-based material as a catalyst and photocatalyst. The scopes of this study can be divided into two parts, which were preparation of cobalt-based catalysts and its catalytic and photocatalytic reactions.

Cobalt Schiff base complexes (cobalt complex) supported on silica was prepared by condensation between 3-aminopropyltrimethoxy silane (APTMS) and cobalt(II) salicylaldehyde. Meanwhile for cobalt complex supported on silica-coated magnetite, APTMS was functionalized on silica-coated magnetite then reacted with cobalt(II) salicylaldehyde. Then, both of these complexes were further treated by calcination process to form cobalt oxide supported on silica-coated magnetite and silica alone. For characterization of these cobalt-based catalysts, numerous methods were conducted such as thermal stability, surface analysis (oxidation state analysis), optical and functional group analysis, morphology, crystallinity, surface area and porosity and water adsorptivity properties.

In order to determine the catalytic efficiency and selectivity, the prepared cobalt-based catalysts were tested in the oxidation of styrene and photodegradation of methylene blue. The reactant and products were analyzed by ultra violet visible spectrometry (UV-vis) for methylene blue and gas chromatography flame ionization detector (GC-FID) for the styrene.

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