A Comparative Study of Hexacyanoferrate-based Prussian Blue Analogue Nanocrystals for Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol

Thomas Wi-Afedzi^a, Fei-Yee Yeoh^{b,}, Ming-Tong Yang^a, Alex C. K. Yip^{c,*}, and Kun-Yi Andrew*

Lin^{a,}*

^a Department of Environmental Engineering & Innovation and Development Center of Sustainable Agriculture & Research Center of Sustainable Energy and Nanotechnology, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan

^b School of Materials and Mineral Resources Engineering, Transkrian Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^c Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

*Corresponding Authors. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw (K.-Y. A. Lin); alex.yip@canterbury.ac.nz (A. C. K. Yip) ; yeoh.usm@gmail.com (F. Y. Yeoh)

Abstract

Catalytic reduction of 4-nitrophenol (4-NP) represents a useful method of converting 4-NP into a more environmentally friendly product, 4-aminophenol (4-AP). Prussian blue (PB) ($\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$) and its Prussian blue Analogues (PBAs) ($\text{M}^{\text{II}}[\text{Fe}(\text{CN})_6]$ PBAs ($\text{M}^{\text{II}} = \text{Mn}, \text{Co}, \text{Ni}, \text{and Zn}$) exhibit hierarchical porous structures, and electrochemical characteristics, making PBAs promising catalysts for 4-NP reduction. Nevertheless, very few literatures report the reduction of 4-NP to 4-AP employing PBAs, and no studies have been ever conducted to evaluate the effects of different M^{II} species of $[\text{Fe}(\text{CN})_6]$ -based PBAs on the catalytic conversion of 4-NP to 4-AP. Herein, we examine the catalytic reductive performance of various $\text{M}^{\text{II}}[\text{Fe}(\text{CN})_6]$ PBAs ($\text{M}^{\text{II}} = \text{Co}, \text{Fe}, \text{Mn}, \text{Ni}, \text{and Zn}$), in the presence of sodium borohydride (NaBH_4), on 4-NP reduction to 4-AP. The catalytic activity of PBAs for 4-NP reduction was in the order $\text{CoFeCN} > \text{NiFeCN} > \text{FeFeCN} > \text{MnFeCN} > \text{ZnFeCN}$. The corresponding activation energies are determined as 32, 43, 46, 47, and 54 kJ/mol for CoFeCN, NiFeCN, MnFeCN, FeFeCN and ZnFeCN, respectively. Especially, CoFeCN shows the highest catalytic activity with a rate constant of 0.457 min^{-1} and a calculated turnover frequency of $6.3 \times 10^{-3} \text{ s}^{-1}$, which are higher than many reported noble metal catalysts because of its high surface area and catalytic activities towards hydrogen generation and hydrogenation. CoFeCN (and NiFeCN) also exhibit excellent reusabilities even after 6 consecutive reduction experiments. These findings demonstrate that PBAs, such as CoFeCN and NiFeCN, are highly advantageous catalysts for reduction of 4-NP and would be promising for reducing other nitro-aromatic compounds.

Keywords: 4-Nitrophenol, Prussian blue analogue, 4-Aminophenol, reduction, Sodium borohydride

1. Introduction

Among various phenolic compounds which are considered as priority pollutants, 4-nitrophenol (4-NP) is one of the frequently occurring by-products, which is hazardous to the environment [1,2]. Contrary to that, the reduction of 4-NP may yield 4-aminophenol (4-AP) which is an important chemical intermediate for the synthesis of pharmaceuticals, polymers, anticorrosive lubricants, and dyes [3–5]. In view of the hazardous effect of 4-NP and the growing demand for 4-AP, direct catalytic conversion of 4-NP to 4-AP is highly desired.

Catalytic reduction of 4-NP has been introduced as a useful method converting 4-NP into 4-AP using NaBH_4 as a reducing agent [3,6,7]. To date, various noble and precious metals such as Ru, Pd, Ag, Pt and Au have been extensively employed for converting 4-NP to 4-AP in the presence of NaBH_4 [8–12]. Although noble metals are known to generate electronic deficient sites which tend to exhibit catalytic activities for hydrogenation reactions, searching for more effective, easy-to-prepare and inexpensive non-noble catalysts have called for increasing researches in this area.

In recent years, coordination polymers, such as metal organic frameworks (MOFs) with hierarchical structures, porosities and multi-functionalities [13], have been considered as promising materials owing to their potential applications in resolving energy and environmental problems [14,15]. Prussian blue (PB), the oldest coordination compound [16], is considered as a class of MOFs [17,18] and therefore shares their numerous characteristics that make them to attract attention in many applications. Interestingly, different Prussian Blue analogues (PBAs) can also be created from the dehydrated prototype PB, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, by substituting other transition metals. PBAs, represented as $\text{M}^{(\text{II})}_3[\text{M}^{(\text{III})}(\text{CN})_6]_2$, have cyanide groups, acting as bridges between two transition metal ions (i.e., two types of metal centers) in octahedral sites. They are chemically stable and easy to prepare yet intriguing because their transition metal ions can exist in different oxidation states while still maintaining the

cubic structure [19]. Frameworks of PBAs also constitute vacancies for balancing charges [20,21]. Owing to their versatility, PBAs have been investigated extensively and are versatile for energy storage [20,22–25], gas storage [26,27], sensors [28–31], drug delivery [17,32,33], and catalysis [34–36].

Nevertheless, very few literatures have reported on the reduction of 4-NP to 4-AP employing PBAs as catalysts. To the best of our knowledge, no studies have been conducted to evaluate the effects of different M^{II} species of $[Fe(CN)_6]$ -based PBAs on the catalytic conversion of 4-NP to 4-AP. In this study, we synthesize different $M^{II}[Fe(CN)_6]$ PBAs (M^{II} = Co, Fe, Mn, Ni, and Zn) and evaluate them for their catalytic performance towards 4-NP reduction to 4-AP via hydrogenation.

2 Experimental

2.1 Materials

All reagents used in this study were reagent-grade and were employed without additional purification. Nickel nitrate ($Ni(NO_3)_2$), $NaBH_4$, 4-NP and zinc nitrate ($Zn(NO_3)_2$) were obtained from Sigma-Aldrich (USA). Potassium hexacyanoferrate ($K_3Fe(CN)_6$) was purchased from J. T. Baker (Germany). Cobalt nitrate ($Co(NO_3)_2$) was received from Choneye Pure Chemicals (Taiwan). Zinc nitrate ($Zn(NO_3)_2$) was obtained Showa Chemical Co. Ltd (Taiwan). Iron nitrate ($Fe(NO_3)_2$) and manganese nitrate ($Mn(NO_3)_2$) were purchased from Merck (Germany). Deionized (DI) water was prepared to less than $18\text{ M}\Omega\cdot\text{cm}$.

2.2 Preparation and Characterization of PBAs

$FeCN$ -based Prussian Blue analogues (PBAs) were synthesized according to reported procedures [37]. In a typical synthesis, 10 mmol of $K_3[Fe(CN)_6]$ was first dissolved in 100 mL of Deionized (DI) water and the resulting solution was dropwise added to another beaker

containing 100 mL of $M^{II}(\text{NO}_3)_2$ solution (0.150 M) (M^{II} = Fe, Mn, Co, Ni and Zn). The mixture was stirred at ambient temperature for 4 h, and precipitate was then collected via centrifugation, washed with DI water thoroughly and dried at 65 °C to afford PBAs. Throughout this study, the abbreviation “ $M^{II}\text{FeCN}$ ” was adopted to denote a certain $M^{II}_3[\text{Fe}(\text{CN})_6]_2$ PBA. For instance, “CoFeCN” was used to denote $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$.

The prepared PBAs were characterized using Powder X-ray diffraction patterns (XRD) of PBAs using an X-ray diffractometer (Bruker D8 Discover, USA) to verify their formations. Microscopic images of the as-prepared PBAs were visualized using scanning electronic microscopy (SEM). Textural properties of PBAs were determined using a volumetric gas adsorption analyzer (Quantachrome Auto IQ, USA) for obtaining N_2 sorption/desorption isotherms. Temperature-programmed reduction (TPR) properties of PBAs were also measured by using a volumetric gas adsorption analyzer equipped with a TCD detector (Quantachrome TPX, USA) for determining chemical absorption of hydrogen. In a typical TPR measurement, 0.1 g of PBA was placed inside a U-shaped quartz tube which would be purged with helium gas at 140 °C for 2 hours and then cooled down to 40 °C, followed by H_2 absorption in the temperature range from 100 to 800 °C. Hydrogen generation from NaBH_4 hydrolysis catalyzed by PBAs was determined by measuring volume of H_2 gas via a water-displacement method. Particle size of PBAs in aqueous medium was measured using a dynamic light scattering (DLS) particle size analyzer (Malvern Zetasizer Nano ZS, UK).

2.3 Catalytic reduction of 4-nitrophenol

In this study, NaBH_4 and 4-NP aqueous solutions were prepared with concentrations of 1 M and 3.6×10^{-3} M, respectively. To a cuvette containing 2.5 mL DI water, 95 μL of 3.6×10^{-3} M aqueous solution of 4-NP was introduced and 137 μL of 1 M aqueous solution of NaBH_4 was added to the solution at a desired temperature, and PBAs (70 μL of 1mg/mL) was added.

After pre-set intervals, UV–vis spectra of reaction mixtures were recorded over the scanning region of 200–500 nm. The quantitative determination of 4-NP was performed by recording the absorbance at different time intervals at 400 nm. The concentration of the NaBH_4 was chosen to exceed the concentration of the 4-NP by far, so that the kinetics of the reduction can be considered as a pseudo-first order reaction with respect to 4-NP [38].

3 Results and discussion

3.1 Characterization

To ensure the formation of PBA, the prepared PBAs were analyzed for their crystalline structures. Fig. 1(a) shows XRD patterns of all PBAs used in this study. While $[(\text{FeCN})_6]^{3-}$ was coordinated with various M^{II} , all PBAs exhibited similar patterns, which agree with the reported XRD pattern of PB [39]. In particular, a number of intense peaks can be observed at $2\theta = 17, 24, 35, 39$ and 43° , corresponding to (2 0 0), (2 2 0), (4 0 0), (4 2 0) and (4 2 2) planes of PB [39]. This special pattern can be attributed to the cubic $\text{M}^{\text{II}}[(\text{FeCN})_6]$ framework, which is comprised of an octahedral $[(\text{FeCN})_6]^{3-}$ complex coordinated with nitrogen-bound Fe^{III} ions. As a result, PBAs were iso-structurally crystallized in the space group of $Fm\bar{3}m$ [27,40].

While the crystalline structures of as-prepared PBAs were almost identical, we further determined their morphologies in Fig. 1(b). FeFeCN seemed to comprise of many fine particles with a size of a few nanometers, but these nanoparticles were closely packed together. On the contrary, MnFeCN was comprised of significantly large clusters. Furthermore, CoFeCN and NiFeCN exhibited a very similar morphology, consisting of rounded particles with sizes of a few tens of nanometers. Nanoscale pores could also be observed between the rounded particles. In addition, ZnFeCN was also found to contain relatively large particles of sizes of a few hundred nanometers. On the other hand, since 4-NP

reduction is an aqueous reaction, particle sizes of these PBAs in water were essential and thus further determined using a DLS particle size analyzer as listed in Table S1. ZnFeCN and MnFeCN appeared to be relatively large, whereas CoFeCN and NiFeCN were moderate, and FeFeCN was smallest. This order of particle sizes of PBAs in water is quite similar to the order of particle size observed based on the SEM images.

Moreover, textural properties of these morphologically different PBAs were also characterized as shown in Fig. 2. One can notice that CoFeCN and NiFeCN exhibited a very similar sorption isotherm of the IUPAC type IV with a small hysteresis loop, signifying the existence of pores as observed in the SEM images. CoFeCN and NiFeCN also adsorbed

Fig. 1. (a) XRD patterns and (b) SEM images of various $M^{II}_3[Fe(CN)_6]_2$ (The scale bar is 100 nm).

considerably higher amounts of N_2 than other PBAs and thus exhibited much higher surface areas of 522 and 520 m^2/g , respectively. In contrast, MnFeCN and ZnFeCN were comprised of large particles, thereby exhibiting much less N_2 adsorption and lower surface areas of 450 and 270 m^2/g . On the other hand, FeFeCN, as an aggregation of fine particles, also revealed a low N_2 adsorption and a surface area of 261 m^2/g but it also exhibited an obvious hysteresis loop, suggesting that it was also porous. Through the characterizations of morphology and textural property, these PBAs, in fact, were quite different.

Fig. 2. N_2 sorption isotherm of the as-synthesized PBAs.

3.2 Catalytic reduction of 4-NP by PBAs

Catalytic activities of various FeCN-based PBAs for 4-NP reduction in the presence of $NaBH_4$ were first investigated by monitoring UV-vis spectral variations of 4-NP solutions.

Fig. 3(a) reveals that the concentration of 4-NP was certainly decreased by FeFeCN but there was a large fraction of 4-NP remaining even after 300 min. In addition, the corresponding peak of 4-AP at 300 nm was quite small. These features suggest that FeFeCN did not efficiently reduce 4-NP even though an extensive reaction time was given. A similar result was observed when MnFeCN was employed for 4-NP reduction and, in fact, the extent of 4-NP reduction by MnFeCN after 300 min was even less than that by FeFeCN.

On the other hand, when CoFeCN was used (Fig. 3(c)), 4-NP was rapidly reduced and completely removed within 8 min. The corresponding peak of 4-AP grew significantly taller over 8 min, indicating that CoFeCN was a highly effective catalyst for reducing 4-NP to become 4-AP. Furthermore, NiFeCN was also able to reduce 4-NP quickly and the resulting 4-AP was also significant (Fig. 3(d)). However, Fig. 3(e) shows that ZnFeCN was unable to reduce 4-NP as the concentration of 4-NP remained almost the same after 300 min and no 4-AP occurred, demonstrating that ZnFeCN was an impotent catalyst for 4-NP reduction. The concentrations of 4-NP and the resulting 4-AP as a function of reaction time were also determined and displayed in Fig. S1 (see the supporting information). These plots of mass balance of phenolic compounds indicate that when 4-NP was converted, it could quickly be converted to 4-AP and no significant adsorption of 4-NP and 4-AP to PBAs could be noticed.

To further quantitatively compare these PBAs, time-dependent variation of 4-NP concentration was expressed as follows:

$$\ln(C_t / C_0) = -kt \quad (1)$$

Where C_t is the concentration of 4-NP at a reaction time ' t ', C_0 is the initial concentration of 4-NP and ' k ' is the first-order rate constant of 4-NP reduction by PBA catalysts in the

Fig. 3. Time-dependent UV-vis absorption spectra of 4-NP (400 nm) and 4-AP (295 nm) during reduction catalysed by different PBAs, (a) FeFeCN (b) MnFeCN (c) CoFeCN (d) NiFeCN and (e) ZnFeCN catalysts at 28 °C. [4-NP (1.22×10^{-4} M), NaBH_4 (4.9×10^{-2} M) and 25 mg/L of the prepared catalysts]

presence of excess NaBH_4 . The corresponding plots of $\ln(C_t/C_0)$ vs. t are displayed as Fig. 4(a), and the pseudo-first-order rate constants are summarized in Table 1. The order of catalytic activities of PBAs for 4-NP reduction was $\text{CoFeCN} > \text{NiFeCN} > \text{FeFeCN} > \text{MnFeCN} > \text{ZnFeCN}$.

Fig. 4. (a) Pseudo-first order plots of 4-NP reduction in the presence of NaBH_4 over different PBAs at 28°C (4-NP (1.22×10^{-4} M)); (b) H_2 generation by NaBH_4 catalyzed by PBAs (NaBH_4 (4.9×10^{-2} M) and 25 mg/L of the prepared catalysts).

Despite the fact that these PBAs exhibited noticeably different surfaces and sizes, either in dry or wet environment, their catalytic activities for 4-NP reduction were obviously not proportional to their surface areas and not directly relevant to their morphologies. Thus, the distinct catalytic activities of these PBAs should be attributed to chemical characteristics of PBAs. Since these PBAs were comprised of the same $\text{M}^{\text{II}}[\text{Fe}(\text{CN})_6]$ framework, the distinct performances of 4-NP reduction should not be attributed to FeCN_6 . Instead, the metal species (M^{II}) bound to FeCN should play a more important role. As various M^{II} species were used, the quite different morphologies of PBAs were also afforded. CoFeCN and NiFeCN actually exhibited much higher surface areas than other PBAs; thus their high catalytic activities might be associated with more reactive surfaces. Additionally, since NaBH_4 was used as a

hydrogen source, which should be decomposed to release hydrogen molecules from NaBH_4 , it was insightful to investigate H_2 generation from NaBH_4 in the presence of these PBAs. Fig. 4(b) shows the initial release of H_2 gas from NaBH_4 in the presence of PBAs. CoFeCN and NiFeCN seemed more effective to facilitate H_2 release from NaBH_4 than other PBAs. Moreover, one can notice that there was an obvious lag for FeFeCN , MnFeCN and ZnFeCN for releasing H_2 from NaBH_4 . This result suggests that CoFeCN and NiFeCN could quickly acquire hydrogen molecules from NaBH_4 while H_2 generation by other PBAs were much slower, validating that CoFeCN and NiFeCN were more catalytically active. This might be because Co and Ni have been proven as highly efficient metal species for decomposing NaBH_4 to generate H_2 [41–44].

On the other hand, since binding of hydrogen molecules to catalysts is considered as an important intermediate reaction for 4-NP reduction [45], temperature-programmed reduction (TPR) analyses of PBAs were conducted in order to realize hydrogenation activities of PBAs in Fig. 5. While these PBAs were comprised of the same $\text{M}^{\text{II}}[\text{Fe}(\text{CN})_6]$ framework, they exhibited very distinct TPR spectra. FeFeCN and MnFeCN seemed relatively difficult to be hydrogenated, whereas CoFeCN and NiFeCN could be more easily hydrogenated. Especially, there was an obvious reduction peak of CoFeCN occurring at 275 °C and no other PBAs could exhibit any reduction peaks < 300 °C. This indicates that CoFeCN revealed a stronger activity of hydrogenation than other PBAs, making CoFeCN the most effective PBA for 4-NP.

Fig. 5. Temperature-programmed reduction analyses of PBAs.

According to the observation above, the potential mechanism of 4-NP reduction to 4-AP by PBAs might be illustrated as shown in Fig. 6. The combination of PBAs (e.g., CoFeCN and NiFeCN) and NaBH_4 induced release of H_2 immediately from NaBH_4 . The resultant H_2 gas would bind to the surface of PBA, where the nitro group of 4-NP was adsorbed. The nitro group was then hydrogenated to become an amine group, and then the resulting 4-AP transferred back to the solution.

Fig. 6. Schematic illustration for the mechanism of 4-NP reduction by PBA in the presence of NaBH_4 .

Overall, CoFeCN seemed to exhibit an even higher catalytic activity than NiFeCN. Previously, cobalt in its pure form has been shown to exhibit a higher catalytic performance than nickel [46]. Thus, CoFeCN could support better catalytic properties than NiFeCN owing to enhanced electron transmission between Co and Fe (than Ni and Fe) when 4-NP is in contact with the surface of CoFeCN. Besides, a number of studies have reported the influence of synergistic effect on enhanced catalytic activity. He *et al.* have attributed the high catalytic activity of their Au–Cu nanocrystals catalyst mainly to synergistic effect between the two metals [47]. Similarly, Lin *et al.* concluded that the synergy between Fe–Co was the main factor behind the excellent catalytic performance of their FeCo nitrogen-doped graphene catalyst towards 4-NP reduction [48]. In this regard, it can be deduced that the synergistic effect of Co–Fe largely contributed to the enhanced catalytic activity of CoFeCN. ZnFeCN, on the other hand, was ineffective towards the reduction of 4-NP probably due to the lack of incomplete *d*-orbitals in Zn^{II} to facilitate the transfer of electrons between BH₄[−] and 4-aminophenolate ions.

Additionally, the determination of the turn over frequency (TOF) made it possible to compare our results with other studies. The TOF, which is given as the turn over number (TON)/time, is defined as the number of reduced reactant molecules (4-NP) per mass of catalyst (PBA) per time or the number of moles of the reduced reactant per mole of catalyst per time [49]. The TOFs of FeFeCN, MnFeCN, CoFeCN and NiFeCN were determined to be 0.009×10^{-3} , 0.002×10^{-3} , 6.3×10^{-3} and $2.44 \times 10^{-3} \text{ s}^{-1}$, respectively. In comparison with reported TOFs of 4-NP by various catalysts (Table 1) [50–55], CoFeCN and NiFeCN exhibited much higher TOFs than most of reported catalysts. Especially, the TOF of CoFeCN appeared to be the highest among various reported materials, including noble metals, signifying the promising catalytic activity of CoFeCN for 4-NP reduction.

Table 1. Comparison of turnover frequency (TOF) for 4-NP reduction over PBAs with different reported catalyst systems

Catalyst	k (min ⁻¹), 28°C	TOF (s ⁻¹)	Reference
FeFeCN	0.013	0.009×10^{-3}	This work
MnFeCN	0.006	0.002×10^{-3}	This work
CoFeCN	0.457	6.31×10^{-3}	This work
NiFeCN	0.193	2.44×10^{-3}	This work
ZnFeCN	< 0.001	-	This work
10 wt.% Ni/TiO ₂		3.83×10^{-3}	50
10 wt.% Ni/Al ₂ O ₃		1.49×10^{-3}	
Ag@Co/RGO		5.30×10^{-3}	51
CeO ₂ /Pd		0.167×10^{-3}	52
Ni-Co-Pd-P		2.00×10^{-3}	53
PtCoY		0.004×10^{-3}	54
Ag-MMT		0.003×10^{-6}	55

3.3 Activation energies of 4-NP reduction using PBAs

To further investigate catalytic activities of PBAs for 4-NP reduction, the effect of temperature on k of 4-NP reduction by various PBAs was studied at different temperatures in order to obtain corresponding activation energies (E_a) via the following Arrhenius equation:

$$\ln k = \ln A - \left(\frac{E_a}{RT} \right) \quad (2)$$

where k is the rate constant, E_a is the activation energy, R is the universal gas constant ($R = 0.008314 \text{ kJ K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (in Kelvin) and A is the pre-exponential factor. Fig. 7 shows plots of $\ln k$ vs $1/T$ of 4-NP reduction by various PBAs; interestingly, regardless of PBA species, $\ln k$ values could be linearly-correlated to $1/T$, indicating that kinetics of 4-NP reduction by PBAs at different temperatures can be properly interpreted by the Arrhenius equation. Accordingly, E_a could be calculated from the slope of each plot and the lowest activation energy of 32.85 kJ/mol was realized for the CoFeCN catalyst while E_a increased to 43.48, 46, and 47 kJ/mol when using NiFeCN, FeFeCN, and MnFeCN, respectively.

Fig. 7. Arrhenius plots ($\ln k$ vs $1/T$) for 4-NP reduction in the presence of different catalysts in the range of 28–50 °C [4-NP (1.22×10^{-4} M), NaBH_4 (4.9×10^{-2} M) and 25 mg/L of the as prepared catalysts]

Table 2 further summarizes various E_a values of reported catalysts comprised of cobalt, nickel, iron and precious metals for comparison with those of PBAs. One can note that PBAs, in fact, exhibited much lower E_a than several precious metal catalysts and CoFeCN could show a comparable or even lower E_a than highly-effective Au-based catalysts[10,54,56–61]. This demonstrates that PBAs, especially CoFeCN and NiFeCN, were very advantageous catalysts for 4-NP reduction.

Table 2. Comparison of activation energies (E_a) for 4-NP reduction over PBAs with different reported catalyst systems

Catalyst	E_a (kJ/mol)	Reference
FeFeCN	47	This work
MnFeCN	46	This work
NiFeCN	43	This work
CoFeCN	32	This work
ZnFeCN	54	This work
PtY	136	
NiY	105	
CoY	60	
PtNiY	119	54
PtCoY	55	
Red PtY	117	
Red PtCoY	48	
Pt NPs	40	56
PS-PEGMA-Ag	62	57
Au/polyelectrolyte brushes	43	58
Au/PMMA	38	
Pt-NPs	44	59
Pd-NPs	44	60
Au/ion-exchange resin	31	10
Magnetic Au-NP	51	61

3.4 Reusability of CoFeCN and NiFeCN

Owing to the significantly higher catalytic activities exhibited by CoFeCN and NiFeCN in earlier tests, they were selected for the reusability experiment to further evaluate their practical catalytic applications. To test for reusability of CoFeCN or NiFeCN, the reduction process was repeated severally using the same catalyst (Fig. 8). After the completion of one catalytic reduction cycle, a fresh batch of 4-NP was added to the reaction mixture without catalyst regeneration. The freshly added 4-NP was easily converted to 4-nitrophenolate by the excess NaBH_4 present in the reaction mixture. Fig. 8 shows that both CoFeCN and NiFeCN exhibited similar catalytic performance even after the 6th consecutive reaction cycle. The corresponding kinetic data of the multiple cycles of 4-NP reduction during the reusability tests were also determined as listed in Table S2. The rate constant of 4-NP reduction, by

using CoFeCN, seemed to decrease slightly from 0.76 to 0.68 min⁻¹. On the other hand, a similar trend for the rate constants of 4-NP reduction by NiFeCN can also be observed. Since the recyclability test in this study was conducted by continuously adding fresh 4-NP and NaBH₄ solutions to the same reactor where the catalyst was retained. Thus, the resulting by-products were accumulated and possibly adsorbed to the catalyst, thereby interfering with interactions between 4-NP and PBAs, and then the reaction kinetics [62].

Nevertheless, CoFeCN and NiFeCN, even without regeneration, were still capable of reducing 4-NP to 4-AP completely and rapidly, indicating the remarkable catalytic activity and high stability of these PBAs in reducing 4-NP to 4-AP.

Fig. 8. Reusability test (C_t/C_0 vs time) of (a) CoFeCN and (b) NiFeCN in reducing 4-NP to 4-AP [4-NP (1.22×10^{-4} M), NaBH₄ (4.9×10^{-2} M) and 25 mg/L of the as prepared catalysts].

4. Conclusion

In summary, the catalytic activity of PBA for 4-NP reduction was in the order CoFeCN > NiFeCN > FeFeCN > MnFeCN > ZnFeCN. The activation energies were found to be 32, 43, 46, 47 and 54 kJ/mol for CoFeCN, NiFeCN, MnFeCN, FeFeCN and ZnFeCN, respectively. Additionally, CoFeCN showed the highest catalytic activity with rate constant (k) of 0.457 min⁻¹ and a calculated TOF value of 6.3×10^{-3} s⁻¹, because of its high surface area and

catalytic activities towards hydrogen generation and hydrogenation. CoFeCN (and NiFeCN) also exhibited higher stability and excellent reusability even after 6 consecutive reduction experiments without regeneration. All data clearly demonstrate that PBA, such as CoFeCN and NiFeCN, are highly advantageous catalysts for reduction of 4-NP and would be promising for reducing other nitro-aromatic compounds.

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Supporting Information
for
**A Comparative Study of Hexacyanoferrate-based
Prussian Blue Analogue Nanocrystals for Catalytic
Reduction of 4-Nitrophenol to 4-Aminophenol**

Thomas Wi-Afedzi^a, Fei-Yee Yeoh^{b,}, Ming-Tong Yang^a, Alex C. K. Yip^{c,*}, and Kun-Yi Andrew
Lin^{a,*}*

^a Department of Environmental Engineering & Innovation and Development Center of Sustainable Agriculture & Research Center of Sustainable Energy and Nanotechnology, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan

^b School of Materials and Mineral Resources Engineering, Transkrian Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^c Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

*Corresponding Authors. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw (K.-Y. A. Lin); alex.yip@canterbury.ac.nz (A. C. K. Yip) ; yeoh.usm@gmail.com (F. Y. Yeoh)

Table S1. Particle sizes of PBAs in water (determined by a DLS particle size analyser).

Catalyst	Average Particle Size from DLS (nm)
CoFeCN	202
NiFeCN	183
MnFeCN	275
FeFeCN	110
ZnFeCN	310

Table S2. *k* constants of the multi-cycles of 4-NP reduction during the reusability tests

Cycle #	<i>k</i> (min ⁻¹)	
	CoFeCN	NiFeCN
1	0.76	0.36
2	0.75	0.35
3	0.73	0.35
4	0.71	0.35
5	0.70	0.34
6	0.68	0.34

Fig. S1 Molar variations of phenolic species during 4-NP reduction by various PBAs: (a) FeFeCN, (b) MnFeCN, (c) CoFeCN, (d) NiFeCN, and (e) ZnFeCN.