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Ultradispersed nickel phosphide on phosphorus-doped carbon with tailored *d*-band center for efficient and chemoselective hydrogenation of nitroarenes

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Abstract: Nickel phosphide is a promising catalyst for hydrogenation of nitroarenes but suffers from sluggish H desorption and low chemoselectivity. Herein, we overcome these problems through reducing the Ni₂P into sub-nanosized clusters, tailoring the *d*-band center of Ni, and coupling them with P-doped carbon. Using DFT calculations, we predicted that electron transfer from P-doped carbon to Ni₂P cluster results in downshift of *d*-band center of Ni that promotes H desorption on highly charged antibonding orbital of Ni-H, and reactant is preferentially adsorbed on P-doped carbon surface through nitro group due to the geometrical hindrance on Ni₂P clusters that leads to good selectivity. Then we developed a chemical anchoring method to fabricate Ni₂P supported on P-doped carbon with high dispersion of 81.3%. The synthesized catalyst delivers high activity and selectivity chemoselective hydrogenation of nitroarenes, and outperforms various noble- and transition-metal catalysts. Moreover, we revealed the origins of the superior performance of catalyst by characterizations, and confirmed the conclusion of DFT calculation. Such concept of tailoring *d*-band center and improving dispersion of active phase can provide insight for design of catalysts for hydrogenation and beyond.

Keywords: Ni₂P, d band center, ultra-dispersion, synergistic effect, selective hydrogenation

1. Introduction

Substituted aromatic amines are important industrial intermediates for pharmaceuticals, agrochemicals, fine-chemicals, dyes and polymers, and most of them are synthesized by chemoselective hydrogenation of corresponding substituted nitro aromatics¹⁻⁶. However, in most cases the hydrogenation of reducible functional groups (*e.g.* –C=O, -Cl and –C=C) also occur with the formation of ineluctable byproducts. Although some noble-metal based catalysts, for example, Pt⁷⁻⁸, Pd⁹⁻¹⁰ and Au¹¹ can achieve good selectivity *via* regulating particle sizes and morphology, alloying with other metals, and coupling with support materials, the expensive price and rare storage limit their applications. Therefore, the development of more low-cost catalyst with high activity and chemoselectivity is very necessary.

Recently intensity research studies have been devoted to designing heteroatom-doped carbon-based catalysts¹²⁻¹⁷, e.g. N/P-doped carbon, for chemoselective hydrogenation of nitroarenes¹⁸⁻¹⁹. Doping highly electronegative heteroatoms into the carbon matrix can effectively improve the electronic density of nearby carbon atoms, and provides activated sites that can exclusively adsorb nitro group and achieves a selectivity of nearly 100%. However, carbon-based catalysts suffer from medium capability in hydrogen activation, so they generally require high reaction temperature, for example, P-doped carbon requires a temperature of 120 °C to reach considerable activity¹⁹. Transition-metal phosphides (TMPs) have also attracted much attention as promising candidates for hydrogen activation due to their Pt-like electronic structure²⁰⁻²⁴. Particularly, nickel phosphide has shown strong ability in hydrogen activation²⁵⁻²⁶ and efficiently catalyze the hydrogenation of nitro or carbonyl group²⁷⁻²⁸ under relatively mild conditions. But it still suffers from two shortcomings: one is poor chemoselectivity in the hydrogenation of nitroarenes due to the non-selective adsorption of various functional groups; the other is the difficulty in release of atomic H for subsequent hydrogenation due to strong affinity. To improve the selectivity, it is necessary to avoid the adsorption of reactants and intermediates on nickel phosphide, so the particle size should be controlled in nano or subnano scale (to get geometrical hindrance^{7,10-11}) by means of fixing them on supports and thus nitro groups can be selectively adsorbed on support materials. To facilitate the desorption of atomic H, it is necessary to weaken the interaction between Ni and H, and a feasible way is to tune the d-band state of Ni to reach low

energy level of H desorption²⁹⁻³⁰, which may be achieved by interaction of doped carbon³¹⁻³². Based on the above considerations, combining nickel phosphide nanoclusters with P-doped carbon may be a promising way to improve the selectivity and activity of Ni₂P for hydrogenation of nitroarenes.

In this work, first by means of DFT calculation, we confirmed that Ni₂P nanoclusters anchored on P-doped carbon (Ni₂P/PC) exhibit a downshifted *d*-band of Ni and exclusive adsorption of reactant on PC, which contribute to facilitated H desorption and spillover for high activity and adsorption of $-NO_2$ groups for high selectivity. Then we developed a chemical anchoring method to fabricate this catalyst with controllable dispersion of Ni₂P clusters. With the dispersion of Ni₂P reaching 81.3%, the optimal Ni₂P/PC-2 catalyst shows a selectivity of >99.9% toward 4-aminobenzaldehyde in hydrogenation of 4-nitrobenzaldehyde, and a large turnover frequency (TOF) of ~147.5 h⁻¹ based on the molar of Ni. Also experimental results reveal the excellent performance is originated from the synergistic effect of Ni₂P nanoclusters for H₂ activation and P-doped carbon support for preferential adsorption of nitro group.

2. Experimental section

Density Functional Theory Calculations. All density functional theory calculations were carried out with Vienna Ab-initio Simulation Package³³⁻³⁴ (VASP). The exchange correlation functional employed was the Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation³⁵⁻³⁶. To locate transition states (TS), the Climbing Images Nudged Elastic Band (CI-NEB) algorithm³⁷ was used. Each transition state was confirmed by vibrational frequency analysis. One-layer slab of graphite was used for modeling carbon materials. The vacuum region was 20 Å. The kinetic energy cutoff of 500 eV was employed. The k-point was set to $2 \times 2 \times 1$ and that of static method was $6 \times 6 \times 1$. The formation energy is defined as the energy difference per unit cell between the nanocrystal and isolated atoms³⁸. The adsorption energies, E_{ads} , are calculated by using the following equation:

 $E_{ads} = E_{adsorbate+surface} - (E_{adsorbate} + E_{surface})$

where E_{ads} is the adsorption energy, $E_{adsorbate+surface}$ is total energy of surface covered with adsorbates, $E_{surface}$ is the energy of clean surface, $E_{adsorbate}$ is the energy of adsorbate. The d-band center, ξ_d is calculated³⁹ by using the following equation:

 $\xi_d = \sum E_d / \sum N_d$

where E_d represents total d-electron energy and N_d represents total d-electron number. And Atomic information of DFT models are given in the Supporting Information.

Synthesis of catalysts. P-doped carbon (PC) was synthesized according to our previously reported method¹⁹. Simply, phytic acid aqueous solution was polymerized under 180 °C and then carbonized at 900 °C under Ar flow. The Ni₂P nanoclusters anchored on P-doped carbon were synthesized by chemical anchoring method. Briefly, nickel nitrate (Ni(NO₃)₂ 6H₂O) and required amounts of citric acid (CA) were dissolved in purified water and mixed, then kept stirring under ambient condition for 12 h to allow the formation of Ni-CA complex. After that, the aqueous solution was mixed with PC and kept stirring for another 12 h to form Ni-CA/PC composite. The sample was then dried under freezing temperature for 12 h in vacuum and further at 60 °C for 1 h, mixed with sodium hypophosphite, and calcined at 400 °C for 1 h under Ar atmosphere to realize phosphorization of nickel. After that, the powders were washed for 3 times using deionized water to remove unconverted sodium hypophosphite, and then dried under 60 °C. The obtained catalyst was referred as Ni₂P/PC-x, where x represents the molar ratio of CA to Ni. As reference, activated carbon (Ni₂P/C) was employed as support by aforementioned synthesis route, in which carbon support was first hydroxylation according to literature (detail in Supporting Information, SI). Bulk Ni₂P catalyst was also synthesized according to the reported procedure (detail in SI).

Characterization. Surface morphologies of catalysts were examined by SEM using a Hitachi S-4800 instrument. TEM images were obtained using a Tecnai G2 F20 transmission electron microscope at 200 kV, with elemental compositions being analyzed by energy dispersive X-ray spectrometer (EDXS). The size distributions of Ni₂P clusters were obtained by statistical analyses carried out for at least 5 images of ~50 Ni₂P clusters from different regions of each catalyst. The crystal structures were recorded using a RigaKu D/max-2500 X-ray diffractometer (XRD) equipped with a Cu K α irradiation source. The element analysis was determined by Vario EL CUBE equipped with METTLER x86 instrument. Elemental composition and bonding information were analyzed using an X-ray photoelectron spectroscopy operated at a pass energy of 187.85 eV (Physical Electronics PHI 1600 ESCA XPS system using a monochromated Al K α X-ray source) and the C 1s peak at 284.6 eV was taken as internal standard. Raman spectra were recorded using a Raman spectrometer (DXR Microscope) and a green semiconductor laser (532 nm) as excitation source. Nitrogen adsorption-desorption isotherms were analyzed with ASAP

Page 5 of 23

ACS Catalysis

2020 physisorption Analyzer at 77 K. FT-IR spectra were recorded on a BioRad FTS 6000 spectrometer. All of the samples were mixed with KBr and pressed into a thin plate for measurement. The Ni content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

Catalytic Hydrogenation. The hydrogenation was conducted in 50 mL autoclave equipped with a PTFE lining, using 0.5 mmol nitroarenes, 5 mL solvent and 10 mg catalyst. The autoclave was purged with N_2 and H_2 (15 bar) respectively for three times, pressurized to 10 bar, and heated to 80 °C for defined time. After the reaction, the autoclave was cooled to room temperature, followed by centrifugation and analysis of a sample by GC-MS (Agilent 5975 equipped with HP-5 capillary column) and GC (Agilent 7820 equipped with FID detector and AT-SE-54 capillary column). TOF was calculated from the reaction rate at 1 h reaction derived by the number of Ni atoms exposed to the catalyst surface (eqs 1 and 2):

$$TOF = n_0 C/tn_{cat}$$
(1)
$$n_{cat} = m_{cat} w Dis_{Ni}/M_{Ni}$$
(2)

where n_0 is the initial molar of substrate, *C* is the conversion of substrates at the reaction of *t*, n_{cat} is the molar of exposed Ni atom, *w* is the mass fraction of Ni in catalysts, M_{Ni} is molar mass of Ni, and Dis_{Ni} is the dispersion of Ni for catalysts.

3. Results and discussion

3.1 DFT design of catalyst. First, we used DFT calculation to confirm our hypothesis for catalyst design by considering Ni₂P cluster anchored on PC support (Ni₂P/PC) and bulk Ni₂P (111) as a reference, with the slab models constructed in Figure S1 (SI). Notably, the adsorption energy of Ni₂P on PC is -1.23 eV, signifying that Ni₂P nanoclusters on PC is very stable. Bader charge analysis (Figure S2, Table S1, SI) shows the valence charge of Ni atom (9.94 |e|) in Ni₂P/PC is more than that of bulk Ni₂P (9.77 |e|), indicating Ni atoms accept electrons from carbon. And the isosurface value shows higher charge density around Ni atom of Ni₂P/PC (**Figure 1a**, Figure S3, SI), which further confirms the electron-transfer from PC to Ni₂P nanoclusters. Such electron-rich effect is expected to tailor the *d*-band of Ni atom. In **Figure 1b**, the density of state (DOS) near the Fermi level (E_f) shows the *d*-band center of Ni in Ni₂P/PC (-1.88 eV) is more far away from E_f than that in Ni₂P (-1.42 eV), indicating a downshift in *d*-band when Ni₂P nanoclusters are anchored on PC. Correspondingly, as shown in **Figure 1c**, the desorption energy of H on Ni₂P/PC

(-0.56 eV) is much lower than that on Ni₂P (-1.12 eV), indicative of more feasible H desorption. Moreover, the length of Ni-H bond on Ni₂P/PC is 1.90 Å, quite longer than intrinsic value of NiH (1.57 Å) and that on Ni₂P (1.65 Å), which further predicts an easier desorption of H from Ni₂P/PC (Figure S4, SI). Generally, the H-Ni interaction can be considered as the coupling between the valence states of H and the *d* states of Ni, which may form bonding and antibonding states. The H-Ni binding is governed by antibonding states, and the filling of antibonding states depend on their energy levels. As the *d*-band center is intervenient between antibonding and bonding, it can be used to describe the strength of H-Ni binding. As illustrated in **Figure 1d**, when *d*-band center of Ni downshifts, the energy level of antibonding states is lowered and easy to be filled, which results in a low desorption energy of H.



Figure 1. (a) Differential charge density in bulk Ni₂P and Ni₂P/PC (Yellow and cyan isosurfaces represent electron accumulation and depletion, respectively; the isosurface value is 0.008 e Å⁻³); (b) Density of states (DOS) of plots of Ni ions in Ni₂P and Ni₂P/PC (*d*-band center of Ni is highlighted in the DOS curve); (c) Desorption energies of dissociated H atoms on bulk Ni₂P and Ni₂P/PC; (d) Schematic illustration of function of downshifted *d*-band on H desorption; (e) Summary of adsorption models of 4-nitrobenzaldehyde on Ni₂P (111) and PC surface of Ni₂P/PC.

Then we considered the selectivity of Ni2P/PC using 4-nitrobenzaldehyde as a model

molecule as shown in Figure 1e. On Ni₂P (111), the adsorption energies of 4-nitrobenzaldehyde via -NO2 and -CHO are calculated as -0.16 and -0.20 eV, respectively, suggesting an equal adsorption of nitro and carbonyl group. Moreover, 4-nitrobenzaldehyde lies parallelly on the catalyst surface with an adsorption energy of -0.41 eV, which is more stable than perpendicular adsorption models, in consistent with reported result that bulk Ni₂P catalyst is low selective for the hydrogenation of 4-nitrobenzaldehyde²⁷⁻²⁸. In addition, the adsorption of 4-nitrobenzaldehyde on other Ni₂P facets, e.g. Ni₂P (100) and Ni₂P (110) were also considered, but all of them show lower adsorption energies, as shown in Figure S5 (SI). For Ni₂P/PC, 4-nitrobenzaldehyde molecule may bind with Ni₂P cluster or PC support. When binding with Ni₂P, 4-nitrobenzaldehyde perpendicularly adsorbs via -NO₂ and -CHO with adsorption energies of -0.06 and -0.09 eV respectively, which is less stable than the case of Ni₂P (111) (Figure S6, SI). Meanwhile, parallel adsorption of 4-nitrobenzaldehyde is not stable owing to the size limit of small Ni₂P cluster and steric hindrance. Alternatively, 4-nitrobenzaldehyde is absorbed on PC via nitro group (with a large adsorption energy of -0.63 eV, more stable than adsorption via carbonyl group (only -0.15eV) and parallel adsorption (+0.32 eV) as shown in Figure S7 (SI), suggesting an excellent selectivity of Ni₂P/PC.

3.2 Controllable synthesis of Ni₂P/PC. Since DFT calculation predict Ni₂P/PC as a promising candidate for selective hydrogenation, we then synthesized this catalyst via a chemical anchoring method. As shown in Figure S8 (SI), the synthesized P-doped carbon shows a typical carbon matrix from the HR-TEM image and broad XRD peak at 24° indexed to graphitic carbon, in agreement with our previous work¹⁹. Then the key to synthesize the sub-nanometer Ni₂P clusters tightly anchored on PC is employing citric acid to fix Ni ions on PC surface, through the interaction between carboxyl groups of CA and acidic hydroxyl groups of PC, as illustrated in **Scheme 1**. As shown in Figure S9 (SI), a decreased signal at *ca*. 1700 cm⁻¹ assigned to C=O in time-dependent IR spectra indicates the Ni-CA complexes are decomposed during the phosphorization process, and the residual Ni ions bonding with the hydroxyl groups are then phosphated, which can be confirmed by reduced acidic sites on Ni₂P/PC (74 µmol/g) compared with PC (108 µmol/g), as witnessed by NH₃-TPD (Figure S10, SI). So this chemical bonding avoids the excessive aggregation of Ni ions and helps to get highly dispersed Ni₂P nanoclusters.



Scheme 1. Schematic illustration for chemical anchoring of Ni ions on P-doped carbon surface via controlled decomposition of Ni-CA.

Importantly, the size of Ni₂P clusters can be regulated by the dosage of CA ligand⁴⁷⁻⁴⁸. With the absence of CA, the Ni₂P particles is ca. 7 nm (Figure 2a), and the faint lattice fringe of d = 0.221nm indexed to plane (111) of Ni₂P²⁵ is observed from HR-TEM image (Figure S11, SI). With increased dosage of CA, the particle size becomes smaller, and no obvious Ni₂P particles can be observed on PC surface with CA/Ni ratio of 2 (Figure 2b-d). The energy-dispersive X-ray (EDX) spectrum and mapping evidences the presence of C, P, and Ni elements in Ni₂P/PC-2 (Figure S12, S13, SI). Moreover, electron-energy loss spectroscopy mapping shows the uniformly dispersed Ni element on PC surface (Figure 2e), further confirming the formation of ultrafine Ni₂P nanoclusters. According to the particle size distributions (Figure 2f, Figure S14, SI), the particle size of Ni₂P decreases in the order of Ni₂P/PC-0 (7.6 nm) > Ni₂P/PC-0.5 (4.5 nm) > Ni₂P/PC-1 $(2.8 \text{ nm}) > \text{Ni}_{2}\text{P/PC-2}$ (ultrafine). Since the chemisorption of CO over Ni_2P can be approximate regarded as monomolecular-layer adsorption, the dispersion of Ni₂P nanoclusters was further calculated by CO chemisorption method (Figure 2f, Table S2, SI). Obviously, the dispersion of Ni₂P nanoclusters increases in the order of Ni₂P/PC-0 (38.5%) < Ni₂P/PC-0.5 (43.4%) < $Ni_2P/PC-1$ (66.2%) < $Ni_2P/PC-2$ (81.3%), in consistent with the particle size distribution, which confirms that CA ligand can reduce the size of Ni₂P clusters. Using the same synthesis procedure, Ni₂P nanoclusters were also loaded on commercial carbon support (Ni₂P/C-2), similarly no obvious nanoparticles were found from TEM image (Figure S15, SI). The dispersion of Ni₂P in Ni₂P/C-2 is 82.1%, similar with that of Ni₂P/PC-2, which further confirms the key role of CA for synthesizing highly dispersed Ni₂P nanoclusters. Nitrogen adsorption-desorption analysis shows that Ni₂P/PC-x catalysts give nearly unchanged BET area (around 700 cm²/g) compared with ~726.83 cm²/g of pristine PC (Figure S16, SI), suggesting a low loading amount of Ni₂P. The

inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis shows the loading amounts of Ni for Ni₂P/PC-x catalysts are around 0.5 *wt.*%, very close to the theoretical value in the synthesis (Table S3, SI). The calculated molar ratio of Ni/P is lower than stoichiometry (2) with the increasing dispersion of Ni₂P nanoclusters, maybe due to unsaturated sites contained in the nanostructure of Ni₂P. Moreover, both Ni and P concentration in bulk are lower than those on surface determined by XPS, suggesting anchored Ni₂P nanoclusters mostly disperse the surface of PC.



Figure 2. HR-TEM images of (a) Ni₂P/PC-0, (b) Ni₂P/PC-0.5, (c) Ni₂P/PC-1 and (d) Ni₂P/PC-2 (scale bar 10 nm); (e) TEM image of Ni₂P/PC-2 (scale bar 50 nm) and corresponding EELS mapping (C, P, Ni elements); (f) Distribution of particle size and dispersion of Ni₂P nanoclusters for Ni₂P/PC; (g) XRD patterns of synthesized catalysts.

In XRD spectra (**Figure 2g**), synthesized catalysts show two peaks at 24° and 44° indexed to graphitic carbon, without any other characteristic peaks of nickel phosphide phase due to the low loading content. To further confirm the formation of Ni₂P, we synthesized Ni₂P/PC with 2.0 *wt.*% loading of Ni (referred as H-Ni₂P/PC). As shown in Figure S17, XRD pattern of H-Ni₂P/PC matches well with that of hexagonal Ni₂P (PDF No.03-0953). Two distinct peaks at 1350 and 1590 cm⁻¹ appear in the Raman spectra (Figure S18, SI), attributed to the defective sp³ hybridized carbon (D band) and the crystallized graphitic sp² carbon (G band), respectively.⁴⁰⁻⁴² Synthesized Ni₂P/PC-x catalysts show higher I_D/I_G values than pristine PC, suggesting that anchored Ni₂P and PC support.

To study the chemical states of Ni₂P/PC-2, X-ray photoelectron spectroscopy (XPS) measurements were conducted. The Ni $2p_{3/2}$ and $2p_{1/2}$ XPS spectra for Ni₂P/PC-2 (Figure 3a, b, Table S4, SI) show three couples of subpeaks at about 852.98 and 856.84 eV, 862.05 and 870.20 eV, 875.19 and 881.59 eV, assigned to Ni^{δ^+}, oxidized Ni species and the corresponding satellite peaks²², respectively, quite similar with that of bulk Ni₂P. The P 2p spectra of Ni₂P/PC-2 (Figure **3c**) can be deconvoluted into four components at binding energies of 129.05, 129.89, 133.21 and 134.46 eV, attributed to P $2p_{3/2}$ and P $2p_{1/2}$ of metal phosphides (P^{δ -}), P-C bond and P-O bond in P-doped carbon^{19,22}, respectively. The presence of Ni^{δ^+} and P^{δ^-} components strongly confirms the formation of nickel phosphide nanoclusters. The fitted C 1s spectra show that Ni₂P/PC-2 contain two carbon components (C-C, C-P) centered at 284.6 and 285.5 eV similar with PC (Figure S19, SI). Specifically, the binding energies of Ni $2p_{3/2}$ and $2p_{1/2}$ peaks for Ni₂P/PC-2 are both shifted negatively compared with those of bulk Ni₂P catalyst (~ 0.12 eV shift for Ni 2p_{3/2} and ~ 0.18 eV shift for Ni $2p_{1/2}$). The binding energies of P $2p_{3/2}$ and $2p_{1/2}$ for Ni₂P/PC-2 also negatively shift in comparison to bulk Ni₂P (~0.26 eV shift for P 2p_{3/2} and ~0.21 eV shift for P 2p_{1/2}) as shown in Figure S20 (SI). Reversely, the binding energy of P 2p of Ni₂P/PC-2 (Figure 3c) is shifted positively compared with that of PC (~0.43 and 0.19 eV shifts for P-C and P-O respectively). These results strongly suggest that Ni₂P clusters have negative charge while PC support shows positive charge, in agreement with DFT calculation.

To further probe the local environment of Ni₂P nanoclusters, CO-probe infrared (IR) spectroscopy was carried out (**Figure 3d**). Ni₂P/PC-0 shows a strong band at 2095 cm⁻¹, assigned

to CO adsorbed on unsaturated Ni^{δ^+} in Ni₂P clusters⁴³. Whereas the CO adsorption band blue shifts gradually from Ni₂P/PC-0.5 to Ni₂P/PC-2, and Ni₂P/PC-2 exhibits the most shift of ~9 cm⁻¹, suggesting a stronger CO adsorption⁴⁴. This indicates that Ni ions in Ni₂P/PC-2 possess higher *d*-band electron density that can form π -back bonding with CO⁴³. Moreover, Ni₂P/PC-x catalysts show decreased intensity of CO adsorption band, which is reasonably assigned to the decreased partial cover caused by the decreased size of Ni₂P clusters, in good agreement with distribution of particle size.



Figure 3. XPS spectra of (a) Ni $2p_{3/2}$ and (b) Ni $2p_{1/2}$ of Ni₂P/PC-2 and Ni₂P; (c) P 2p spectra of Ni₂P/PC-2 and PC; (d) CO-probe molecule IR of Ni₂P/PC-x and Ni₂P/C-2.

3.3 Catalytic selective hydrogenation of nitroarenes using Ni₂P/PC. We evaluated the catalytic hydrogenation performance over the Ni₂P/PC catalysts using 4-nitrobenzaldehyde as a model reactant under mild conditions (T=80 °C and P=10 bar). The catalytic behavior of P-doped carbon, Ni₂P, Ni₂P/PC-2 and Ni₂P/C-2 catalysts was shown in **Figure 4**. When P-doped carbon is used as the catalyst, no catalytic hydrogenation product is observed even in 20 h, indicating P-doped carbon cannot activate hydrogen unless the reaction temperature is increased to 120 °C, as we mentioned aforehand¹⁷. When bulk Ni₂P is used as the catalyst, 100% conversion is

observed in 20 h. However, the chemoselectivity to aminobenzaldehyde is only 56.5% with a large amount byproduct of carbonyl group reduction. When Ni₂P nanoclusters are anchored onto PC (Ni₂P/PC-2), it exhibits the best activity with a full conversion in 5 h and TOF (calculated at 1 h reaction) reaching ~147.5 h⁻¹. More importantly, the chemoselectivity of 4-aminobenzaldehyde can approach >99.9%, and the amount of byproducts is below the detection limitations of gas chromatography-mass spectrometry (GC-MS) as shown in Figure S21, SI. In addition, Ni₂P/C-2 shows very low activity because neither Ni₂P nanoclusters nor carbon support can adsorb the reactant. On the other side, PC is capable of adsorbing reactant due to improved electronic density of carbon atoms nearby the dopants.



Figure 4. Catalytic activity and chemoselectivity of synthesized catalysts for hydrogenation of 4-nitrobenzaldehyde. (a) Time course of conversion of 4-nitrobenzaldehyde; (b) Chemoselectivity and TOF of 4-aminobenzaldehyde. Reaction condition: 0.5 mmol 4-nitrobenzaldehyde, 10 mg of catalysts (1.5 mol% Ni), 4 mL of ethanol, 80 °C and 10 bar H₂.

The kinetic profile in hydrogenation over Ni₂P/PC-2 reveals the conversion of 4-nitrobenzaldehyde changes linearly with the reaction time, suggesting the hydrogenation reaction follows pseudo-zero-order kinetics. Several additional experiments at different concentration of 4-nitrobenzaldehyde (0.05 M, 0.15 M and 0.20 M) were performed (Table S5, entries 16-18, SI), and the TOF is 64.1, 63.0 and 63.5 h⁻¹ respectively, suggesting the reaction conversion is independent on the concentration of reactant. The dependence profile of reaction rate on 4-nitrobenzaldehyde concentration and hydrogen pressure was further considered (Figure S22, SI). The correlation coefficients of 4-nitrobenzaldehyde concentration is the rate-determining step in this

reaction. The Arrhenius plot gives an activation energy of 24.5 kJ·mol⁻¹ over Ni₂P/PC-2 (Figure S23, SI), lower than noble metal catalysts, such as Au-Pt⁴⁵ (31 kJ·mol⁻¹), Ni⁴⁶ (54.5 kJ·mol⁻¹) and Cu³⁰ (61.4 kJ·mol⁻¹), and much lower than the bulk Ni₂P (79.2 kJ·mol⁻¹). The activation energy is significantly lowered over Ni₂P/PC-2, which clearly demonstrates that hydrogen desorption is promoted by downshifted *d*-band of Ni as DFT calculation predicted. Furthermore, the Ni₂P/PC-2 performs higher activity than previously reported noble-metal (Table S6, SI) and transition-metal catalysts (Table S7, S8, SI) under similar reaction conditions. In order to demonstrate the stability and recyclability of Ni₂P/PC-2, we reused the catalyst in the reaction up to 10 times. The selectivity of aniline keeps almost constant in all runs, although the conversion goes down a little (Figure S24, SI). TEM and XPS characterizations confirm the morphology and structure of the catalyst are well retained after the recycling tests (Figure S25, S26, SI), further demonstrating the excellent catalytic stability.

Furthermore, we explored the hydrogenation of 14 other industrially interesting nitroarenes using Ni₂P/PC-2 as catalyst and obtained the corresponding anilines in excellent yield and selectivity (**Table 1**). Interestingly, halogen substituted nitrobenzenes were reduced to the corresponding chloroanilines soothly without any dehalogenation (**Table 1**, entries 5-6). This catalyst is able to selectively hydrogenate nitro-group to corresponding amino-group with full conversion and remains other unsaturated functional groups such as -OH, -COOH, -CN, -C=C and -C=C unchanged (**Table 1**, entries 1-4, 10, 13-16). Especially for the hydrogenation of 3-nitrostyrene, it gives a conversion of ~96.1% with a high selectivity toward 3-aminostyrene around 4 h mark. Even reaction time is prolonged to 8 h with the selectivity maintained constant. Moreover, DFT calculation can also demonstrate high selectivity as shown in Figure S27, SI. Ni₂P/PC-2 is active and selective for substrates with either electron-withdrawing or electron-donating groups, suggesting it serves as a versatile catalyst for the selective hydrogenation of substituted nitroarenes.

Table 1. Hydrogenation of Functionalized Nitroarenes UsingNi2P/PC-2 as Catalyst.

Entry Substrate Trouter Time (ii) Con./Set. (70)	Entry	Substrate	Product	Time (h)	Con./Sel. (%)
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Page 14 of 23

1					
2 3 4 5 6	1		COOH NH2	5	99.2/>99.9
7 8 9	2	OH NO ₂	OH NH ₂	5	98.2/>99.9
10 11 12 13	3	OH NO ₂	OH NH2	5	93.5/>99.9
14 15 16	4	OH NO ₂	OH NH2	5	94.6/>99.9
17 18 19 20	5		CI NH2	9	97.4/>99.9
21 22 23 24	6	NO ₂	NH ₂	4.5	99.0/>99.9
24 25 26 27	7	Me NO ₂	Me NH ₂	10	95.0/>99.9
28 29 30 31	8	OMe NO ₂	OMe NH ₂	10	89.6/>99.9
32 33 34	9	NO ₂	NH ₂	10	98.3/>99.9
35 36 37 28	10	NO ₂	NH2	6	98.4/>99.9
39 40 41	11	Br	Br	9	83.6/>99.9
42 43 44	12			4	90.5/>99.9
45 46 47 48	13	NO ₂	NH ₂	8.5	>99.9/>99.9
49 50 51 52	14	NO ₂	NH2	5	>99.9/>99.9
52 53 54	15	NO ₂	NH ₂	4	96.1/>99.0
56 57 58	16	NO2	NO2	8	100/>99.0

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Reaction conditions: 0.5 mmol substrate, 10 mg Ni₂P/PC-2, 5 mL ethanol,

10 bar H₂, 80 °C.

3.4 Origins of high activity and chemoselectivity for Ni₂P/PC. To understand how the dispersion of Ni₂P clusters affect the selective hydrogenation of 4-nitrobenzaldehyde, Ni₂P/PC-x were tested under the same reaction condition (Figure 5a). Ni₂P/PC-2 delivers the best catalytic activity (taking 5 h for full conversion), and other catalysts with lower Ni₂P dispersion exhibit relatively lower catalytic performance (taking 5.5, 6.5 and 10 h to reach full conversion for Ni₂P/PC-1, Ni₂P/PC-0.5 and Ni₂P/PC-0 respectively). Correspondingly, their reaction rates are in order of 20.41 mol·L⁻¹·h⁻¹ (Ni₂P/PC-2) > 18.54 mol·L⁻¹·h⁻¹ (Ni₂P/PC-1) > 15.50 mol·L⁻¹·h⁻¹ $(Ni_2P/PC-0.5) > 10.13 \text{ mol} \cdot L^{-1} \cdot h^{-1} (Ni_2P/PC-0)$ as revealed in **Figure 5b** and S28. SI. The catalytic activity is further characterized by TOF as the function of Ni₂P dispersion (size). As shown in Figure 5c, although higher dispersion of Ni₂P shows a relatively lower TOF value, Ni₂P dispersion shows a significant effect on chemoselectivity of 4-nitrobenzaldehyde to 4-aminobenzaldehyde (Figure 5d). When the Ni₂P dispersion is low, 4-nitrobenzaldehyde can be adsorbed in parallel on Ni₂P, so both -CHO and -NO₂ can be reduced, resulting in poor chemoselectivity. Therefore, Ni₂P/PC-0 with lowest Ni₂P dispersion (38.5%) delivers the lowest chemoselectivity of $\sim 60.1\%$. With the increasing of Ni₂P dispersion, the adsorption of reactant on Ni₂P nanoclusters can be repressed due to geometric hindrance, which benefits the preferential adsorption of 4-nitrobenzaldehyde via nitro group on PC support, and thus delivers the superior chemoselectivity.



Figure 5. Effects of particle size on the catalytic performance of 4-nitrobenzaldehyde hydrogenation. (a) Catalytic profiles of various catalysts with different particle size/dispersion of Ni_2P nanoclusters as a function of time and (b) corresponding reaction rate constants; (c) plot of the particle size/dispersion and their TOFs, (d) plot of the particle size/dispersion and their selectivity.

To better understand the underlying factors that afford the selective hydrogenation of 4-nitrobenzaldehyde, attenuated total reflection infrared spectra (ART-IR) was carried out to understand the adsorbed behaviors of $-NO_2$ and -CHO over Ni₂P/PC-2, Ni₂P and P-doped carbon (**Figure 6a-c**). For Ni₂P/PC-2, when nitrobenzene is used as the substrate, the asymmetric and symmetric IR vibration frequencies of $-NO_2$ at 1520 and 1343 cm⁻¹ appear²³. When 4-nitrobenzaldehyde is applied as the probe molecule, also only these two peaks attributed to $-NO_2$ obviously appear while no vibrations of -CHO present. For the adsorption of benzaldehyde, no vibrations of -C=O (*ca.* 1700 cm⁻¹)¹¹ present, suggesting that Ni₂P/PC-2 can easily absorb nitro group but does not absorb aldehyde group. In contrast, there are several characteristic peaks

attributed to -NO₂ and -CHO for bulk Ni₂P catalyst, which indicates Ni₂P adsorbs both -NO₂ and -CHO non-selectively, quite different from the case of Ni₂P/PC-2. Moreover, P-doped carbon shows similar signals with Ni₂P/PC-2, suggesting a preferential adsorption of 4-nitrobenzaldehyde on PC *via* nitro group. These results also confirm that over Ni₂P/PC-2 the reactant is adsorbed on PC support rather than on Ni₂P.



Figure 6. ATR-IR spectra of absorbed species on (a) $Ni_2P/PC-2$, (b) bulk Ni_2P and (c) PC; (d) In situ FT-IR spectra of PC and $Ni_2P/PC-2$ after being exposed under H₂ at 80 °C for 30 min.

We then conducted *in-situ* FT-IR measurements to investigate the activation behavior of H_2 on Ni_2P nanoclusters and PC support (**Figure 6d**). This spectrum of PC exposed in the H_2 at 80 °C exhibits no obvious peaks, confirming H_2 molecule cannot be activated on PC under the reaction temperature. It has been reported that H_2 is able to dissociate into H atoms separately binding with Ni and P atoms²⁴. Actually, when Ni₂P/PC-2 exposed in the H_2 atmosphere, a weak signal at 2350 cm⁻¹ corresponding to the stretching vibration of P-H⁴⁷ appears, which indicates H_2 molecule is activated and dissociated on Ni₂P rather than on PC support.

4. Conclusion

In summary, we have reported an outstanding catalyst for selective hydrogenation of nitroarenes by reducing the Ni₂P into sub-nanosized clusters, tailoring the *d*-band center of Ni, and coupling them with P-doped carbon. A chemical anchoring method was developed to fabricate Ni₂P with controllable dispersion of 81.3% on P-doped carbon. The electron-transfer from P-doped carbon to Ni₂P clusters results in downshift of *d*-band center of Ni, which promotes H desorption on highly charged antibonding orbital of Ni-H, resulting in outstanding activity. The adsorption of reactant is preferentially adsorbed on P-doped carbon surface through nitro group, and the adsorption on Ni₂P nanoclusters is suppressed due to the geometrical hindrance, leading to excellent selectivity. Therefore, the optimized catalyst (Ni₂P/PC-2) shows excellent activity, selectivity and stability in the hydrogenation of nitroarenes, much better than many reported noble- and transition-metal catalysts.

Supporting Information

Supplementary experimental procedure, DFT calculation results, supplemental figures and tables (Figure S1-S28 and Table S1-S8) and MS spectra of products.

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