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Project title	Nickel-based heterogeneous catalysts for nitroarene reduction

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Program	Bachelor of Science in Applied Chemistry
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Nickel-based heterogeneous catalysts for nitroarene reduction

by

Mr. Khandhinat Watanaudomkiat

In Partial Fulfillment for the Degree of Bachelor of Science
Program in Applied Chemistry (International Program)
Department of Chemistry, Faculty of Science
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Abstract

Silica-supported nickel (Ni/Q6) and silica-supported nickel phosphide (Ni$_2$P/Q6) catalysts were synthesized via wetness impregnation method using different metal loading amounts. The synthesized materials were characterized and confirmed the successful preparation of catalysts using X-ray diffraction (XRD), N$_2$ adsorption-desorption, and CO chemisorption. The characterization results showed that the use of 6% loading amount of Ni gave the highest surface area, highest pore volume, and highest metal dispersion among the synthesized materials. The synthesized catalysts were tested for their catalytic capabilities via the reduction reactions of 4-nitrophenol and several other nitroarenes to their corresponding aminoarenes. The catalytic results showed that the supported nickel phosphide catalyst with 6% nickel loading (6NiP-Q6) exhibited the highest catalytic activity and the reaction was completed within 5-6 min. The high reaction rate using 6NiP-Q6 as the catalyst could be mainly due to its higher metal dispersion and higher surface area. Lastly, the reusability test was performed to determine the sustainability and efficiency of the synthesized catalysts. It was confirmed that the catalysts could be reused up to four times without a significant loss in efficiency.

Keywords: Nickel phosphide, Nitroarenes, 4-NP, Reduction reaction, Non-noble metal catalysts

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List of Abbreviations

4-AP	4-aminophenol
4-NP	4-nitrophenol
4-NP anion	4-nitrophenolate anion
xNi-Q6	Silica Q6-supported nickel catalyst with x percent nickel loading
xNiP-Q6	Silica Q6-supported nickel phosphide catalyst with x percent nickel loading
BET	Brunauer-Emmett-Teller
CO	Carbon monoxide
KBH_4	Potassium borohydride
MCM-41	Mobil Composition of Matter No. 41 (name of a mesoporous material)
$NaBH_4$	Sodium borohydride
Ni/Q6	Silica Q6-supported nickel catalyst
Ni_2P/Q6	Silica Q6-supported nickel phosphide catalyst
Q6	Commercial amorphous silica with an average pore size of 6 nm
XRD	X-Ray diffraction

Chapter 1 – Introduction

1.1   Introduction to the research problem and significance

Nowadays, the environmental concerns are increasing in significance around the world due to the growth of various industries. Water pollution is one of the problems arising from the industrial wastes. 4-nitrophenol (4-NP) is an industrial waste which is generally released into the water and affects the ecosystem due to its carcinogenicity and mutagenicity problems. Furthermore, its resistance to conventional biodegradation and water treatment needs to be concerned. Thus, it has been researched and studied over the years for the elimination of 4-NP in water treatment process. One of the methods that gains interests is the catalytic reduction with the use of noble metal catalysts because of the ability to produce 4-aminophenol (4-AP), a precursor in synthesis of dyes, medicines, etc. which is the beneficial product. However, noble metals are expensive; therefore, cheaper metals are being investigated to replace noble metals. Hence, this project will investigate the capability of nickel-based catalysts and determine if they can be an economically efficient choice as catalysts for 4-NP reduction.

1.2   Literature review

1.2.1   Nitroarenes

1.2.1.1   4-Nitrophenol (4-NP)

Nitroarenes are a large class of molecules which are nitro-substituted derivatives of aromatic hydrocarbons. Structurally, nitroarenes have at least one nitro ($-NO_2$) group covalently bonded to aromatic hydrocarbons.[1]

4-nitrophenol (4-NP) is one of nitroarenes that is being studied in this research. It is generally used in the production of pesticides, explosives, dyes, and pharmaceutical drugs.[2,3] However, 4-NP is recognized as a potential industrial pollutant due to its carcinogenicity and mutagenicity according to U.S. Environmental Protection Agency.[2] From the industrial

production process, 4-NP is usually released along with wastewater as it is difficult to eliminate by conventional water treatment methods. With the presence of nitro group and aromatic ring, it gains high chemical stability and resistance to biodegradation process.[3,4]

### 1.2.1.2 Methods for removal of 4-NP from wastewater

With the high stability and toxicity of 4-NP, it has been extensively studied to search for methodologies to eliminate it and obtain safer environment for nature. Various methods have been proposed throughout the years[2,5] including photodegradation using visible light and photocatalysts,[6] adsorption using nanoparticles,[7,8] microbial degradation using bacteria as biocatalysts,[9] catalytic reduction using metal catalysts and reducing gents.[2]

Among the reported methodologies, one of the most extensively investigated approaches is catalytic reduction due to the advantages of 4-aminophenol (4-AP), the product of 4-NP reduction.[3,10] 4-AP is an important precursor for the synthesis of medicines, dyes, photographic developers, anti-corrosion additives in paints, etc.[2,4,10-12] As such, not only catalytic reduction can eliminate the toxicity of 4-NP in wastewater, it can also produce another important chemical for industrial use.[3]

In early studies of the process to reduce 4-NP and some other nitroarenes, iron/acid catalysts were used. However, the Fe-FeO sludge produced in the process became another pollutant and caused another environmental problem.[2,3] Another reduction method was later proposed to avoid the sludge problem. Sodium borohydride ($NaBH_4$) was used as a reducing agent and noble metals such as gold, silver, and palladium were used as catalysts. The results were favorable due to faster reaction time, not leaving unwanted byproducts, and easy to monitor by observing the disappearance of yellow color of 4-NP.[2]

The mechanism of the proposed method was to use $NaBH_4$ as a reducing agent and convert 4-NP into 4-nitrophenolate anion (4-NP anion). $NaBH_4$ can also associate with water to produce hydrogen radicals (Equation 1.1) for another process, which is to replace oxygen from nitro group with hydrogen (Equation 1.2). In addition, to make these processes occur,

catalyst is necessary to increase kinetic potential of the reaction since the overall reaction is kinetically unfavorable in the absence of catalysts.[2] The overall reaction was summarized as Equation 1.3.

$$BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2 \tag{1.1}$$

$$(1.2)$$

$$(1.3)$$
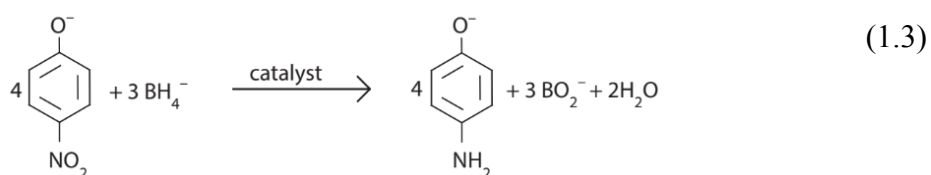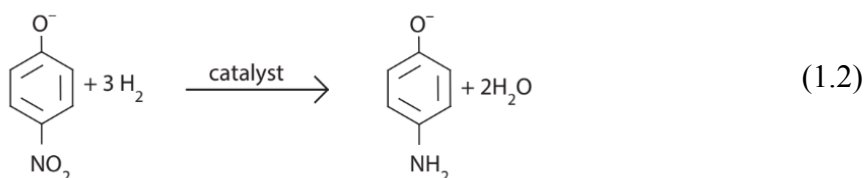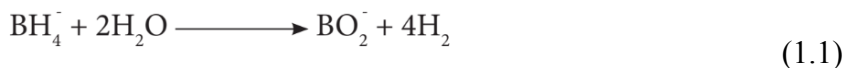
As NaBH4 was used both to convert 4-NP to 4-NP anion and to associate in water, it is used in an excess amount to drive the reaction to go forward and prevent the oxidation of the produced 4-AP.[2]

To monitor the reaction process, UV-Vis spectroscopy can be applied by measuring the absorption peaks of the solution. With 4-NP having peak at 317 nm, and the peak moves to 400 nm when it is converted to 4-NP anion. After 4-AP is produced, the peak can be observed at 300 nm. However, as the intensity of 4-NP anion is much higher than that of 4-AP, the reaction process can be observed by the lowering intensity of the peak at 400 nm.[2]
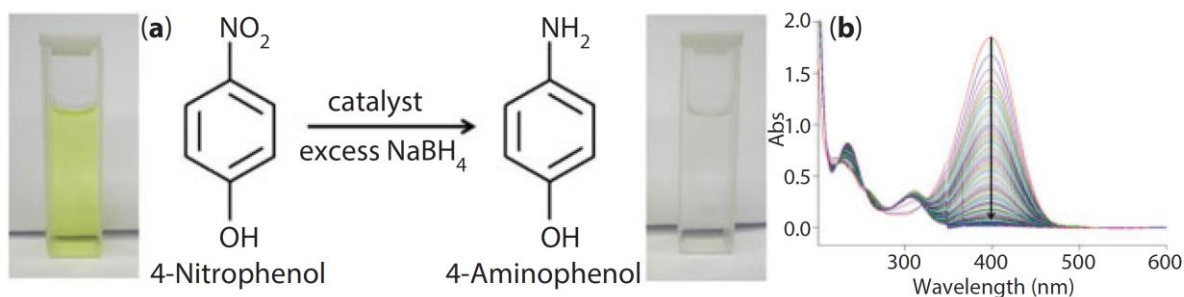
Figure 1.1 (a) The observation of color change in reduction of 4-NP to 4-AP with excess NaBH4 and catalyst. (b) Typical UV-Vis spectrum of 4-NP reduction. Illustration of decreasing intensity at 400 nm and slightly increasing intensity at 300 nm.

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1.2.1.3 Catalysts for conversion of 4-NP to 4-AP

As mentioned in the previous section, the catalysts and procedures for catalytic reduction has been changed over the years from iron/acid catalysts to noble metals. However, noble metals have major drawbacks due to their high price, rendering the method to be economically inefficient.[3,12] To solve this problem, non-noble transition metals including Ni, Co, Fe, and Mo have been tested as catalysts which are less costly and gain more attention to substitute noble metals.[12,13]

1.2.1.4 Other nitroarenes

Apart from 4-nitrophenol, there are many other derivatives of nitroarenes. This includes but not limited to nitrotoluenes and nitroanilines. These compounds also have industrial applications. For example, nitrotoluenes can be used in production of explosives,[14,15] and nitroanilines in dyes, polymers, and medicines.[16] These compounds are also toxic to health of humans and animals, and not environmental friendly when they are released.[14-16] Thus, they should be eliminated after industrial usage and before releasing to the environment.

There are reports that these compounds can be reduced using various catalysts.[17,18] Hence, it is worth mentioning and studying the reduction of them with non-noble metal catalysts.

1.2.2 Nickel-based catalysts for reduction reactions

1.2.2.1 Nickel catalysts

The catalysts to be used in this research are nickel-based. Nickel is a metal which is abundant in nature and not costly.[19,20] Thus, it is one of the promising choices to be used as a substitution of noble metals and is used as catalysts in various fields. Zhu et al. reported its high potential as catalyst in hydrogenation of biodiesel using bentonite as support.[19] Favero et al. also reported the synthesis of nickel/α-diimine catalytic systems with mesoporous MCM-41 support which showed good behavior in ethylene polymerization.[20]

In applications of nickel-based catalysts for reduction reactions, Lope et al. reported the use of nickel along with copper to reduce nitrogen oxide gas into nitrogen and carbon dioxide with carbon monoxide as reducing agent.[21] There was also a report from Romanazzi et al. of using polymer supported nickel catalysts to reduce various nitroarenes. Although the reaction time was longer than an hour, it showed an ability to be used repeatedly.[22] Thus, nickel is an interesting non-noble metal to be used in reduction of nitroarenes including 4-NP.

1.2.2.2 Nickel phosphide catalysts

Among nickel catalysts, nickel phosphide is one of the catalysts to be studied due to its high stability and activity.[23] It has been used in hydrodenitrogenation and phenol hydrodeoxygenation reactions in recent years and showed high capability in those reactions.[23,24] There was also the report of using different nickel phosphide phases such as Ni_2P and $Ni_{12}P_5$ (without catalyst support) to reduce 4-NP with KBH_4 as reducing agent. The result was satisfying as the conversion was complete in less than 20 minutes. Specifically, the use of $Ni_2P/Ni_{12}P_5$ showed best results with complete conversion in 8 minutes.[3] As both nickel and nickel phosphide have received satisfactory results over the recent years, they are interesting to be studied for their ability to reduce nitroarenes in this research.

1.3 Objectives

There are three main objectives in this project. The first objective is to successfully synthesize and characterize nickel-based catalysts for the reduction of 4-NP and several other nitroarenes. The next objective is to study the catalytic performance of the synthesized catalysts. The third objective is to confirm the efficiency of the synthesized catalysts especially in reusability and capability.

Chapter 2 – Experimental Section

2.1   Materials

2.1.1   Chemicals

Ammonium phosphate (Honeywell Fluka, USA)

Citric acid monohydrate (Wako, Japan)

Nickel (II) nitrate hexahydrate (Merck, Germany)

Silica Support Q-6 (Fuji Silysia, Japan)

Sodium borohydride (Sigma-Aldrich, USA)

3-Nitroaniline (Sigma-Aldrich, USA)

4-Nitroaniline (Sigma-Aldrich, USA)

4-Nitrophenol (Alfa Aesar, USA)

4-Nitrotoluene (Sigma-Aldrich, USA)

5-chloro-2-nitroaniline (Sigma-Aldrich, USA)

2.1.2   Instruments

Calcination machine (CARBOLITE Type: RHF 16/3)

Centrifuge machine

Electric drying oven (Memmert UMH00)

Metal chemisorption analyzer (BEL-METAL-3)

N_2 adsorption-desorption analyzer (BELSORPII-mini)

UV-Vis spectrophotometer

X-ray diffractometer (Rigaku RINT2200)

2.2   Catalyst Preparation

A commercial amorphous silica Q-6 (Fuji Silysia Chemicals, Japan) with an average

pore diameter of 6 nm was used as the supporting material in preparation of nickel-based

catalysts in this work. The silica support was dried overnight at 110 °C before use. The silica

supported nickel phosphide catalyst (Ni$_2$P/Q6) was synthesized by a wetness impregnation method using the Ni/P molar ratio of 1:2. Firstly, 1.69 g of nickel (II) nitrate hexahydrate as the nickel (Ni) source and 1.73 g of ammonium phosphate as the phosphorus (P) source were mixed. Then, 2 mmol of citric acid monohydrate and 100 mL of deionized water were then added to the mixture .and stirred for 20 min. Then, 5 g of Q6 support was added to the mixture and heated at 80 °C under magnetic stirring for 6 h The obtained solid was dried at 110 °C in an oven overnight, followed by calcination at 500 °C for 3 h. The resulting solid was then reduced in H$_2$ atmosphere at 600 °C for 3 h. The obtained product was designated as 6NiP-Q6.

The same procedure was conducted to synthesize silica supported nickel phosphide with different nickel loadings: 10% and 15% wt.% of Ni while the Ni/P molar ratio was kept constant at 1:2.

The silica supported nickel catalyst (Ni/Q6) was also synthesized. The same synthesis procedure was conducted without the addition of ammonium phosphate. The obtained product was designated as 6Ni-Q6.

2.3   Catalyst Characterization

2.3.1   CO chemisorption

BEL-METAL-3 temperature programmed machine was used to measure metal dispersion on the supporting material. Briefly, 0.07 g of each calcined sample was reduced in a U-tube glass under a pretreatment process of BEL-METAL-3. By making pulses of CO gas through the reduced catalysts, the percentage of metal dispersion can be determined by the number of CO molecules bonded with the Ni active sites in the sample.

2.3.2   XRD analysis

X-ray diffraction (XRD) analysis was performed with Rigaku RINT2200 to identify the phase composition of the samples. The analysis procedure was conducted within the 2θ range of 10 – 80° and Cu K$_\alpha$ radiation (40 kV, 40 mA).

2.3.3 N₂ adsorption-desorption

BELSORPII-mini was used in N$_2$ adsorption-desorption technique to determine the textural properties of the synthesized materials. Briefly, 0.04 g of each sample was dried at 200 °C for 3 h and degassed to remove unwanted gases. The process was performed at 77.4 K by adding liquid nitrogen followed by adsorption until the pressure reached atmospheric pressure, then degassed to vacuum for desorption.

2.4   Reduction of 4-nitrophenol (4-NP)

The synthesized nickel-based catalysts and the support including 6NiP-Q6, 10NiP-Q6, 15NiP-Q6, and 6Ni-Q6 were tested in the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The pure Q6 supporting material was also tested for comparison. Briefly, 10 mg of each catalyst was added in a beaker along with 10 mg of NaBH$_4$. Next, 15 mL of deionized water and 30 mL of aqueous 4-NP solution (20 ppm, pH 7) were added into the beaker and stirred constantly at room temperature for 10 min. The samples were collected every minute and monitored the disappearance of 4-NP at the absorption peak of 400 nm with UV-Vis spectrophotometer.

2.4.1   Effect of catalyst loading

To study the effect of catalyst loading, 0, 5, 10, and 15 mg of 6NiP-Q6 were added into separate beakers along with 10 mg of NaBH$_4$. Next, 15 mL of deionized water and 30 mL of aqueous 4-NP solution (20 ppm, pH 7) were added into the beaker and stirred constantly at room temperature for 10 min. The sampling procedure was conducted in the same manner as Section 2.4.

2.4.2   Effect of pH of 4-NP solution

To study the effect of pH, the reactions with different pH values (6, 7, 8, 9, 10) of 4-NP solution were performed using 6NiP-Q6 as the catalyst. The experimental procedure was conducted in the same manner as Section 2.4.

2.4.3 Effect of temperature

To study the effect of temperature, 6Ni-Q6 was used as a catalyst in this section. 25 mL of deionized water and 30 mL of aqueous 4-NP solution (20 ppm, pH 7) were added into the beaker. The beaker was then heated with hot water bath until the temperature in the beaker reached 40 °C. Then, 10 mg of the catalyst and 10 mg of $NaBH_4$ were added into the beaker and stirred constantly for 10 min. The sampling procedure was conducted in the same manner as Section 2.4.

2.5 Reduction of other nitroarenes

To study the reaction of other nitroarenes, the aqueous solutions of 3-nitroaniline, 4-nitroaniline, 4-nitrotoluene, and 5-chloro-2-nitroaniline were used instead of 4-NP. Each solution had the same conditions as 4-NP which were 20 ppm and pH 7. The experimental procedure was conducted in the same manner as Section 2.4.

2.6 Catalyst Reusability

To investigate the stability of the synthesized catalysts, the catalyst reusability using 6NiP-Q6 as the representative catalyst was performed. Briefly, after the reaction was completed as explained in Section 2.4, The catalyst was then separated from the solution by centrifugation at the speed of 4,000 rpm for 10 min. The obtained catalyst was then used for the next run without the washing or drying process.

Chapter 3 – Results and Discussion

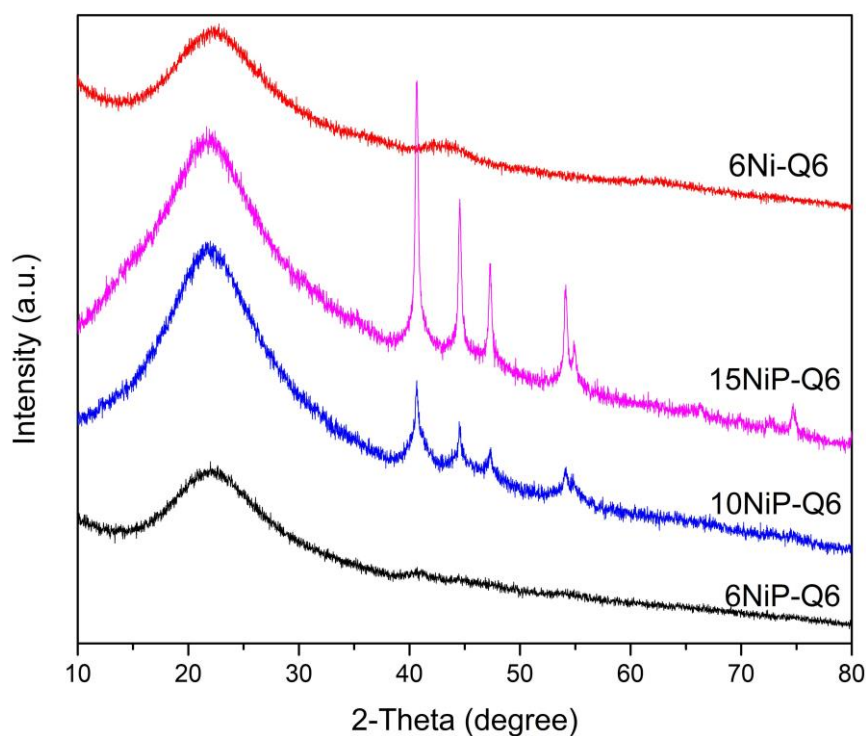## 3.1 Catalyst characterization

3.1.1 XRD analysis

Figure 3.1 XRD diffraction patterns of the synthesized materials.

XRD analysis was performed to identify the phase composition of the samples and the results were shown in Figure 3.1. A broad peak was found at around $2\theta = 22º$ for all materials, indicating the presence of amorphous silica. In 10NiP-Q6 and 15NiP-Q6, there were sharp peaks at 40.8º, 44.8º, 47.6º, and 54.4º[25], corresponding to the (111), (201), (210), and (300) planes[26] of Ni_2P phase (JCPDS 03-0953)[27], respectively. In addition, the peaks of 15NiP-Q6 were sharper with higher intensity compared to those of 10NiP-Q6 due to the larger crystallite size of Ni_2P particles in 15NiP-Q6. Meanwhile, those peaks were not found in 6NiP-Q6, implying the well-dispersion of Ni_2P particles on the Q6 support. In other words, the sizes of particles were too small to be detected by the XRD method. This phenomenon also applied to

6Ni-Q6 as there was no significant peak shown in the spectrum, except the broad peak of amorphous silica and a broad peak with very low intensity at around 41-42°.
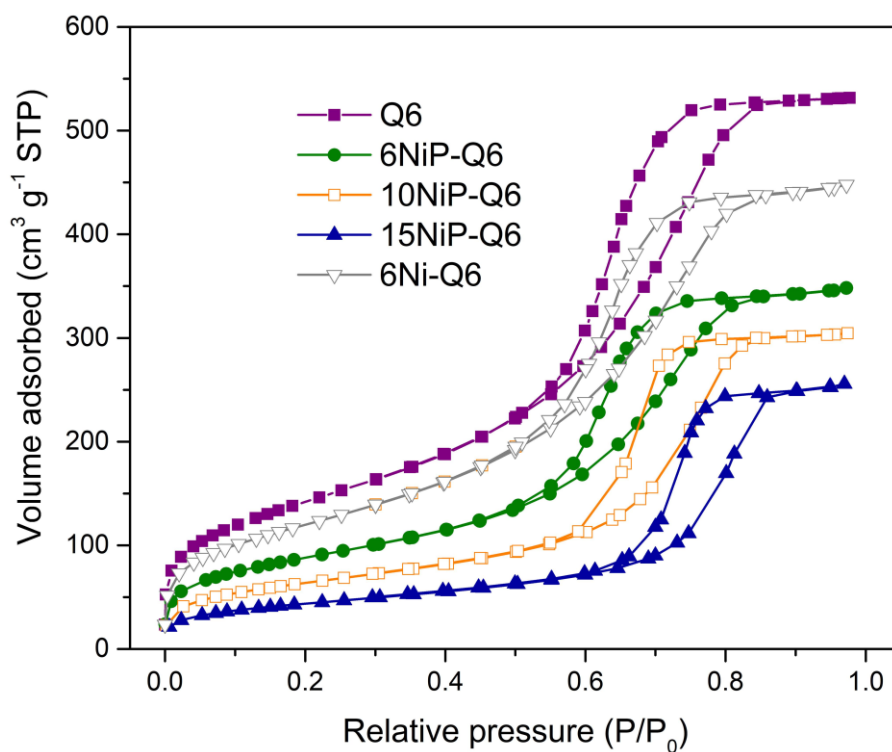
3.1.2 N$_2$ adsorption-desorption

Figure 3.2 N$_2$ adsorption desorption isotherms of the synthesized materials.

N$_2$ adsorption-desorption was performed to determine the surface area and pore volume of the synthesized materials. The adsorption isotherms of the synthesized materials showed the hysteresis loop in all materials (Figure 3.2), which confirmed type-IV isotherm that represents the mesoporous structure. In addition, the surface area of the materials was calculated using the BET method and the results were shown in Table 3.1. 6Ni-Q6 had the largest surface area and pore volume among all synthesized catalysts, while 6NiP-Q6 had the largest surface area and pore volume among nickel phosphide catalysts. In addition, all Ni- and Ni$_2$P doped materials had lower surface area and pore volume than the Q6 support, confirming the successful impregnation of Ni and Ni$_2$P species on the Q6 surface.

Table 3.1 Physical and chemical properties of the synthesized materials.

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Metal dispersion (%)	CO uptake (μmol/g)
Q6	512	0.83	-	-
6NiP-Q6	321	0.54	9.84	105.2
10NiP-Q6	232	0.48	5.34	91.1
15NiP-Q6	158	0.40	2.81	71.8
6Ni-Q6	434	0.70	22.60	241.6

3.1.3   CO chemisorption

CO chemisorption was performed to measure the metal dispersion on the supporting material (Q6). The percentage of metal dispersion was calculated from the mole of CO adsorbed divided by the initial mole of Ni added. Among the Ni_2P-doped materials, the results showed that the increase of Ni_2P percentage led to the decrease in metal dispersion percentage. Specifically, the metal dispersion of 6NiP-Q6, 10NiP-Q6, and 15NiP-Q6 were found to be 9.84%, 5.34%, and 2.81%, respectively. 6NiP-Q6 showed well dispersion of Ni_2P species (9.84%) and better than other Ni_2P doped materials. In case of Ni-Q6, the result showed much better dispersion of Ni species (22.60%) on the surface of Q6. The reason of 6Ni-Q6 to perform better dispersion than 6NiP-Q6 was probably due to the blockage of Ni by some of the phosphates from P source which were not reduced during catalyst preparation step. Those phosphates covered the surface of the Ni sites and this phenomenon thus interrupted the CO binding with the Ni active sites and therefore exhibited lower metal dispersion. This characterization technique also supports the disappearance of XRD peaks in 6NiP-Q6 and 6Ni-Q6.
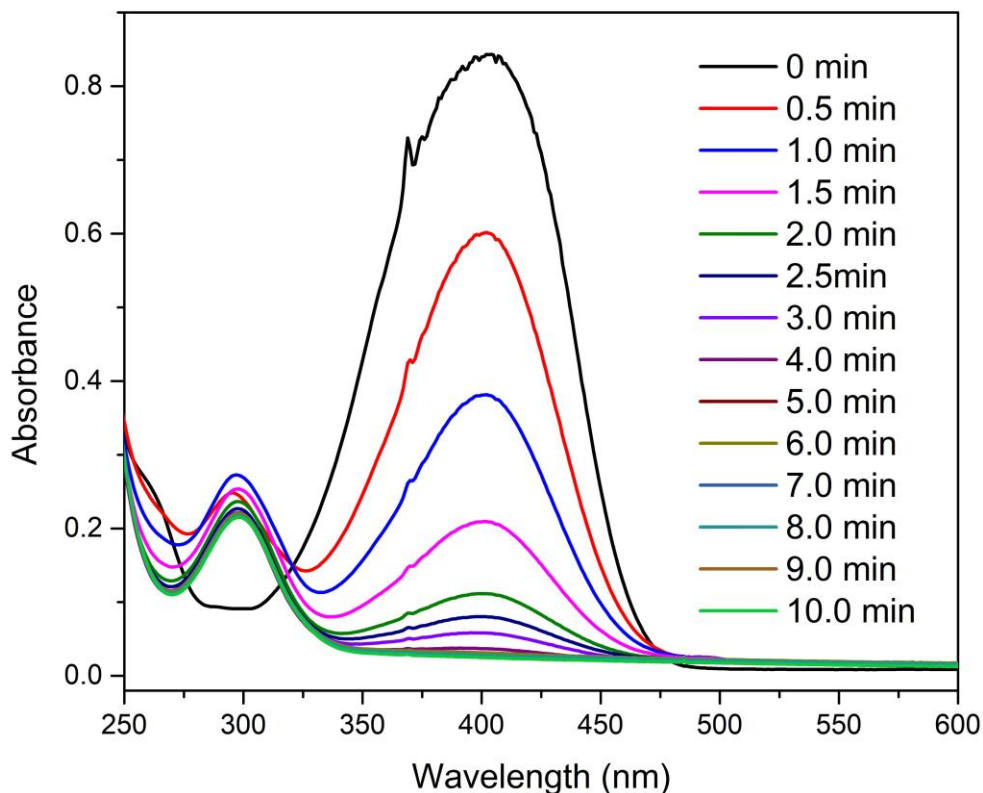
3.2   Catalytic activity

Figure 3.3 UV-Vis spectra of the reduction of 4-NP in the presence of 6NiP-Q6 catalyst, showing the decreasing intensity of the peak at 400 nm and increasing intensity of the peak at 300 nm over time.

The catalytic activities of the synthesized catalysts for 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) were monitored using UV-Vis spectroscopy. The main peaks to be monitored were at 400 nm and 300 nm as shown in Figure 3.3. The results showed the reduction of 4-NP (400 nm) and the production of 4-AP (300 nm) over time. Also, the decreasing intensity of 4-NP was more clearly observed as compared to the increasing intensity of 4-NP. Therefore, the peak to be monitored would be at 400 nm and plotted of (C/C_0) versus time will be presented in the following sections.
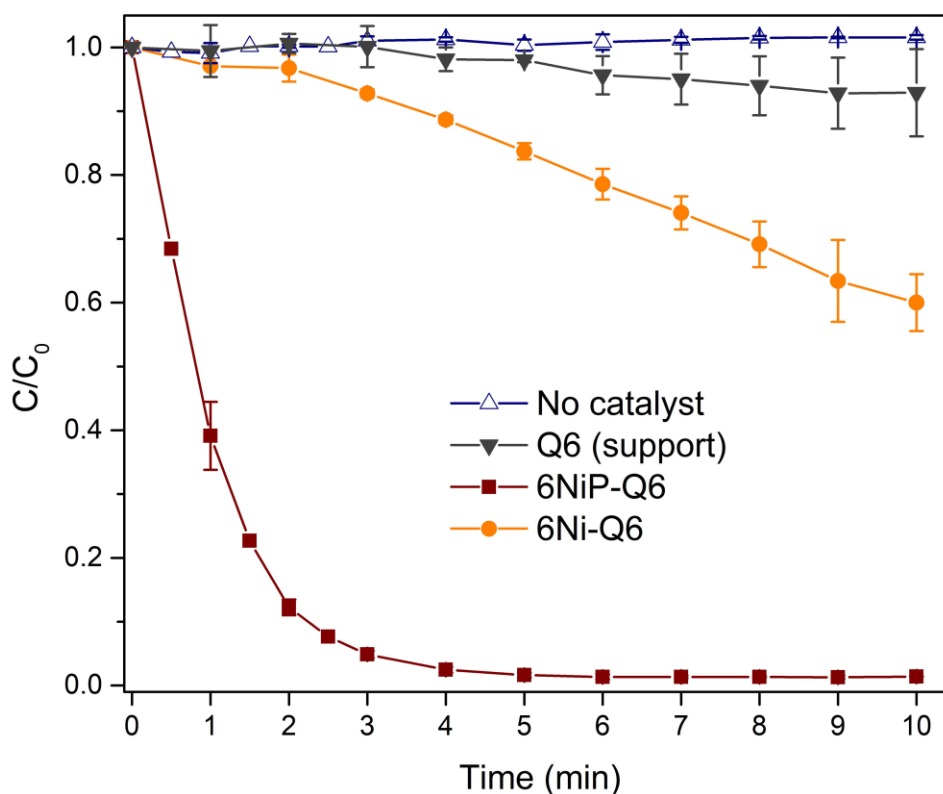
3.2.1 Effect of different catalysts

Figure 3.4 Time-dependent concentrations of 4-NP reduced over various catalysts.

Figure 3.4 showed the results of how much 4-NP was reduced with the use of different catalysts in the reaction system. According to the results, 4-NP was not reduced without the presence of catalyst. This was to be expected as this reaction lacked kinetic potential to drive reaction forward.[2] Thus, this confirmed that the use of catalysts was necessary for increasing kinetic potential to reduce 4-NP with $NaBH_4$. In case of the use of pure Q6 support as the catalyst, the results showed that after 10 min of reaction, 4-NP was reduced in insignificant amount with the presence of Q6 support without the impregnation with non-noble metal catalysts. In the reaction with 6Ni-Q6 as a catalyst, roughly 40% of 4-NP was reduced after 10 min of reaction. Although it took longer than 10 min, it was not the surprising result as the previous research regarding the use of Ni on a polymer support reported that it took longer than an hour.[22] This confirmed that Ni catalysts had the potential to drive the reduction of 4-NP to occur, but the rate was still sluggish and the activation energy of this reaction was not lowered

down enough to react at room temperature. The last reaction in this section was the use of 6NiP-Q6 as a catalyst. The reaction was completed with all of 4-NP was reduced within 5 to 6 min. The presence of phosphide greatly enhanced the reaction rate of the reaction and acted as a better electron transfer media from the electron donor (BH_4^-) to the electron acceptor (4-NP).[3]

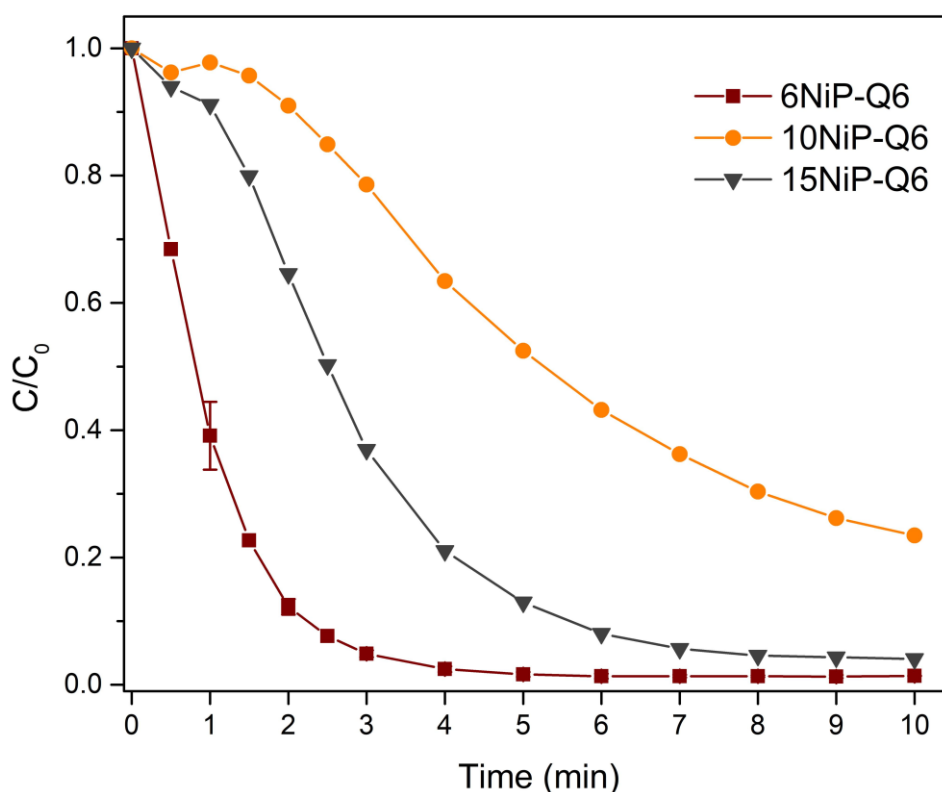### 3.2.2 Effect of percentage of Ni_2P in the catalysts

Figure 3.5 Time-dependent concentrations of 4-NP reduced over various percentage of Ni_2P.

In this section, Q6-supported nickel phosphide catalysts with three different percentages of nickel phosphide: 6%, 10%, and 15% were investigated for their catalytic reduction activity of 4-NP. The results showed that 6NiP-Q6 was the catalyst that exhibited the highest reaction rate with the complete reaction within 5 to 6 min. Meanwhile, the reaction rate of 15NiP-Q6 was slower with the completion at around 8 to 9 min, and 10NiP-Q6 performed slowest with incomplete reaction after 10 min. The reason of 6NiP-Q6 to perform better catalytic activity was because 6NiP-Q6 had higher surface area and smaller Ni_2P particle sizes. Thus, 6NiP-Q6 could come into contact with more 4-NP species in the solution, resulting in better reaction rate.
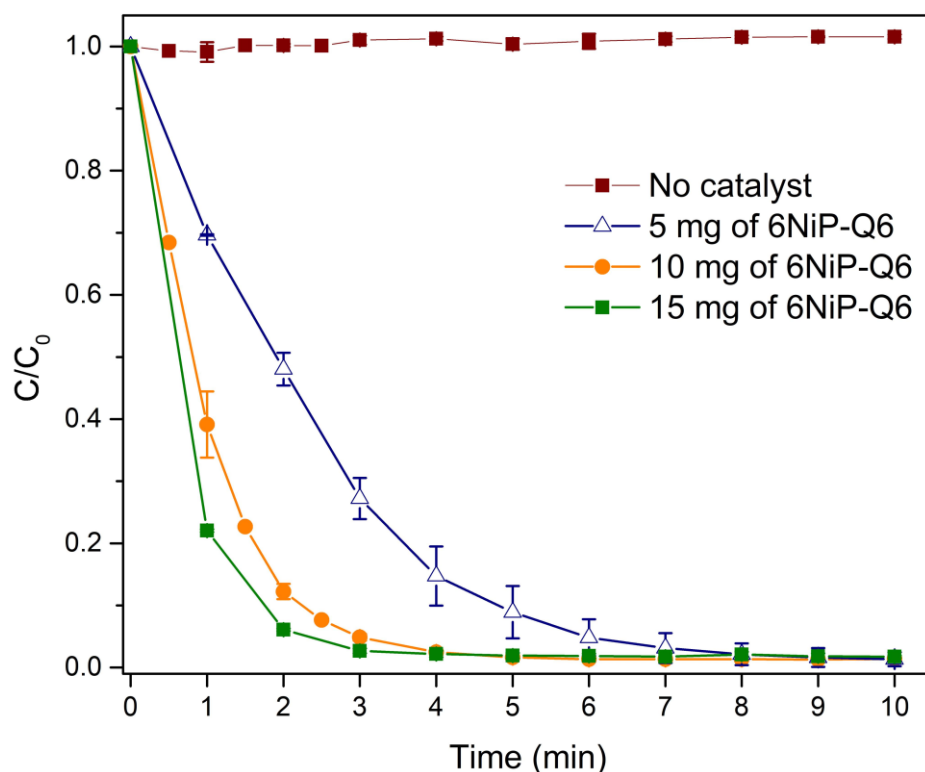
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3.2.3 Effect of catalyst loading

Figure 3.6 Time-dependent concentrations of 4-NP reduced over Ni2P catalysts in various loading amounts.

In this section, 6NiP-Q6 was used as the representative catalyst for investigating the effect of catalyst loading. The results showed that the use of 10 mg and 15 mg of catalyst loading did not give much difference in terms of kinetics and activity. The difference was just that adding 15 mg made the reaction to proceed faster than adding 10 mg during the first 3 min. However, the catalytic activities were similar after 4 min of reaction and both reactions were completed at the same time. Meanwhile, the use of 5 mg of 6NiP-Q6 caused the reaction to proceed a bit slower with the reaction to be completed after reaching 9 minutes. For the slower rate of adding 5 mg, it was probably due to the lack of catalyst amount to contact with 4-NP molecules to complete the reaction. Meanwhile, 10 mg of the catalyst was just enough amount to let all catalyst contact with all 4-NP molecules and adding 15 mg did not significantly change the result. This could confirm that 10 mg of 6NiP-Q6 was the optimum loading amount for the reduction of 4-NP under the condition used in this work.
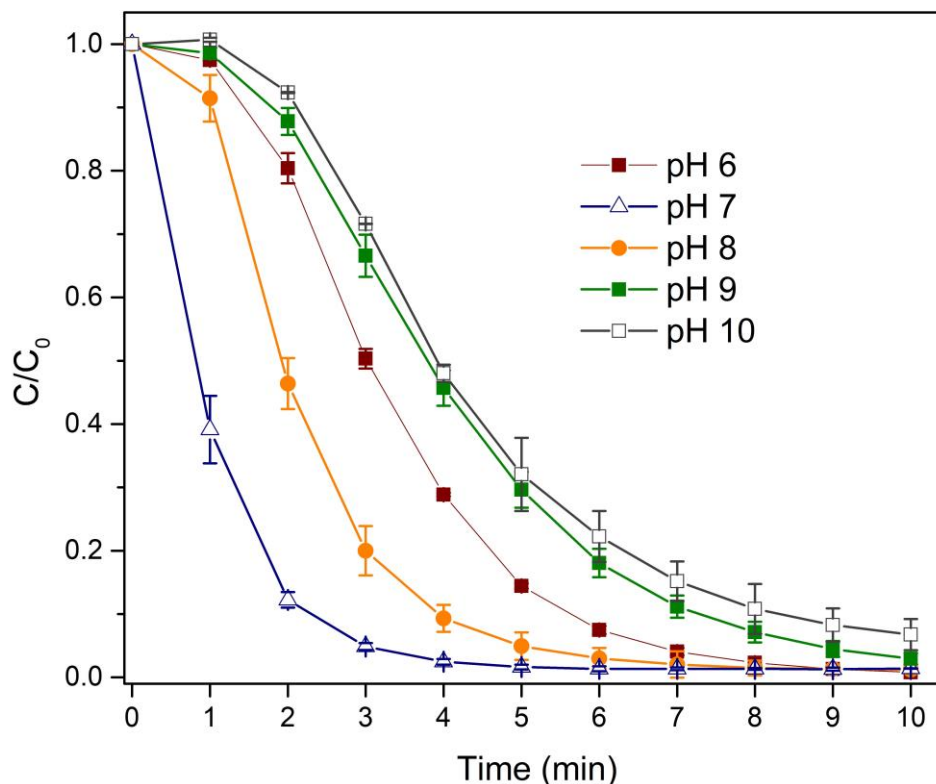
3.2.4 Effect of pH of 4-NP solution

Figure 3.7 Time-dependent concentrations of various pH values of 4-NP in the presence of 6NiP-Q6 catalyst.

4-NP solution with different pH values from 6 to 10 were prepared to study the effect of pH in this reaction. The results showed that 4-NP could be reduced best when the reaction is neutral as the reaction at pH 7 was completed before others. Also, the higher pH value was away from 7, the slower the reaction was. This may imply that the proton dissociation in water which are the properties of acids and bases disturbed the overall reaction system and hindered the reaction rate. In addition, the reaction at pH 6 showed that the reaction was slower than the reaction at pH 8. This may also imply that the proton donation property of acids caused greater disturbance in the reaction system than the proton receiving property of bases. Thus, the optimum condition regarding the acidic and alkaline of the reaction is to perform in neutral condition.
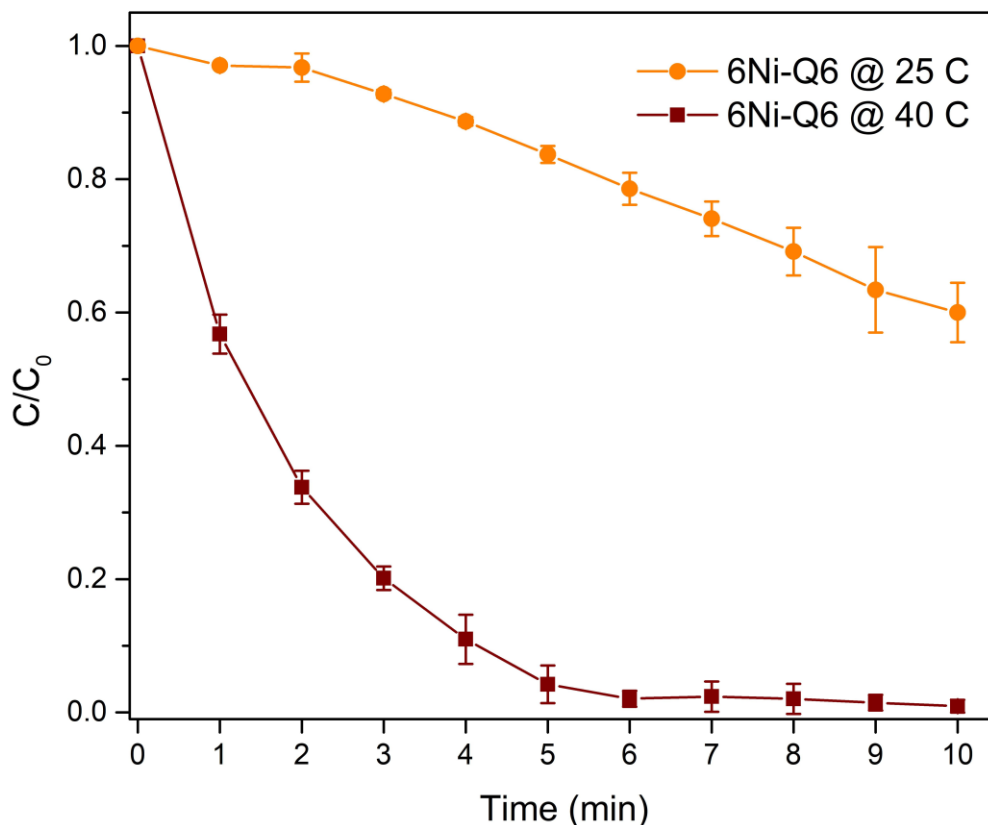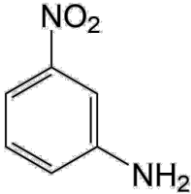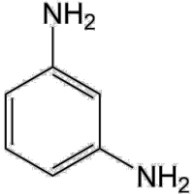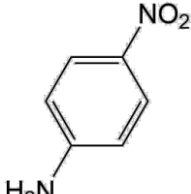
3.2.5 Effect of reaction temperature
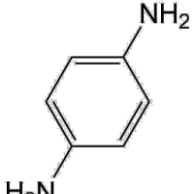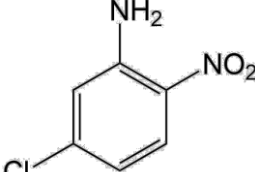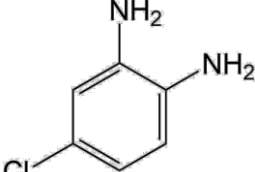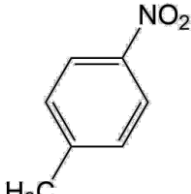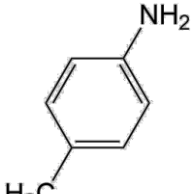
Figure 3.8 Time-dependent concentrations of 4-NP reduced over 6Ni-Q6 at 25 ºC and 40 ºC.

In this section, the catalyst used was 6Ni-Q6 to study the effect of temperature. The results showed that at a higher temperature (40 ºC) could speed up the reaction. When the reaction was at room temperature, the reaction was not complete after 10 min of reaction. Meanwhile, the reaction was completed at 6 min when the reaction was conducted at 40 °C which was at the similar speed as using the 6NiP-Q6 as catalyst. The results indicated that the sluggish rate of reactions in nickel catalysts (without phosphide) were due to insufficient activation energy in room temperature. Thus, by raising temperature, the reaction could speed up and became comparable to nickel phosphide.

3.2.6   Reduction of other nitroarenes

Table 3.2 Catalytic activity of 6NiP-Q6 for different group substituted nitroarene compounds.

Entry	Starting material	Product	Time (min)	Conversion (%)
1	3-nitroaniline	1,3-diaminobenzene	5	100
2	4-nitroaniline	1,4-diaminobenzene	5	100
3	5-chloro-2-nitroaniline	4-chloro-1,2-diaminobenzene	7	100
4	4-nitrotoluene	4-aminotoluene	8	100

*Reaction conditions: 30 mL of starting materials (20 mmol, pH 7), 10 mg of $NaBH_4$, 10 mg of 6NiP-Q6, 15 mL of deionized water, reactions performed at room temperature.

Four different nitroarenes were used to study the catalytic capability of the synthesized catalysts, in which 6NiP-Q6 was used as the representative. The results showed that the rate of these nitroarenes reduction were not much different from 4-NP with the complete reaction within 5-8 min. Thus, these results confirmed that 6NiP-Q6 had the capability to reduce not only 4-NP, but various nitroarenes in a short period of time.

3.2.7 Catalyst reusability
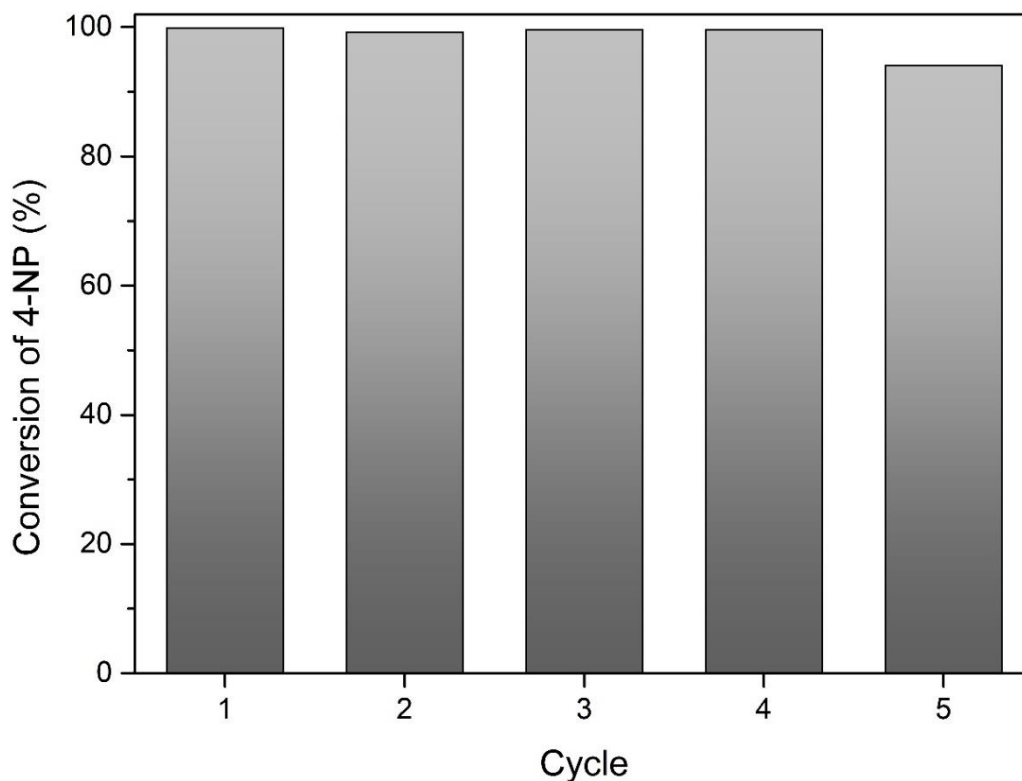
Figure 3.9 Catalyst reusability test of 6NiP-Q6 for five reaction cycles.

6NiP-Q6 was used as the representative catalyst for the study of catalyst reusability. The reduction of 4-NP was conducted by the catalyst and the process was repeated for 5 times. Between each cycle, the catalyst was separated from the solution by centrifugation without any other treatment. The results showed that the conversion of 4-NP remained 100% for the first 4 cycles (Figure 3.9). However, the conversion of 4-NP in the fifth cycle was slightly decreased but was still effective with more than 90% conversion. This confirmed the stability of Ni_2P as catalyst in 4-NP reduction and showed the high potential to be used for multiple times without the significant loss in efficiency.

Chapter 4 – Conclusion

Nickel and nickel phosphide catalysts (Ni/Q6 and Ni$_2$P/Q6) were successfully synthesized using wetness impregnation method. The synthesized materials were characterized by X-ray diffraction, N$_2$ adsorption-desorption, and CO chemisorption. The XRD diffractogram confirmed the successful synthesis with the observed peaks corresponding to the database and implied the metal dispersion on the Q6 support. N$_2$ adsorption-desorption showed how different nickel loadings affected the surface area and the pore volume of the synthesized products. In addition, CO chemisorption results confirmed the metal dispersion of each catalyst.

The catalytic performance tests were conducted by the reduction of 4-nitrophenol (4-NP) using NaBH$_4$ as the reducing agent . 6NiP-Q6 exhibited the highest catalytic activity despite containing the least loading amount of nickel phosphide. This outcome was due to the better metal dispersion and higher surface area to contact with 4-NP in the solution. For nickel catalyst without phosphide (6Ni-Q6), the satisfying result could be archived but the reaction temperature needed to be raised to 40 °C. Other nitroarenes were also used in the study and the results showed that the synthesized catalysts could also reduce them within a short period of time as well.

Lastly, as 6NiP-Q6 showed the highest performance, it is a promising non-noble metal catalyst to replace expensive noble metal catalysts for the reduction of 4-NP with satisfying efficiency. Moreover, the catalyst could also be reused without losing efficiency for at least four cycles. Thus, 6NiP-Q6 was the catalyst that was efficient both capability and economically.

4.1 Suggestions for future research

There are several suggestions regarding the study of nickel phosphide catalysts. As the one that loaded the least metal performed well with higher surface area and better dispersion on the support, decreasing the amount and synthesizing even lower amount of nickel may be an interesting option to find the minimum loading amount that still maintain the satisfying results. The next suggestion may be using more diverse choices of nitroarenes to test the capability and selectivity of the catalysts. Another suggestion is to try varying concentrations of 4-NP to be used as samples as well as varying $NaBH_4$. There was a literature that explained about the difference in concentration that can affect the rate of the reaction.[2] Using different concentrations to find the optimum condition for using the catalysts in this project may provide better information to apply in the actual work. The last suggestion that came into the author's mind was to try applying the methodology used in this project in real water treatment and use real 4-NP-polluted water as samples. This may confirm how practical the methodology is to be used in real cases.

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Biography

Mr. Khandhinat Watanaudomkiat was born on 5th of March 1999. He graduated from Columbia International School in Saitama, Japan and achieved Ontario Secondary School Diploma as a certificate. Currently, he is studying in fourth year for the Bachelor of Science in Applied Chemistry (BSAC) program majoring in Industrial Chemistry and Management, the Department of Chemistry, Faculty of Science, Chulalongkorn University. He will graduate with his B.Sc. in 2021 with high chance of receiving honor degree. He is planning to continue his studies for master's degree, with the university and course are being considered at the moment.