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Pd modified prussian blue frameworks: Multiple electron transfer pathways for improving catalytic activity toward hydrogenation of nitroaromatics



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ABSTRACT

Prussian blue analogs (PBAs) exhibit potential as low-cost and eco-friendly nanocatalysts that can be fabricated with ease. However, the PBA framework structure suffers from poor electronic conductivity, which limits the catalytic efficiency for this class of materials. Noble metals represent an alternative class of materials that display inherent catalytic activity but suffer from aggregation, ultimately reducing the amount of accessible catalytic sites. Herein, we demonstrate a combinatory approach that circumvents the known disadvantages with these classes of catalytic materials in which PBA-supported nanocatalysts were synthesized. These composite materials exhibit excellent catalytic activity for the reduction of nitroaromatics to aminoaromatics while displaying long-term cycling stability, which is attributed to the availability of multiple electron transfer pathways. Overall, this work opens the study on the assembly of PBA-supported heterogeneous nanocatalysts and potentially paves the way toward future applications.

1. Introduction

Catalysts are quite useful for the fabrication of chemical products [1–12]. In particular, highly active and selective catalysts play an important role in the conversion of nitroaromatics to aminoaromatics used in the fabrication of pesticides, dyes, explosives, and pharmaceuticals [13–15]. Thus far, the development of stable catalysts used for these conversion reactions has remained a challenge due to many disadvantages, such as agglomeration, loss of activity, and poor selectivity of the catalysts [16–22]. To date, great advances have been achieved through the use of nanocatalysts, which exhibit highly improved catalytic activity that originates from the innovative design of composite nanocatalysts [23–28]. However, drawbacks for this class of materials

include synthesis strategies that require multiple steps and the need for the use of expensive instruments. Therefore, the development of catalysts targeted for use in practical applications should be designed in a way that can address the aforementioned issues.

Prussian blue analogs (PBAs), also known as porous coordination polymers, have been garnering extensive attention in various fields, including batteries, gas sensors, and catalysis, among others, owing to inherent advantages, such as high electrochemical activity, stable framework structures, and ease of fabrication [29–36]. In the chain of cation–CN–cation, through which the electron can flow which affects the chemical properties. In the coordination, the metal cations can interact with either carbon or nitrogen atoms. Thus, the PBA performance is comprehensively determined by the containing species [37]. PBAs

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possess a high density of uniformly-dispersed active sites and open channels, which facilitate the transport and diffusion of both reactant substrates and products [38-40]. Furthermore, PBAs offer the potential for the incorporation of alternative catalytically active species to frameworks, further highlighting the advantages of these heterogeneous systems. In this context, the synergy between nanoparticles (NPs), a class of materials commonly supported on heterogeneous frameworks, and PBAs is of great significance in the catalytic prowess of these composite materials [41-43]. While previous reports have partly addressed the activity of PBAs toward reduction of nitroaromatics to aminoaromatics [44], limited catalytic activities of PBAs are attributed to the poor electronic conductivity resulting from the cyanide bridges in these materials. Therefore, we hypothesized that a modification of the cyanide linkers may potentially yield more efficient electron transport pathways, ultimately resulting in greater activity and higher performance in these hydrogenation reactions.

Noble metal NPs, such as Pd, have been established as highly active catalysts for the hydrogenation of nitroarenes and other reductions [45–48]. Unfortunately, noble metal NPs are typically thermodynamically unstable and tend to aggregate during catalytic reactions due to the high surface energy of small NPs. As a result, catalytic activities are significantly reduced due to the decrease in accessible active sites upon aggregation of NPs. Porous skeleton materials as intrinsic heterogeneous supports can potentially offer sufficient spatial confinement to prevent NP aggregation, resulting in the generation of stable and well-dispersed NPs.

The disadvantages of aggregation and poor conductivity related to catalysts comprised of bare noble metal NPs and PBAs, respectively, can potentially be simultaneously circumvented through the careful fusion of these two classes of materials. As such, we were motivated to evaluate the catalytic activity of PBAs@Pd heterogeneous composite materials for the reduction of nitroaromatics to aminoaromatics in order to probe this hypothesis. These composite materials can be easily prepared through a wet chemical method in an aqueous bath; in a typical synthesis, Pd ions are introduced into an aqueous solution containing the as-prepared PBAs, followed by a reductive growth process of Pd NPs inside and on the surfaces of the PBAs. Six types of hexacyanoferrate (III)-based PBAs (MnHCFe, FeHCFe, CoHCFe, NiHCFe, CuHCFe, and ZnHCFe) were prepared, and out of these materials, FeHCFe exhibits the highest activity for nitroaromatic reduction. In order to explore the performance of PBAs as potential nanocatalyst supports, Pd NPs were decorated on the bare FeHCFe support in the presence of a reductant (Pluronic F-127). Relative to FeHCFe, the synthesized FeHCFe@Pd displays improved catalytic activity, reusability, and selectivity for the reduction of a diverse range of nitroaromatics to the corresponding aminoaromatics, which we attribute to the multiple electron transfer pathways constructed in this composite material.

2. Experimental

2.1. Preparation of PBAs

All reagents were purchased from Sigma Aldrich and used without any further purification. The PBA powders were prepared by mixing 0.1 mol of FeSO₄·7H₂O, MnSO₄·H₂O, NiSO₄·6H₂O, ZnSO₄·7H₂O, CuSO₄·5H₂O, or CoSO₄·7H₂O aqueous solutions with 0.1 mol of a K₃Fe (CN)₆ aqueous solution, followed by constant stirring at 25 °C. Precipitation was immediately observed after mixing the two solutions. Thereafter, the suspension was subjected to high-power ultra-sonication to uniformly disperse the formed products. The ensuing powders were collected and washed with deionized water several times using filtration, and well-cleaned products were dried in a vacuum oven.

2.2. Preparation of FeHCFe@Pd

The FeHCFe@Pd heterogeneous nanocatalyst was prepared by

adding 0.15 g of Pluronic F-127 into a 100 mL of aqueous solution containing the as-prepared FeHCFe NPs (0.1 mol). Sequentially, 0.02 g of K_2PdCl_4 was dissolved in this mixed solution under vigorous stirring and a high-power ultra-sonication for achieving the dispersion. The synthesized heterogeneous nanocatalyst FeHCFe@Pd was separated from the solution via filtration and dried in a vacuum chamber. The Pd NPs loaded on carbon support was also synthesized via a similar method for being used as a reference.

2.3. Material characterizations

The structures of the synthesized nanocatalysts were determined using X-ray diffraction (XRD, D8 Advance). Morphologies were observed using transmission electron microscopy (TEM, JEOL JEM-F200) combined with energy-dispersive X-ray spectroscopy (EDX). Cyanide linkers were detected using Fourier transform infrared (FT-IR, Nicolet iS50) spectroscopy and Raman spectroscopy (LabRAM HV Evolution, HORIBA). Surface chemical bonding features were measured by X-ray photoelectron spectroscopy (XPS, AXIS-HSi) using an Al Ka source. Thermal stability was verified using thermogravimetric analysis (TGA, Simultaneous DTA/TGA analyzer); the sample was heated from room temperature to 700 °C at a temperature ramp of 10 °C min⁻¹ under nitrogen flow. Local ion (Fe and Co) environment was studied by Fe and Co K-edge X-ray absorption near edge structure (XANES) spectroscopy, which was recorded on the CRG-FAME (BM30B) beamline with an incident radiation energy selected by using a pair of Si(220) crystals. Small-angle X-ray scattering (SAXS) was assigned for detecting the decorated Pd NPs. Energy-filtered transmission electron microscopy (EFTEM) was employed for the elemental mapping. The surface area of the FeHCFe@Pd product was analyzed with Brunauer-Emmett-Teller BET through the gas adsorption-desorption method. The amounts of different metal species were measured by inductively coupled plasmaatomic emission spectrometry (ICP-AES).

2.4. Catalytic characterizations

The catalytic activities of the as-prepared PBAs and FeHCFe@Pd were assessed in a model reaction for the reduction of nitroaromatics to aminoaromatics in the presence of the reductant NaBH₄ at room temperature in an aqueous medium. Solutions mentioned in these studies were prepared with deionized water without any organic additives. The catalysts were separated from reaction systems by centrifugation after reaction completion. In a typical procedure, 5 mg of the as-prepared PBAs were dispersed in 30 mL of deionized H₂O, and then, 0.1 mmol of the nitroaromatic was added into the reaction system; constant stirring yielded a uniform solution. Next, the reductant solution (containing NaBH₄, 1.2 mmol) was added to the reaction mixture, which was stirred for 5 min at room temperature. A study on the reusability of the composite FeHCFe@Pd catalyst was conducted by reusing the separated and well-washed catalyst for the subsequent runs. Yields of the aminoaromatic products were determined using gas chromatography-mass spectrometry (GC-MS, Agilent 7890A Gas chromatograph and 5977A Mass selective detector). Furthermore, well-controlled experiments were conducted for 2, 5, and 10 min using 5, 10, 20 mg of catalysts for the optimization of hydrogenation conditions.

3. Results and discussion

Bivalent transition metal ion nodes with an increasing main quantum number are deployed to construct the PBAs, and the as-prepared PBAs can be mass fabricated in a facile manner. Crystal phases of the PBAs identified using XRD are shown in Fig. 1, and the characteristic peaks are well-indexed in the patterns. A common cubic crystal structure is observed for the prepared products, except for the ZnHCFe, which exhibits a different, slightly distorted monoclinic crystal structure that is likely caused by the repulsion between Zn^{2+} nodes and Fe



Fig. 1. XRD patterns of the products: (a) CoHCFe, (b) CuHCFe, (c) FeHCFe, (d) MnHCFe, (e) NiHCFe, (f) ZnHCFe.

 $[(CN)_6]^{4-}$. Lattice parameters of around 10.12 Å (a = b = c) are verified for the cubic PBAs; MnHCFe has an enlarged lattice parameter of around 10.44 Å (Table S1). The monoclinic ZnHCFe with enhanced lattice parameters of (10.95, 13.16, 18.12 Å) is depicted in comparison with others (Table S1).

Morphologies of the PBAs have been observed using TEM, and following an ultra-sonication treatment, all products show a similar morphology for NPs with a size of around 20 nm (Fig. 2). This small particle size results in the generation of more accessible active sites, which is a crucial parameter in the context of catalytic hydrogenation reactions. Furthermore, the high specific surface area that results from small NPs is beneficial for the additive loading of other metals, such as Pd.

The Fe *K*-edge XANES spectra reveal the local structure around Fe ions inside the products, and a typical feature of the pre-region in Fe *K*edge XANES spectra is illustrated by the data for CoHCFe and FeHCFe (Fig. 3a). In these systems, $3d^5$ electron orbital in high-spin Fe(III) splits into $3de_g$ and $3dt_{2g}$ owing to the octahedral crystal field. Electron transitions from the 1s core level to the split orbitals are demonstrated by the peaks in the pre-region A of Fe *K*-edge XANES spectra (Fig. 3b) [49]. In the edge-region (B), sharp peaks at 7131 eV for both CoHCFe and FeHCFe suggest the same oxidation state of Fe ions in the products (Fig. 3a), and a similar pattern for both CoHCFe and FeHCFe is also observed in the C region. The valance state of Co ions in CoHCFe is measured by examining the *K*-edge XANES spectrum (Fig. 3c); a sharp peak at 7725 eV in the B region demonstrates the bivalent Co(II), followed by a C region. Raman spectroscopy has been deployed to verify the vibrational states of the cyanide functional groups in representative mono-metal and bi-metal ion-constructed PBAs (Fig. 3d). A typical Raman shift at 2070 cm⁻¹ (A_{1g}) for FeHCFe is observed, and dual peaks at higher Raman shifts of 2100 (A_{1g}) and 2160 (E_g) cm⁻¹ are observed in the spectrum for CoHCFe. The three transform modes for cyanide are A_{1g} , E_g , and T_{1u} ; the former two are Raman active, and the last one is infrared. A mixed breathing mode for A_{1g} (volume-changing mode) reveals that the central metal ions are coordinated by the stretched and contracted cyanides, which forms by mixing with low-wavenumber modes. Furthermore, the E_g (shape-changing) modes form by mixing with high-wavenumber vibrations [50].

The catalytic activities of the bare PBAs were evaluated in a model reaction in which nitrobenzene was reduced to aminobenzene in the presence of a reductant, aqueous NaBH₄. The highest yield of 33% for aminobenzene is achieved using the bare FeHCFe catalyst (Table S2), demonstrating the potential for FeHCFe as a catalyst in this reaction. To further improve the catalytic activity, Pd NPs were loaded into FeHCFe NPs to create electron transfer pathways on the FeHCFe support.

A schematic illustration of the Pd loading method is depicted in Fig. 4; the process is eco-friendly as the synthesis occurs in water, and this reaction can be easily used scaled up. Upon completion of the reaction, high-powered ultra-sonication is employed to obtain a uniform dispersion and refinement of the particle sizes. The decorated Pd NPs with a size of around 5 nm are observed in TEM images (Fig. 5). A uniform decoration of Pd NPs on FeHCFe NPs is observed in TEM images obtained for the composite material (Fig. 5c and d). EDX



Fig. 2. TEM images of the synthesized products: (a) FeHCFe, (b) CoHCFe, and (c) NiHCFe.



Fig. 3. K-edge XANES spectra of (a) Fe, (b) magnified A region in (a), and (c) Co. (d) Raman spectra of the FeHCFe and CoHCFe products.

mapping shows a better supporting effect for FeHCFe than that of the carbon substrate, displaying larger and agglomerated Pd NPs (Fig. S1). Furthermore, the loaded Pd NPs and uniformly distributed species have been analyzed by EFTEM (Fig. S2). The high-power ultra-sonication of a mixture of these small, uniform Pd NPs combined and an effective surfactant results in the generation of more accessible active sites during the reduction reaction.

XRD analysis was employed to characterize Pd-loaded FeHCFe (Fig. 6a), and the characteristic peaks for PBAs with a face-central cubic

crystal structure is observed both before and after Pd loading. The absence of characteristic Pd peaks suggests the presence of small Pd NPs, which is corroborated by the small particle sizes observed in the TEM images (Fig. 5), and the nanocomposite shows reduced peak intensities after Pd loading relative to data collected for the sample before Pd loading. The structure of the composite nanocatalyst is further confirmed by FT-IR spectroscopic analysis (Fig. 6b). Strong peaks at 3310 cm⁻¹ (OH– stretching vibrations) and 1580 cm⁻¹ (HOH–– bending vibrations) shown by both bare FeHCFe and FeHCFe@Pd are attributed



Fig. 4. Schematic demonstration for the synthesis of the FeHCFe@Pd catalyst.



Fig. 5. TEM images for FeHCFe (a, b) without and (c, d) with Pd nanocatalysts.

to residual H_2O molecules [51]. In addition, sharp characteristic peaks at 2120 cm⁻¹ are associated with in-plane vibrations of the cyanide bridges [52,53]. It is worth noting that the characteristic peak of

cyanide linkers significantly changed from twin peaks to a mono-peak after Pd loading (Fig. 6c). The intensity of the peak at 2130 cm⁻¹ reduced while the peak intensity at 2165 cm⁻¹ increased after Pd loading,



Fig. 6. (a) XRD patterns, (b,c) FT-IR spectra, and (d) TGA curves of FeHCFe with (red) and without (black) Pd nanocatalysts. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Deconvoluted XPS spectra of the prepared FeHCFe@Pd catalyst.

suggesting an interaction between Pd NPs and the cyanide bridges in FeHCFe [54].

Thermal stabilities of the as-prepared FeHCFe catalyst before and after Pd loading were ascertained using TGA (Fig. 6d) in which the loss of absorbed water molecules (10 wt.%) was observed in the initial range up to approximately 200 °C. In the temperature range of 200–500 °C, the as-prepared FeHCFe shows a steady thermal stability, whereas a gradual weight decay is observed for FeHCFe@Pd, suggesting poor thermal stability. This data is consistent with the PXRD data in which reduced crystallinity was observed for FeHCFe@Pd relative to that of the bare FeHCFe (Fig. 6a). Next, the surface area and porosity of the FeHCFe@Pd were estimated using BET analysis (Fig. S3). The composite material exhibits a typical adsorption-desorption isotherm curve and displays a surface area of 294 m² g⁻¹ similar to the previous report [55]. Furthermore, the FeHCFe@Pd shows a pore size distribution comprised of meso- and micro-pores (4 nm in average pore radius and 0.3 cm³ g⁻¹ in volume, Fig. S3).

The surface chemical properties of FeHCFe@Pd were studied using XPS (Fig. 7). The presence of the cyanide linkers is confirmed by the deconvoluted C 1s and N 1s spectra (Fig. 7a and b), and the Fe cation nodes through the observation of the Fe 2p spectrum (Fig. 7c). The bonding nature of Fe and Pd ions was verified by the deconvoluted Fe 2p and Pd 3d spectra in which the data suggest that the Pd NPs are fixed on the frameworks. The O 1s spectrum detected in the product is illustrative of the residual water molecules still present in the sample. Furthermore, the composite product was quantitatively analyzed through XPS measurements, where a mass ratio of 1.5% Pd relative to FeHCFe was observed, suggesting the successful loading of Pd NPs onto the framework (Table S3).

Pd *K*-edge XANS analysis of the composite nanocatalyst (FeHCFe@ Pd) was employed to verify the valance states of Pd component (Fig. 8a). A peak at 24,366 eV (Pd²⁺) further affirms the bonding feature between Pd and FeHCFe at the interface, and a peak located at 24,388 eV suggests the elemental Pd in FeHCFe@Pd. In addition, SAXS characterization was used to analyze Pd NPs that were unable to be detected by normal XRD analysis due to their small size, and a sharp peak at around 0.6 degrees was observed (Fig. 8b). XANS and SAXS measurements were also performed on commercial samples of Pd on carbon, and the similarities between spectra for this sample and the composite sample validate the loading of Pd NPs on FeHCFe (Fig. 8).

Next, the catalytic activity of FeHCFe@Pd was established in the



Fig. 8. (a) XANS and (b) SAXS spectra of the FeHCFe@Pd catalyst (solid line) and commercial Pd NPs on carbon (dot line).

reduction of nitrobenzene to aminobenzene in aqueous NaBH₄. A high yield of 98% is obtained, which can be attributed to the loaded Pd NPs (Table 1). After hydrogenation, a transparent solution can be obtained, suggesting completion of the reaction (Fig. S4). In addition, the

Table 1

Reduction of nitroaromatic substrates catalyzed by $\mbox{FeHCFe}\ensuremath{@Pd}\xspace$ using $\mbox{NaBH}\xspace_4$ reductant.



Reaction conditions: NaBH_4 1.2 mmol, nitromatics 1 mmol, catalyst 5 mg, time 5 min.



Fig. 9. Repeated cycling studies for the reduction of nitrophenol to aminophenol by using the FeHCFe@Pd catalyst.

FeHCFe@Pd composite nanocatalyst is also active towards other nitroaromatic substrates with a diverse range of functional groups, including $-NH_2$, -Br, -Cl, $-CH_3$, and -OH (Table 1), demonstrating the generality of this catalytic system in the context of nitrobenzene reductions. In all cases, FeHCFe@Pd selectively reduces the nitro functional group to the corresponding amino group (Table 1), showing

an excellent performance for this catalyst for broad catalytic reduction applications. Furthermore, the durability of the FeHCFe@Pd composite nanocatalyst was investigated using the reduction of nitrophenol to aminophenol in aqueous NaBH₄ as a model reaction, and the catalytic activity was preserved as 82% yield to the desired product was observed after 5 consecutive reduction cycles (Fig. 9). One possible reason for this reduced catalytic activity is the loss of composite catalyst, FeHCFe@Pd, as it adheres to the walls of the tube during centrifugation after each reaction, which is consistent with the formation of thin film that can be observed on the tube walls. To confirm the immobility of Pd in FeHCFe, the used FeHCFe@Pd catalyst was further analyzed by ICP-AES for the Pd amount on the FeHCFe support, and by XPS to elucidate the bonding environment inside the composite catalyst. The results from these experiments indicate the composite nanocatalyst contains 0.54% Pd within the composite material, suggesting the existence of Pd species. In addition, composite catalyst was also analyzed after a reaction by XPS, and the data indicate the existence of Pd species in the composite product, together with others, such as C, N, Fe (Fig. S5).

Turnover frequency (TOF), an important parameter for the evaluation of catalytic activity, is calculated on the basis of the turnover number, or amount of reactant consumed per amount of catalyst, per unit time. The composite FeHCFe@Pd exhibits a TOF value of around 1.43 s^{-1} , suggesting high catalytic activity for this material. In addition, full conversion of the same amount of nitrophenol (0.1 mmol) can be obtained by a smaller amount of catalyst (5 mg) within 5 min, which can be visually discerned according to the color change between 2 and 5 min (Fig. S6).

A systematic comparison of the catalytic performance between the composite nanocatalyst in this study, FeHCFe@Pd, and previously reported noble metal-containing catalytic materials is provided in Table S4. Compared to the other catalysts, which are typically synthesized via multiple wet-chemical and high-temperature heat treatment approaches [56–58], a relatively facile synthesis process is used for preparing the composite nanocatalyst in this report. Furthermore, FeHCFe@Pd exhibits high catalytic activity as complete conversion of 0.1 mmol of nitrophenol is achieved within a short time range of 5 min (Table 1).

The underlying mechanisms for the excellent catalytic activity of the FeHCFe@Pd composite catalyst can potentially be ascribed to the inherent high activity of Pd, as well as multiple electron transfer pathways present in the composite system (Fig. 10). Upon incorporation of Pd NPs on the FeHCFe framework, the number of electron transfer pathways increase from the original pathway in FeHCFe (i.e., NaBH₄ to FeHCFe to nitroaromatics, Fig. 10a) to at least four total potential pathways in FeHCFe@Pd (i: NaBH₄ to FeHCFe to nitroaromatics; ii: NaBH₄ to Pd to nitroaromatics; iii: NaBH₄ to Pd to FeHCFe to nitroaromatics; iii: NaBH₄ to FeHCFe to nitroaromatics; Fig. 10b); a synergetic effect is simultaneously displayed in FeHCFe@Pd, resulting in superior catalytic performance for this system.

4. Conclusions

In summary, six hexacyanoferrate(III)-based PBAs were synthesized through the use of an ultrasound sonication approach, including Mn-, Fe-, Co-, Ni-, Cu-, and Zn-based materials, and characterized using multiple spectroscopic methods. Next, these PBAs were examined for their catalytic performance in the reduction of nitroaromatics in aqueous NaBH₄, and it was found that the identity of the metal in the PBA greatly influenced the catalytic activity. FeHCFe exhibits a 33% yield for the reduction of nitrobenzene to aniline, which is the highest catalytic activity for this reaction among these PBA-based catalysts. In order to further improve the catalytic performance for this class of materials, catalytically active Pd NPs were incorporated in FeHCFe in order to build more electron transfer pathways in this system. Following characterization of the composite material and confirmation of successful Pd loading into the robust PBA framework, this material



Fig. 10. Schematic illustration for (a) mono- and (b) multiple-pathway reduction reactions.

was tested for the same catalytic reaction and exhibited a significant improvement in catalytic activities with near-quantitative conversions achieved. We propose the improvement in catalytic activity for FeHCFe@Pd originates from the introduction of multiple new electron transfer pathways, as well as the highly improved conductivity, that results upon the combination of porous PBAs and catalytically active Pd NPs. Overall, these results provide insight into the construction of framework materials using PBAs as supports and the engineering of electron transfer tunnels.

Credit Author Statement

Kaiqiang Zhang and Kent O. Kirlikovali: Writing- Reviewing and Editing; Joo Hwan Cha, Se Yeon Jeon, Vamegh Rasouli, and Mehdi Ostadhassan: Visualization, Investigation; Omar K. Farha, Ho Won Jang, Rajender S. Varma, and Mohammadreza Shokouhimehr: Project administration and Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110967.

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