



# Article High-Performance Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol over Pt Nanoparticles Supported on Co-Al LDH Nanosheets

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**Abstract:** In this study, a Pt@Co-Al LDH hybrid structure was fabricated by assembling the metal precursor  $PtCl_6^{2-}$  with the exfoliated LDH nanosheets followed by in situ reduction by NaBH<sub>4</sub>. The morphology, composition and microstructure of the hybrid were characterized by FESEM, HRTEM, XRD, XPS and BET techniques. Pt nanoparticles (NPs) with an average particle size of 3.1 nm were successfully and uniformly loaded on the surface of LDH nanosheets. The catalytic activity of the Pt@Co-Al LDH hybrid was tested for the reduction of 4-nitrophenol, which is one of the most frequent pollutants in wastewater effluent from the pharmaceutical and textile industries. The hybrid displays superior catalytic activity and stability in the reduction of 4-NP under environmental conditions with NaBH<sub>4</sub> as a reducing agent. The hybrid can be recovered in a simple way and still shows high catalytic activity after five reuses.

**Keywords:** Co-Al LDH; platinum nanoparticles; 4-nitrophenol reduction; exfoliation/restacking; heterogeneous catalysis

## 1. Introduction

Currently, water quality pollution is receiving increasing attention. Nitrophenol compounds are considered as priority pollutants due to their biologically harmful properties at low concentrations [1–3]. Among them, 4-nitrophenol is an indispensable substance in the pharmaceutical and textile industries. Over-absorption by the human body can lead to serious consequences such as neurological poisoning, which can seriously damage human health [4,5]. For this reason, a lot of research has been carried out with the expectation of its efficient removal from wastewater. In addition, 4-aminophenol (4-AP) is a crucial chemical intermediary for the production of polymers, pigments, anticorrosive lubricants and medicines [6]. The catalytic reduction of 4-NP to 4-AP is essential in view of the hazardous effects of 4-NP on the human body and the demand for 4-AP in drug synthesis. Thus, for the catalytic conversion of 4-NP to 4-AP under moderate conditions, it is highly desirable to develop a highly effective and easily recoverable catalyst.

The great efficiency of metal nanoparticles, particularly noble metal NPs, as heterogeneous catalysts in various liquid-phase catalytic processes has generated a great deal of interest in them [7–9]. To date, various noble metal NP catalysts have been widely used to convert 4-NP to 4-AP, such as Pd, Pt, Au, Ag [10–16]. However, the small size of noble metal NPs also leads to high surface energy, making them highly susceptible to agglomeration. To address this problem, noble metal NPs are usually immobilized on specific carriers (such as metal oxides and nitrides, molecular sieves, carbon materials and polymer matrices) to



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). improve their stability and recyclability [17–20]. However, the uneven distribution of noble metal nanoparticles or lack of strong host–guest interactions can still result in poor catalytic activity and reduced stability. Consequently, the choice of an appropriate host material and immobilization strategies is crucial for solving the aforementioned challenges [21–23].

For the past few years, layered double hydroxides (LDHs) have become highly sought after as catalyst carriers due to their two-dimensional transition-metal-based nature. One of the main advantages of LDHs is their adjustable composition, with the proportion of metal ions and counter-anions being easily modifiable. Additionally, LDHs offer a tunable structure, allowing for control of the number of layers and spacing between them. With a large surface area, high anion-exchange capacity and the ability to be easily functionalized with other materials [24–26], LDHs have become a popular choice for catalyst development. There are various ways to achieve noble metal NP modification on a carrier surface. For example, Zhang et al. anchored Au nanoclusters with sizes of 1.4 nm on carbonized natural lotus leaf flakes by an impregnation technique. The AuNCs@C-lotus leaf showed good catalytic reduction performance towards 4-NP [27]. Murayama et al. explored the effect of different deposition methods on the loading of Au nanoparticles onto Nb<sub>2</sub>O<sub>5</sub>. By comparing the catalytic oxidation performance of CO, it was found that Au/Nb<sub>2</sub>O<sub>5</sub> synthesized by the deposition reduction (DR) method exhibited optimal catalytic activity [28]. Liang et al. used a sol-gel immobilization method to adjust the particle size of Pt NPs loaded on SBA-15. The nanoparticles were found to exhibit optimal catalytic performance for decalin at a particle size of 3.5 nm [29]. In the past decades, the exfoliation chemistry of LDHs has become a research hotspot due to the unique structural features and fascinating physical, electronic and chemical properties of ultrathin 2D LDH nanosheets [30]. Considering their high charge density, the direct exfoliation of LDHs is quite difficult, and a two-step process is often required: the introduction of anions with weak affinity to layers, followed by the exfoliation step [31,32]. The exfoliated LDH nanosheets with electrostatically interacting surface characteristics are deemed to be an excellent option for loading noble metal active species, which facilitates a high degree of dispersion of noble metal NPs over the catalysts [33].

In this study, uniformly distributed Pt NPs with sizes of 3.1 nm were successfully supported on the surface of exfoliated Co-Al LDH nanosheets without using any stabilizing agent. As shown in Scheme 1, the carbonate form of Co-Al LDH was first converted to nitrate form through two consecutive ion-exchange steps. The LDH-NO<sub>3</sub> was swollen and exfoliated in formamide to obtain a Co-Al LDH nanosheet colloid. Then, the noble metal precursor  $PtCl_6^{2-}$  was assembled with the exfoliated Co-Al LDH nanosheets by electrostatic interaction, followed by the in situ reduction by NaBH<sub>4</sub>. The Pt@Co-Al LDHs were finally aggregated together with the addition of a concentrated alkaline solution. The obtained hybrid Pt@Co-Al LDH exhibits excellent catalytic performance and reusability during the conversion of 4-NP to 4-AP with NaBH<sub>4</sub> as a reducing agent. The catalyst was ready for the next use after a simple centrifugal separation and washing step. After five consecutive uses, its catalytic activity still reached 94.8% of the initial catalytic activity.



Scheme 1. Schematic illustration for the synthesis of Pt@Co-Al LDH.

# 2. Experimental Section

## 2.1. Chemicals

 $CoCl_2 \cdot 6H_2O$ , AlCl<sub>3</sub>  $\cdot 6H_2O$ , urea, 4-nitrophenol, NaBH<sub>4</sub>, NaNO<sub>3</sub> and NaCl were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). H<sub>2</sub>PtCl<sub>6</sub>  $\cdot 6H_2O$  was supplied by Shanghai Tengzhun Biotechnology Co., Ltd. (Shanghai, China). All chemicals were of reagent grade and were used directly without further purification.

## 2.2. Preparation of Co-Al LDH

Co-Al LDH intercalated with carbonate (LDH-CO<sub>3</sub>) was synthesized by the urea hydrolysis method [34,35]. First, 37.5 mL of an aqueous solution containing  $CoCl_2 \cdot 6H_2O$  (0.1 M),  $AlCl_3 \cdot 6H_2O$  (0.05 M) and urea (0.35 M) was mixed and then transferred into a Teflon-lined stainless-steel autoclave after stirring, under hydrothermal heating at 100 °C for 24 h. The products were cooled at room temperature, collected by centrifugation and washed several times using deionized water and ethanol to remove impurities, and the final precipitate was dried under vacuum at 60 °C to obtain 0.6 g of a pink-colored powder.

#### 2.3. Anion Exchange and Exfoliation of Co-Al LDH

LDH-CO<sub>3</sub> (0.2 g) was dispersed into 200 mL of deionized water containing 1 M NaCl and 3.3 mM HCl under a nitrogen atmosphere for 24 h. After thorough washing with water and drying, 0.17 g of LDH-Cl was obtained. The as-prepared LDH-Cl was then treated with 170 mL of NaNO<sub>3</sub>-HNO<sub>3</sub> solution (1.5 M NaNO<sub>3</sub> and 5 mM HNO<sub>3</sub>) to obtain 0.12 g LDH-NO<sub>3</sub>. The anion-exchange product LDH-NO<sub>3</sub> (0.1 g) was mixed with formamide (100 mL) in a flask under nitrogen protection. The mixture was stirred under vigorous magnetic stirring for two days. After centrifugation at 2000 rpm for 10 min, unexfoliated particles were removed, leaving a pink translucent colloidal suspension of exfoliated Co-Al LDH nanosheets (0.95 mg/mL).

## 2.4. Preparation of Pt@Co-Al LDH Hybrid

First, 1 mL of chloroplatinic acid ( $H_2PtCl_6$ , 5 mM) was added to 100 mL of the LDH nanosheet colloidal suspension under a nitrogen atmosphere to load Pt NPs onto Co-Al LDH nanosheets. Excess NaBH<sub>4</sub> solution (molar ratio of NaBH<sub>4</sub>/H<sub>2</sub>PtCl<sub>6</sub> = 10) was dissolved in 10 mL of water and dropped into the solution. Flocculation was achieved by adding 2 M KOH solution. The final product was washed several times with deionized water and ethanol and then dried overnight at 60 °C under vacuum to obtain 75 mg of Pt@Co-Al LDH. The Pt content in the hybrid was measured to be 3.2 wt% by XPS analysis.

### 2.5. Catalyst Characterization

The X-ray diffraction (XRD) (X 'pert Pro, PANalytical BV, Almelo, The Netherlands) spectra of the samples were collected with a scanning range between 5° and 70° and Cu K $\alpha$  radiation ( $\lambda$  = 1.54 A). A high-resolution scanning electron microscope (FESEM-7600F, Japan Electronics Co., Ltd., Tokyo, Japan) and transmission electron microscope (JEOL JEM-2100F, Japan Electronics Co., Ltd., Tokyo, Japan) combined with energy-dispersive X-ray spectra (EDS-mapping) were used to analyze the morphologies of the samples. The surface chemical state of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Escalab 250Xi, Thermo Fisher Scientific Inc., Waltham, MA, USA) with Al-K $\alpha$  radiation (h $\nu$  = 1486.6 eV). The zeta potential of the samples was measured by a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Malvern, UK).

#### 2.6. Evaluation of Catalytic Performance

To assess the catalytic performance of Pt@Co-Al LDH, the hydrogenation of 4-NP to 4-AP was carried out as a model reaction. During a typical experiment, 20  $\mu$ L of Pt@Co-Al LDH (3 mg mL<sup>-1</sup>) dispersion and 100  $\mu$ L of freshly prepared NaBH<sub>4</sub> (0.2 M) solution were combined in a quartz cell. Then, 1 mL of 4-NP solution with an initial concentration of 0.1 mM was added to initiate the reduction reaction. The absorbance of the reactant (4-NP)

and product (4-AP) was measured using an Evolution 220 UV-Vis Spectrophotometer at specified time intervals within the wavelength range of 250–550 nm. In order to assess the reusability of Pt@Co-Al LDH, the catalyst underwent a thorough rinsing process with deionized water and ethanol, followed by drying under vacuum at 60 °C, before being reused in a subsequent run. All experiments were repeated at least three times, and the mean values were reported.

## 3. Results and Discussion

#### 3.1. Characterization of Pt@Co-Al LDH Hybrid

The XRD analysis in Figure 1 reveals the crystal structures of the products. Co-Al LDH-CO<sub>3</sub> exhibits a series of reflections at 11.7°, 23.5°, 34.8°, 39.2°, 46.8°, 59.7° and 60.9°, consistent with the (003), (006), (012), (015), (018), (110) and (113) crystal planes of the LDH-CO<sub>3</sub> phase [36,37], respectively. These peaks agree well with the published data (JCPDS No. 51-0045), and the high intensity of the diffraction peaks confirms the high crystallinity of the Co-Al LDH-CO<sub>3</sub> (Figure 1a). Because of the high affinity of CO<sub>3</sub><sup>2-</sup> ions to LDH layers, an exchange into other anions is required before exfoliation [38]. The (00*l*) reflections of Co-Al LDH-Cl were shifted to lower 2 $\theta$  angles, and the basal spacing was increased from 7.5 to 7.8 Å (Figure 1b), demonstrating that decarbonation was successfully conducted after the salt–acid treatment. After further exchange by NO<sub>3</sub><sup>-</sup> ions, the basal spacing was increased to 8.9 Å (Figure 1c). The results are consistent with previous work [35,39].



**Figure 1.** XRD patterns of (**a**) Co–Al LDH–CO<sub>3</sub>, (**b**) Co–Al LDH–Cl, (**c**) Co–Al LDH–NO<sub>3</sub>, (**d**) Pt@Co–Al LDH.

Co-Al LDH-NO<sub>3</sub> was treated with formamide, and the mixture formed a pink transparent colloidal solution. Tyndall light scattering can be seen clearly (Figure S1), confirming that the exfoliated LDH nanosheets form a homogeneous colloidal suspension with the formamide solution. Zeta potential is an important indicator for assessing the stability of colloidal suspension systems. The zeta potential of Co-Al LDH nanosheets was measured to be 35.6 mV (Figure S2). The positive zeta potential of LDH particles is due to the special electric double layer and structural positive charge on the LDH surface [40]. When the noble metal precursor  $PtCl_6^{2-}$  solution was added to the LDH colloid, the value of zeta potential dropped to 31.4 mV, and no precipitation was observed in the system (Figure S3). This indicates that the system still remains stable and confirms the assembly of  $PtCl_6^{2-}$  with LDH nanosheets via electrostatic forces [35]. The XRD spectra of Pt@Co-Al LDH show three characteristic peaks at 11.7°, 23.5° and 34.8°, corresponding to the (003), (006)

and (012) crystal planes of Co-Al LDH-CO<sub>3</sub>, respectively (Figure 1d). It can be concluded that the crystal structure of LDH has been reconstructed. However, the decrease in the intensity of its characteristic peaks and the broadening of the peaks indicate the decrease in the crystallinity of the composite. The characteristic peaks attributed to Pt NPs are not observed in the figure, which is caused by the low content and uniform distribution of Pt elements [41].

To exhibit the surface morphology of Co-Al LDH and Pt@Co-Al LDH, SEM and TEM images are shown in Figure 2. Figure 2a shows Co-Al LDH shale-shaped crystals with a lamellar structure that contains irregular edges, ranging in size from 1 to 4  $\mu$ m. The final hybrid Pt@Co-Al LDH also presents a sheet-like structure, but with much lower crystallinity and smaller particle size. It is suggested that the sheets formed in the LDH host material experienced a fracture caused by strong stirring during the exfoliation process. The carbonyl group on formamide can form a hydrogen bond with the hydroxyl group on Co-Al LDH, whereas the amino group is not able to bind tightly to the nitrate ion. Under the solvation effect and vigorous stirring, Co-Al LDH is exfoliated into smaller nanosheets [42,43]. In order to gain further insight, we performed HRTEM analysis on the prepared hybrid. As shown in Figure 2c, the morphology of layer stacking can be observed clearly. The Pt NPs with an average particle size of 3.1 nm are uniformly distributed on the LDH nanosheets. In addition, we measured the *d*-spacing (inter-atomic spacing) of Pt NPs to be 0.22 nm (Figure 2d), which is consistent with the plane of (111) [44,45].



**Figure 2.** SEM images of (**a**) Co–Al LDH–CO<sub>3</sub> and (**b**) Pt@Co–Al LDH; HRTEM images of Pt@Co–Al LDH (**c**,**d**).

As shown in Figure 3, the STEM image coupled with the Pt element mapping further demonstrates the homogeneous dispersion of Pt NPs on the Co-Al LDH nanosheets. Meanwhile, three other elements (Co, Al and O) together constitute the LDH nanosheets. Furthermore, as expected, the atomic ratio of Co and Al elements is 2:1 according to EDX analysis.



**Figure 3.** High-angle annular dark-field STEM image of Pt@Co–Al LDH (**a**) and elemental analysis of Co, Al, O and Pt elements (**b–e**); EDX analysis of Pt@Co–Al LDH (**f**).

XPS analysis demonstrated the chemical states and surface composition of the samples, and the results are shown in Figure 4 and Figure S4. The Co 2p high-resolution spectrum of the Pt@Co-Al LDH (shown in Figure 4a) exhibits the presence of two spin-orbital twin peaks at 781.8 and 797.7 eV attributed to  $Co^{3+} 2p_{3/2}$  and  $Co^{3+} 2p_{1/2}$ , respectively. In addition, two satellite peaks at 787.0 and 803.6 eV indicate the presence of high-spin bivalent  $Co^{2+}$  in Co-Al LDH [36]. It can be found from Figure 4a that there is no obvious difference in the cobalt valence state between Pt@Co-Al LDH and pure LDH. For the Pt 4f signal in Figure 4b, the presented  $4f_{7/2}$  and  $4f_{5/2}$  peaks are found at 70.6 and 74.7 eV, respectively, and agree well with the values of the zerovalent Pt in the metallic state [2,46,47]. In addition, XPS analysis revealed that the weight percentage of Pt in the complex is 3.2%.



Figure 4. The high-resolution XPS spectra of (a) Co 2p and (b) Pt 4f of Pt@Co-Al LDH.

As plotted in Figure 5, the N<sub>2</sub> adsorption–desorption isotherms of Pt@Co-Al LDH display a type IV isotherm shape with a narrow hysteresis loop (H3-type) in the P/P<sub>0</sub> range of 0.6–1.0, demonstrating the presence of mesoporous structures. The pore size analysis curve of Pt@Co-Al LDH further reveals that the majority of pore diameters lie in the range of 2–4 nm. Table 1 summarizes the additional structural characteristics of pure LDH and the hybrid. The BET surface area of Co-Al LDH was determined to be 8 m<sup>2</sup> g<sup>-1</sup>. By contrast, the hybrid has an over four times larger BET surface area (35 m<sup>2</sup> g<sup>-1</sup>). Furthermore, the pore volume of Pt@Co-Al LDH is much higher than that of pure LDH. This can be ascribed to the house-of-cards structure of the hybrid originated from the aggregation of the LDH nanosheets during the restacking process. Similar phenomena have been repeatedly observed in previous works [48–50]. The larger specific surface area and higher porosity not only favor the mass transfer of reactants, but also expose a large number of Pt active sites on the LDH nanosheets during the reduction process.



**Figure 5.** N<sub>2</sub> adsorption–desorption isotherms and pore size distribution curve (inset) of (**a**) Co–Al LDH and (**b**) Pt@Co–Al LDH.

Material	$\mathrm{S/m^2~g^{-1}}$	A/nm	$P/cm^3 g^{-1}$
Co-Al LDH	8	6.1	0.04
Pt@Co-Al LDH	35	4.5	0.15
	11	1	

Table 1. The structural characteristics of Co-Al LDH and Pt@Co-Al LDH.

S—specific surface area, A—average pore diameter, P—pore volume.

# 3.2. Catalytic Performance of Pt@Co-Al LDH Hybrid

The catalytic reduction activity and kinetics of the obtained catalyst for the reduction from 4-NP to 4-AP were first investigated under environmental conditions using UV-Vis analysis. After the addition of NaBH<sub>4</sub>, the light yellow solution immediately turned bright yellow, indicating the formation of the 4-nitrophenolate ion (4-NP<sup>-</sup>) in an alkaline environment (Figure 6a). When using Pt@Co-Al LDH as a catalyst, the absorbance for 4-NP at 400 nm decreased quickly, while the absorbance for 4-AP at 300 nm increased at the same time (Figure 6b). The solution completely faded to colorless within only 3 min, evidencing the complete conversion from 4-NP to 4-AP by Pt@Co-Al LDH [2,18,51,52]. When the catalyst was removed or replaced with pure Co-Al LDH, the absorbance at 400 nm remained the same even after 24 h. This indicates that the system requires a catalyst to proceed and that pure Co-Al LDH has no catalytic effect (Figure 6d). This confirms that the supported Pt NPs are the key to the high catalytic activity of Pt@Co-Al LDH [53].



**Figure 6.** UV–Vis spectra (**a**) of 4–NP solution before (black) and after (red) the addition of NaBH<sub>4</sub>, measured after various time periods, showing 4–NP reduction in the presence of Pt@Co–Al LDH (**b**), without catalyst (**c**) and in the presence of Co–Al LDH (**d**).

The kinetics of the reduction reaction were evaluated by measuring the changes in the absorbance at 400 nm using UV-Vis absorption spectra during reaction time. Owing to the excess amount of NaBH<sub>4</sub>, its consumption can be considered negligible, and the reduction can be presumed to follow the pseudo-first-order kinetic model. Accordingly, the rate constant ( $k_{app}$ ) can be obtained by the plot of ln( $C_t/C_0$ ) vs. reaction time [27,51,54].

$$\ln\frac{C_t}{C_0} = \ln\frac{A_t}{A_0} = -k_{app}t$$

where  $C_0$  is the initial 4-NP concentration,  $C_t$  is the 4-NP concentration at time t,  $A_0$  is the initial integral absorbance and  $A_t$  is the integral absorbance at time t. The rate constant  $k_{app}$  of Pt@Co-Al LDH hybrid can be calculated to be  $16.1 \times 10^{-3} \text{ s}^{-1}$ , and its specific rate constant k' can be calculated from the ratio of  $k_{app}$  to catalyst mass as 268.3 s<sup>-1</sup> g<sup>-1</sup>. In Table 2, the catalytic activity of Pt@Co-Al LDH is compared with that of other reported Pt-loaded catalysts. The higher  $k_{app}$  value of our catalyst reflects its superior catalytic performance in the reduction of 4-NP. As revealed in the TEM analysis, the excellent catalytic activity of the Pt@Co-Al LDH is related to the presence of small, highly dispersed Pt NPs on the surface, which provide a large number of active sites for effective contact with the reactants and fast interfacial electron transfer between Pt NPs and 4-NP.

Catalyst	Reaction Conditions (4-NP, NaBH <sub>4</sub> , Cat.)	$k_{app} imes 10^3 \ ({ m s}^{-1})$	Time (min)	Ref.
Pt NPs@C-PZS	0.1 mM, 5 mM, 0.2 mg	4.6	16	[55]
Pt/MMZ	0.03 mM, 0.016 mM, 2 mg	5.35	14	[56]
Pt/meso-CeO <sub>2</sub>	0.1 mM, 5 mM, 0.3 mg	6.0	8	[57]
Fe2O3-Pt@DSL-Pt	0.1 mM, 41 mM, 0.5 mg	6.32	10	[58]
PtNi/MoS <sub>2</sub>	0.1 mM, 80 mM, 1 mg	9.2	5	[59]
Co-doped CuO NPs	0.06 mM, 4 mM, 1 mg	43.8	3.5	[60]
Pt@Co-Al LDH	0.1 mM, 20 mM, 0.06 mg	16.1	3	This work

**Table 2.** Comparison of the catalytic performance of Pt@Co-Al LDH with other reported Pt-loaded catalysts for 4-NP reduction.

In addition, the effects of catalyst dosage and NaBH<sub>4</sub> concentration on the reduction of 4-NP were studied (Figure 7). All the reactions followed the pseudo-first-order kinetic model. Increasing the catalyst dosage from 0.03 to 0.12 mg reduced the time required for the complete conversion due to the increase in active sites. And the conversion of 4-NP is significantly increased with increasing NaBH<sub>4</sub> concentration because BH<sub>4</sub><sup>-</sup> ions obtained from dissociation initiate the reduction reaction.



**Figure 7.** Kinetics of the catalytic reduction of 4–NP over Pt@Co–Al LDH at different catalyst dosages (**a**) and NaBH<sub>4</sub> concentrations (**b**).

Thermodynamic analysis of the catalytic system was performed by varying the reaction temperature from 15 to 45 °C. The results show that the catalytic reduction rate strongly depends on the reaction temperature (shown in Figure 8). The time required for complete conversion of 4-NP at 15 °C was 6 min, which decreased to 75 s as the temperature was increased to 45 °C. The efficiency of the reaction increases due to enhanced interaction between reactants and the decomposition of NaBH<sub>4</sub> at higher temperatures [61,62]. The Arrhenius equation is commonly used to determine the activation energy of a catalytic process. The equation is as follows:

$$\ln k_{app} = -\frac{E_a}{RT} + \ln A$$

where *A* is the Arrhenius constant,  $E_a$  is the activation energy and *R* is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). The activation energy of the catalytic reduction of 4-NP by Pt@Co-Al LDH can be determined to be 36.63 kJ mol<sup>-1</sup> from the slope of the plot of ln  $k_{app}$  vs. 1/T (Figure S5).



**Figure 8.** Kinetics of the catalytic reduction of 4-NP over Pt@Co-Al LDH at different temperatures: (a) 15 °C, (b) 25 °C, (c) 35 °C and (d) 45 °C.

According to the experimental results and previous literature [63–65], a rational mechanism of the reduction process of 4-NP to 4-AP catalyzed by Pt-decorated LDH is proposed (Scheme 2). Firstly, the reactants including 4-NP<sup>-</sup> and  $BH_4^-$  ions are adsorbed onto the alkaline catalyst surface. The  $BH_4^-$  ions dissociate and contact the active site Pt NPs to form Pt-hydride bonds. Then, nitro groups in 4-NP<sup>-</sup> ions interact with hydride ions to generate a Pt complex. Finally, 4-NP transforms to 4-AP by different hydro-deoxygenation steps. The product is detached from the catalyst, making the active site available for the next catalytic cycle to proceed. The synergetic effect between LDH and Pt NPs contributes to the excellent catalytic activity of Pt@Co-Al LDH hybrids. In addition, highly dispersed Pt NPs enhance the reaction rate by increasing the rate of electron transfer between  $BH_4^-$  and 4-NP. And LDH nanosheets facilitate the adsorption of the oppositely charged reactants, and the relatively high porosity formed by the stacking of exfoliated LDH nanosheets favors the mass transfer process in the catalytic process.

For heterogeneous catalysts, the recycling performance is extremely important for further industrialization. In this study, Pt@Co-Al LDH was recycled and reused five times. As shown in Figure 9, the degradation rate was 99.1% in the first cycle. The activity of the catalyst remained at a high level (94.8%) even after five cycles, confirming the high stability of 2D LDH substrates for the catalytic reduction application. Also, in order to further confirm the stability of Pt@Co-Al LDH structure, we characterized the recovered catalyst by XRD, TEM and XPS analysis, as shown in Figures S6–S9. The original and recovered catalysts showed no significant changes in the crystal structure and morphology. And Pt NPs were still uniformly dispersed on Co-Al LDH nanosheets after successive cycles. The Pt content in the recycled catalyst was determined to be 3.1 wt%, which was slightly lower than that in the initial catalyst (3.2 wt%), indicating that the Pt leaching was negligible.



**Scheme 2.** A possible mechanism for the catalytic reduction of 4–NP to 4–AP catalyzed by Pt@Co–Al LDH.



Figure 9. Recyclability of Pt@Co-Al LDH catalyst for the reduction of 4-NP.

# 4. Conclusions

In summary, a novel catalyst Pt@Co-Al LDH was synthesized via the exfoliation/ restacking route. The metal precursor  $PtCl_6^{2-}$  ions were assembled onto the surface of LDH nanosheets by electrostatic interaction and then underwent in situ reduction by NaBH<sub>4</sub>. Various analyses including XRD, SEM, TEM and XPS indicated the successful synthesis of Pt@Co-Al LDH hybrid. Pt NPs were uniformly dispersed on Co-Al LDH nanosheets, and the average particle size was 3.1 nm. The Pt@Co-Al LDH hybrid exhibits

superior catalytic activity towards the catalytic reduction of 4-NP to 4-AP at ambient conditions. The reaction rate constant  $k_{app}$  reaches  $16.1 \times 10^{-3} \text{ s}^{-1}$ . The Pt@Co-Al LDH hybrid demonstrates excellent stability and recyclability. There is no noticeable decline in its catalytic performance after five consecutive uses.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst14030284/s1. Figure S1. Tyndall phenomenon of LDH nanosheet colloidal dispersion. Figure S2. Zeta potential of Co-Al LDH nanosheets. Figure S3. Zeta potential of PtCl<sub>6</sub><sup>2–</sup>@Co-Al LDH nanosheets. Figure S4. XPS survey spectra of Co-Al LDH and Pt@Co-Al LDH. Figure S5. Arrhenius plot for catalytic reduction of 4-NP in the presence of Pt@Co-Al LDH. Figure S6. XRD patterns of the original and recycled Pt@Co-Al LDH catalyst. Figure S7. HRTEM image of the recycled Pt@Co-Al LDH. Figure S8. XPS survey spectrum of the recycled Pt@Co-Al LDH. Figure S9. The high-resolution XPS spectra of (a) Co 2p, (b) Al 2p and Pt 4f for the recycled Pt@Co-Al LDH.

**Author Contributions:** C.X.: writing—original draft, writing—review and editing. Y.Q.: methodology. X.Y.: visualization. Z.G.: supervision, data curation. Z.W.: investigation. C.L.: software. Y.S.: formal analysis. J.M.: project administration. L.L.: conceptualization, resources. All authors have read and agreed to the published version of the manuscript.

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#### References

- Fu, H.; Zhang, A.; Jin, F.; Guo, H.; Huang, W.; Cheng, W.; Liu, J. Origami and layered-shaped ZnNiFe-LDH synthesized on Cu(OH)<sub>2</sub> nanorods array to enhance the energy storage capability. *J. Colloid Interface Sci.* 2022, 607, 1269–1279. [CrossRef] [PubMed]
- El-Bahy, Z.M. Preparation and characterization of Pt-promoted NiY and CoY catalysts employed for 4-nitrophenol reduction. *Appl. Catal. A* 2013, 468, 175–183. [CrossRef]
- Neal, R.D.; Inoue, Y.; Hughes, R.A.; Neretina, S. Catalytic reduction of 4-nitrophenol by gold catalysts: The influence of borohydride concentration on the induction time. J. Phys. Chem. C 2019, 123, 12894–12901. [CrossRef]
- 4. Narayanan, K.B.; Sakthivel, N. Heterogeneous catalytic reduction of anthropogenic pollutant, 4-nitrophenol by silverbionanocomposite using *Cylindrocladium floridanum*. *Bioresour*. *Technol*. **2011**, *102*, 10737–10740. [CrossRef] [PubMed]
- Ahmad, M.M.; Mushtaq, S.; Al Qahtani, H.S.; Sedky, A.; Alam, M.W. Investigation of TiO<sub>2</sub> nanoparticles synthesized by sol-gel method for effectual photodegradation, oxidation and reduction reaction. *Crystals* 2021, *11*, 1456. [CrossRef]
- Wi-Afedzi, T.; Yeoh, F.-Y.; Yang, M.-T.; Yip, A.C.K.; Lin, K.-Y.A. A comparative study of hexacyanoferrate-based Prussian blue analogue nanocrystals for catalytic reduction of 4-nitrophenol to 4-aminophenol. Sep. Purif. Technol. 2019, 218, 138–145. [CrossRef]
- Chen, Z.; Xu, B.; Wang, X.; Zhang, L.; Yang, X.; Li, C. Sandwich-like MIL-100(Fe)@Pt@MIL-100(Fe) nanoparticles for catalytic hydrogenation of 4-nitrophenol. *Catal. Commun.* 2017, 102, 17–20. [CrossRef]
- Liu, B.; Yan, S.; Zhang, A.; Song, Z.; Sun, Q.; Huo, B.; Yang, W.; Barrow, C.J.; Liu, J. Insight into catalytic mechanisms for the reduction of nitrophenol via heterojunctions of gold nanoclusters on 2D boron nitride nanosheets. *ChemNanoMat* 2019, *5*, 784–791. [CrossRef]
- Karki, H.P.; Ojha, D.P.; Joshi, M.K.; Kim, H.J. Effective reduction of p-nitrophenol by silver nanoparticle loaded on magnetic Fe<sub>3</sub>O<sub>4</sub>/ATO nano-composite. *Appl. Surf. Sci.* 2018, 435, 599–608. [CrossRef]
- 10. Lee, S.J.; Yu, Y.; Jung, H.J.; Naik, S.S.; Yeon, S.; Choi, M.Y. Efficient recovery of palladium nanoparticles from industrial wastewater and their catalytic activity toward reduction of 4-nitrophenol. *Chemosphere* **2021**, *262*, 128358. [CrossRef]
- 11. Mejía, C.H.; van Deelen, T.W.; de Jong, K.P. Activity enhancement of cobalt catalysts by tuning metal-support interactions. *Nat. Commun.* **2018**, *9*, 4459–4466. [CrossRef] [PubMed]

- 12. Islam, M.T.; Saenz-Arana, R.; Wang, H.; Bernal, R.; Noveron, J.C. Green synthesis of gold, silver, platinum, and palladium nanoparticles reduced and stabilized by sodium rhodizonate and their catalytic reduction of 4-nitrophenol and methyl orange. *New J. Chem.* **2018**, *42*, 6472–6478. [CrossRef]
- 13. Menumerov, E.; Hughes, R.A.; Neretina, S. Catalytic reduction of 4-nitrophenol: A quantitative assessment of the role of dissolved oxygen in determining the induction time. *Nano Lett.* **2016**, *16*, 7791–7797. [CrossRef]
- Pandey, S.; Mishra, S.B. Catalytic reduction of p-nitrophenol by using platinum nanoparticles stabilised by guar gum. *Carbohydr.* Polym. 2014, 113, 525–531. [CrossRef] [PubMed]
- 15. Akilandaeaswari, B.; Muthu, K. One-pot green synthesis of Au-Ag bimetallic nanoparticles from Lawsonia inermis seed extract and its catalytic reduction of environmental polluted methyl orange and 4-nitrophenol. *J. Taiwan Inst. Chem. Eng.* **2021**, 127, 292–301. [CrossRef]
- 16. Baran, N.Y.; Çalışkan, M.; Baran, T. Pd@MgAl LDH/2-ThCA: A sustainable, active and recyclable nanocatalyst system for the rapid and efficient catalytic reduction of organic pollutants. *Inorg. Chem. Commun.* **2023**, *157*, 111333–111346. [CrossRef]
- 17. Wang, X.; Tan, F.; Wang, W.; Qiao, X.; Qiu, X.; Chen, J. Anchoring of silver nanoparticles on graphitic carbon nitride sheets for the synergistic catalytic reduction of 4-nitrophenol. *Chemosphere* **2017**, *172*, 147–154. [CrossRef]
- Tian, X.; Zahid, M.; Li, J.; Sun, W.; Niu, X.; Zhu, Y. Pd/Mo<sub>2</sub>N-TiO<sub>2</sub> as efficient catalysts for promoted selective hydrogenation of 4-nitrophenol: A green bio-reducing preparation method. *J. Catal.* 2020, 391, 190–201. [CrossRef]
- 19. Tian, X.; Zahid, M.; Sun, W.; Zhu, Y. Facile fabrication of TiO<sub>2</sub> with 3D hierarchical structure and its supported Pd catalysts for high catalytic hydrogenation performance of 4-nitrophenol to 4-aminophenol. *Appl. Surf. Sci.* **2021**, 566. [CrossRef]
- Wu, Z.; Zhu, J.; Wen, W.; Zhang, X.; Wang, S. Spherical covalent organic framework supported Cu/Ag bimetallic nanoparticles with highly catalytic activity for reduction of 4-nitrophenol. *J. Solid State Chem.* 2022, 311, 123116–123123. [CrossRef]
- 21. Malik, M.A.; Alshehri, A.A.; Patel, R. Facile one-pot green synthesis of Ag–Fe bimetallic nanoparticles and their catalytic capability for 4-nitrophenol reduction. *J. Mater. Res. Technol.* **2021**, *12*, 455–470. [CrossRef]
- Ye, W.; Yu, J.; Zhou, Y.; Gao, D.; Wang, D.; Wang, C.; Xue, D. Green synthesis of Pt–Au dendrimer-like nanoparticles supported on polydopamine-functionalized graphene and their high performance toward 4- nitrophenol reduction. *Appl. Catal. B* 2016, 181, 371–378. [CrossRef]
- Xia, B.; He, F.; Li, L. Preparation of bimetallic nanoparticles using a facile green synthesis method and their application. *Langmuir* 2013, 29, 4901–4907. [CrossRef] [PubMed]
- 24. Sun, F.; Zhou, Y.; You, Z.; Xia, H.; Tuo, Y.; Wang, S.; Jia, C.; Zhang, J. Bi-functional Fe<sub>3</sub>O<sub>4</sub> / Au/CoFe-LDH sandwich-structured electrocatalyst for asymmetrical electrolyzer with low operation voltage. *Small* **2021**, *17*, 2103307–2103320. [CrossRef] [PubMed]
- Yi, H.; Liu, S.; Lai, C.; Zeng, G.; Li, M.; Liu, X.; Li, B.; Huo, X.; Qin, L.; Li, L.; et al. Recent advance of transition-metal-based layered double hydroxide nanosheets: Synthesis, properties, modification, and electrocatalytic applications. *Adv. Energy Mater.* 2021, *11*, 2002863–2002888. [CrossRef]
- 26. Wei, C.; Yan, X.; Zhou, Y.; Xu, W.; Gan, Y.; Zhang, Y.; Zhang, N. Morphological control of layered double hydroxides prepared by co-precipitation method. *Crystals* **2022**, *12*, 1713. [CrossRef]
- Zhang, A.; Liu, B.; Liu, S.; Li, M.; Zheng, W.; Deng, L.; Liu, J. Novel approach to immobilize Au nanoclusters on micro/nanostructured carbonized natural lotus leaf as green catalyst with highly efficient catalytic activity. *Chem. Eng. J.* 2019, 371, 876–884. [CrossRef]
- 28. Murayama, T.; Haruta, M. Preparation of gold nanoparticles supported on Nb<sub>2</sub>O<sub>5</sub> by deposition precipitation and deposition reduction methods and their catalytic activity for CO oxidation. *Chin. J. Catal.* **2016**, *37*, 1694–1701. [CrossRef]
- 29. Liang, Y.; Zhao, B.; Tang, Q.; Liu, L.; Dong, J. Adjusting Pt nanoparticle size on SBA-15 by a sol-immobilisation method towards naphthalene hydrogenation. *Catal. Lett.* **2022**, *152*, 3489–3497. [CrossRef]
- Yu, J.; Wang, Q.; O'Hare, D.; Sun, L. Preparation of two dimensional layered double hydroxide nanosheets and their applications. *Chem. Soc. Rev.* 2017, 46, 5950–5974. [CrossRef]
- Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. Macromolecule-like aspects for a colloidal suspension of an exfoliated titanate. pairwise association of nanosheets and dynamic reassembling process initiated from It. J. Am. Chem. Soc. 1996, 118, 8329–8335. [CrossRef]
- 32. Abe, R.; Shinohara, K.; Tanaka, A.; Hara, M.; Kondo, J.N.; Domen, K. Preparation of porous niobium oxides by soft-chemical process and their photocatalytic activity. *Chem. Mater.* **1997**, *9*, 2179–2184. [CrossRef]
- 33. Xu, J.; Liu, X.; Zhou, Z.; Deng, L.; Liu, L.; Xu, M. Platinum nanoparticles with low content and high dispersion over exfoliated layered double hydroxide for photocatalytic CO<sub>2</sub> reduction. *Energy Fuels* **2021**, *35*, 10820–10831. [CrossRef]
- 34. Huang, S.; Cen, X.; Peng, H.; Guo, S.; Wang, W.; Liu, T. Heterogeneous ultrathin films of poly(vinyl alcohol)/layered double hydroxide and montmorillonite nanosheets via layer-by-layer assembly. *J. Phys. Chem. B* 2009, *113*, 15225–15230. [CrossRef]
- Liu, Z.; Ma, R.; Osada, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. Synthesis, anion exchange and delamination of Co-Al layered double hydroxide: Assembly of the exfoliated nanosheet/polyanion composite films and magneto-optical studies. *J. Am. Chem. Soc.* 2006, *128*, 4872–4880. [CrossRef] [PubMed]
- 36. Li, C.; Guo, R.; Zhang, Z.; Wu, T.; Yue, C.; Pan, W. Loading metal nanoparticles on the CoAl-LDH/CGCNN S-scheme heterojunction for efficient photocatalytic CO<sub>2</sub> reduction under visible light. *Sep. Purif. Technol.* **2023**, *322*, 124266–124276. [CrossRef]
- Tao, J.; Yu, X.; Liu, Q.; Liu, G.; Tang, H. Internal electric field induced S–scheme heterojunction MoS<sub>2</sub>/CoAl LDH for enhanced photocatalytic hydrogen evolution. *J. Colloid Interface Sci.* 2021, 585, 470–479. [CrossRef] [PubMed]

- 38. Ma, R.; Liu, Z.; Li, L.; Iyi, N.; Sasaki, T. Exfoliating layered double hydroxides in formamide: A method to obtain positively charged nanosheets. *J. Mater. Chem.* **2006**, *16*, 3809–3813. [CrossRef]
- 39. Chen, Y.; Jing, C.; Zhang, X.; Jiang, D.; Liu, X.; Dong, B.; Feng, L.; Li, S.; Zhang, Y. Acid-salt treated CoAl layered double hydroxide nanosheets with enhanced adsorption capacity of methyl orange dye. *J. Colloid Interface Sci.* **2019**, *548*, 100–109. [CrossRef]
- Huang, S.; Peng, H.; Tjiu, W.W.; Yang, Z.; Zhu, H.; Tang, T.; Liu, T. Assembling exfoliated layered double hydroxide (LDH) nanosheet/carbon nanotube (CNT) hybrids via electrostatic force and fabricating nylon nanocomposites. *J. Phys. Chem. B* 2010, 114, 16766–16772. [CrossRef] [PubMed]
- Shi, W.; Zhang, B.; Lin, Y.; Wang, Q.; Zhang, Q.; Su, D.S. Enhanced chemoselective hydrogenation through tuning the interaction between Pt nanoparticles and carbon supports: Insights from identical location transmission electron microscopy and X-ray photoelectron spectroscopy. ACS Catal. 2016, 6, 7844–7854. [CrossRef]
- 42. Mao, N.; Zhou, C.H.; Tong, D.S.; Yu, W.H.; Lin Cynthia, C.X. Exfoliation of layered double hydroxide solids into functional nanosheets. *Appl. Clay Sci.* 2017, 144, 60–78. [CrossRef]
- 43. Chen, C.; Tao, L.; Du, S.; Chen, W.; Wang, Y.; Zou, Y.; Wang, S. Advanced exfoliation strategies for layered double hydroxides and applications in energy conversion and storage. *Adv. Funct. Mater.* **2020**, *30*, 1909832–1909849. [CrossRef]
- 44. Tian, H.; Yu, Y.; Wang, Q.; Li, J.; Rao, P.; Li, R.; Du, Y.; Jia, C.; Luo, J.; Deng, P.; et al. Recent advances in two-dimensional Pt based electrocatalysts for methanol oxidation reaction. *Int. J. Hydrogen Energy* **2021**, *46*, 31202–31215. [CrossRef]
- 45. Qian, Q.; Yu, G.; Zhao, Q.; Zhang, X. One-step hydrothermal preparation of bilayer films of NiCo LDH/Pt loaded on nickel foam surface for HER catalytic activity. *New J. Chem.* **2023**, *47*, 1040–1044. [CrossRef]
- 46. Cai, T.; Zhang, P.; Shen, X.; Huang, E.; Shen, X.; Shi, J.; Wang, Z.; Sun, Q. Synthesis of Pt-loaded NiFe-LDH nanosheets on wood veneer for efficient gaseous formaldehyde degradation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 37147–37154. [CrossRef]
- Jang, S.W.; Dutta, S.; Kumar, A.; Hong, Y.R.; Kang, H.; Lee, S.; Ryu, S.; Choi, W.; Lee, I.S. Holey Pt nanosheets on NiFe-hydroxide laminates: Synergistically enhanced electrocatalytic 2D interface toward hydrogen evolution reaction. ACS Nano 2020, 14, 10578–10588. [CrossRef]
- Lin, B.; He, L.; Zhu, B.; Chen, Y.; Gao, B. Visible-light photocatalytic activity of mesoporous nanohybrid assembled by tantalotungstate nanosheets and manganese ions. *Catal. Commun.* 2012, 29, 166–169. [CrossRef]
- 49. Gu, T.H.; Gunjakar, J.L.; Kim, I.Y.; Patil, S.B.; Lee, J.M.; Jin, X.; Lee, N.S.; Hwang, S.J. Porous hybrid network of graphene and metal oxide nanosheets as useful matrix for improving the electrode performance of layered double hydroxides. *Small* **2015**, *11*, 3921–3931. [CrossRef] [PubMed]
- 50. Karthikeyan, J.; Fjellvag, H.; Bundli, S.; Sjastad, A.O. Efficient exfoliation of layered double hydroxides; effect of cationic ratio, hydration state, anions and their orientations. *Materials* **2021**, *14*, 346. [CrossRef] [PubMed]
- Zahid, M.; Almashhadani, H.A.; Jawad, S.F.; Khan, M.F.; Ismail, A. Stabilization of Pt nanoparticles within MOFs for selective hydrogenation of hazardous 4-nitrophenol to valuable 4-aminophenol: Confinement and synergistic effect. *J. Solid State Chem.* 2022, 316, 123565–123574. [CrossRef]
- 52. Kiani, Z.; Zhiani, R.; Khosroyar, S.; Motavalizadehkakhky, A.; Hosseiny, M. UiO-66/btb/Pd as a stable catalyst reduction of 4-nitrophenol into 4-aminophenol. *Inorg. Chem. Commun.* **2021**, *124*, 108382–108388. [CrossRef]
- 53. Kharlamova, T.S.; Salina, M.V.; Svetlichnyi, V.A.; Salaev, M.A.; Stadnichenko, A.I.; Mamontov, G.V. CeO<sub>2</sub>-supported Pt–Ag bimetallic catalysts for 4-nitrophenol reduction. *Catal. Today* **2022**, *384–386*, 12–24. [CrossRef]
- Wu, Y.; Hao, W.; Li, X.; Qin, L.; Zhang, T.; Kang, S.-Z. An efficient integrated catalyst for the reduction of 4-nitrophenol in a continuous flow system: Ag nanoparticles loaded graphene nanosheets immobilized on Ti meshes. *Diam. Relat. Mater.* 2022, 126, 109135–109141. [CrossRef]
- Fu, J.; Wang, S.; Wang, X.; Yan, Y.; Wang, K.; Gao, M.; Xu, Q. Facile preparation of highly dispersed Pt nanoparticles supported on heteroatom-containing porous carbon nanospheres and their catalytic properties for the reduction of 4-nitrophenol. *J. Porous Mater.* 2017, 25, 1081–1089. [CrossRef]
- Subhan, F.; Aslam, S.; Yan, Z.; Yaseen, M.; Marwat, A.; Ahmad, A. Catalytic reduction of nitrophenol and MB waste water using homogeneous Pt NPs confined in hierarchically porous silica. *J. Environ. Chem. Eng.* 2021, *9*, 105567–105578. [CrossRef]
- Wang, Q.; Zhang, Y.; Zhou, Y.; Zhang, Z.; Xue, J.; Xu, Y.; Zhang, C.; Sheng, X.; Kui, N. Nanocasting synthesis of an ordered mesoporous CeO<sub>2</sub>-supported Pt nanocatalyst with enhanced catalytic performance for the reduction of 4-nitrophenol. *RSC Adv.* 2016, *6*, 730–739. [CrossRef]
- 58. Gao, Y.; Fang, J.; Zhang, Y.; Zhang, C.; Zhao, S.; Zhou, Y.; Huang, M.; Sheng, X. Novel synthesis of Fe<sub>2</sub>O<sub>3</sub>–Pt ellipsoids coated by double-shelled La<sub>2</sub>O<sub>3</sub> as a catalyst for the reduction of 4-nitrophenol. *Appl. Organomet. Chem.* **2018**, *32*, 4208–4219. [CrossRef]
- Akbarzadeh, E.; Bahrami, F.; Gholami, M.R. Au and Pt nanoparticles supported on Ni promoted MoS<sub>2</sub> as efficient catalysts for p-nitrophenol reduction. J. Water Process Eng. 2020, 34, 101142–101150. [CrossRef]
- 60. Sharma, A.; Dutta, R.K.; Roychowdhury, A.; Das, D.; Goyal, A.; Kapoor, A. Cobalt doped CuO nanoparticles as a highly efficient heterogeneous catalyst for reduction of 4-nitrophenol to 4-aminophenol. *Appl. Catal. A* **2017**, *543*, 257–265. [CrossRef]
- 61. Kassem, A.A.; Abdelhamid, H.N.; Fouad, D.M.; Ibrahim, S.A. Catalytic reduction of 4-nitrophenol using copper terephthalate frameworks and CuO@C composite. *J. Environ. Chem. Eng.* **2021**, *9*, 104401–104410. [CrossRef]
- 62. Aykut, E.; Sert, M.; Sert, E. Catalytic activity of MOF derived CuFe@C catalysts for catalytic reduction of 4-nitrophenol. *J. Water Process Eng.* **2023**, *54*, 103970–103983. [CrossRef]

- 63. Bogireddy, N.K.R.; Pal, U.; Kumar, M.K.; Domínguez, J.M.; Gomez, L.M.; Agarwal, V. Green fabrication of 2D platinum superstructures and their high catalytic activity for mitigation of organic pollutants. *Catal. Today* **2021**, *360*, 185–193. [CrossRef]
- 64. Mejia, Y.R.; Reddy, N.K. Bogireddy Reduction of 4-nitrophenol using green-fabricated metal nanoparticles. *RSC Adv.* 2022, 12, 18661–18675. [CrossRef] [PubMed]
- Bogireddy, N.K.R.; Sahare, P.; Pal, U.; Méndez, S.F.O.; Gomez, L.M.; Agarwal, V. Platinum nanoparticle-assembled porous biogenic silica 3D hybrid structures with outstanding 4-nitrophenol degradation performance. *Chem. Eng. J.* 2020, 388, 124237–124250. [CrossRef]

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