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On-demand, Ultrasensitive Hydrogenation System Enabled by Precisely Modulated Pd-Cd Nanocubes

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ABSTRACT: The pursuit of efficient hydrogenation nanocatalysts with a desirable selectivity towards intricate substrates is state-of-the-art research but remains a formidable challenge. Herein, we report a series of novel PdCd_x nanocubes (NCs) for the ultrasensitive hydrogenation reactions with flexible tuning feature. Obtaining a desirable conversion level of the substrates (e.g., 4-nitrophenylacetylene (NPA), 4-nitrobenzaldehyde (NBAD) and 4-nitrostyrene (NS)) and competitive selectivity for all potential hydrogenation products have been achieved one by one under optimized hydrogenation conditions. The performance of these PdCd_x NCs displays an evident dependence on both the composition and the use of Cd and a need for a distinct hydrogen source (H₂ or HCOONH₄). Additionally, for the selectivity of hydrogen to be suitably high, the morphology of the NCs has a very well-defined effect. Density functional theory calculations confirmed the variation of adsorption energy for the substrate and hydrogenation products by carefully controlled introduction of Cd, leading to a desirable level of selectivity for all potential hydrogenation products. The PdCd_x NCs also exhibit excellent reusability with negligible activity/selectivity decay and structural/composition changes after consecutive reactions. The present study provides advanced strategy for the rational design of superior hydrogenation nanocatalysts to achieve a practical application for desirable and selective hydrogenation reaction efficiency.

INTRODUCTION

Selectivity is fundamental to heterogeneous hydrogenation and is of great scientific and industrial interest.¹⁻³ Currently, noble metals (e.g., Pd and Pt) that can readily activate hydrogen (H₂) are the best choice for the hydrogenation of unsaturated hydrocarbons.^{2, 4-6} Unfortunately, precise control of the hydrogenation of the desirable product over bare noble metals is challenging, which usually results in a low selectivity. In general, a highly selective noble-metal nanocatalyst should primarily hydrogenate the reactant whilst avoiding consecutive hydrogenation of the desired product. In fact, the hydrogenation selectivity of noble metals can be encouraged by the introduction of a second metal or organic/inorganic compound,⁷⁻¹⁶ since this can lower the

hydrogen dissociation ability of the active noble metal and reduce the binding energy of the desired products on nanocatalysts. However, with previously reported nanocatalysts, it remains a difficult task to selectively reduce the substrate with multiple unsaturated functional groups (e.g., alkynes, alkenes, aldehydes and nitroarene) while obtaining potential hydrogenation products with a desired selectivity.^{4, 6, 17} Nevertheless, achieving selective hydrogenation in the presence of competing unsaturated functional groups is of a great importance to the pharmaceutical and chemical industry because many specific hydrogenation products are difficult to produce by simple organic synthesis.^{18, 19} Therefore, it is a highly desirable yet formidable challenge to achieve a sufficient

level of selectivity of intricate substrates to on-demand hydrogenation products.

To achieve precise hydrogenation performance, the nature of the nanocatalyst (size, compositions and morphology, etc.) must be carefully controlled, which provides an ensemble control of the adsorption of hydrogenation sources, reactants and products.²⁰⁻²⁵ As predicted by our theoretical study, the adsorption energy of hydrogen sources on different PdCd_x nanocatalysts can be readily controlled (table S1), for which PdCd nanocatalysts may potentially possess desirable performance for selective hydrogenation. Here in this work, we have introduced Cd into Pd to form PdCd_x NCs as a potential electrocatalyst for the hydrogenation based on flexible control of compositions. We have developed a series of PdCd_x nanocubes (NCs) (*x* = 0.53, 0.67, 0.82 and 1.13) for the selective hydrogenation of 4-nitrophenylacetylene (NPA) with both nitro and alkynyl groups. Remarkably, a desirable level of selectivity with a switchable feature for all five potential hydrogenation products, and an excellent reusability have been achieved over these systematically tuned PdCd_x NCs under optimal hydrogenation conditions. The detailed theoretical study revealed that the tuning of the adsorption energy for the substrate and hydrogenation products by the precise introduction of Cd plays a key role in obtaining a competitive selectivity. Significantly, the outstanding hydrogenation performance of PdCd_x NCs can be readily applied to other intricate substrates (i.e., 4-nitrobenzaldehyde (NBAD) and 4-nitrostyrene (NS)), making it a practical potential hydrogenation nanocatalyst system with a very competitive selectivity for fine chemicals and beyond.

EXPERIMENTAL SECTION

Chemicals. Bis(acetylacetonate)palladium(II) (Pd(acac)₂, 99%), sodium tetrachloropalladate(II) (Na₂PdCl₄, > 98%), oleylamine (C₁₈H₃₇N, OAm, > 70%), oleic acid (C₁₈H₃₄O₂, OA, > 85%), polyvinylpyrrolidone (PVP, K30) and commercial Pd/C (10 wt%, 2-5 nm Pd nanoparticles) were all purchased from Sigma-Aldrich. Cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O, CdAc₂·2H₂O > 99.99%) and ricinoleic acid (C₁₈H₃₄O₃, RA, > 97%) were purchased from Aladdin. DL-mandelic acid (C₈H₈O₃, > 99%) was purchased from Energy Chemical. Benzoin (C₁₄H₁₂O₂, > 98%) was purchased from Acros. 4-Nitrophenylacetylene (C₈H₂NO₂, NPA, > 99%) was purchased from Beijing HWARD Chem. Cyclohexane (C₆H₁₂, analytical reagent, ≥ 99.5%), ethanol (C₂H₆O,

analytical reagent, ≥ 99.7%), N, N-Dimethylformamide (DMF, ≥ 99.5%), formic acid (CH₂O₂, analytical reagent, ≥ 99.9%), acetone (C₃H₆O, ≥ 99.9%) and sodium iodide (NaI, analytical reagent, ≥ 99.9%) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ cm⁻¹) used in all experiments was obtained by passing through an ultra-pure purification system (Aqua Solutions).

Synthesis of PdCd_x NCs and PdCd_{0.82} NPs. In a typical preparation of PdCd_{0.82} NCs, Pd(acac)₂ (7.6 mg), CdAc₂·2H₂O (8.8 mg), DL-mandelic acid (150.0 mg), OAm (4 mL) and OA (1 mL) were added to a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for approximately 0.5 h. The resulting homogeneous mixture was heated from room temperature to 160 °C for approximately 0.5 h and kept at 160 °C for 5 h in an oil bath. After cooling to room temperature, the colloidal products were collected by centrifugation and washed with a cyclohexane/ethanol mixture. For the syntheses of PdCd_{0.53}, PdCd_{0.67}, and PdCd_{1.13} NCs, all the conditions are similar to those of PdCd_{0.82} NCs, except for changing the amount of CdAc₂·2H₂O to 4.4 mg, 6.6 mg, and 11.0 mg, respectively. The preparation of PdCd_{0.82} NPs is similar to that of PdCd_{0.82} NCs, except for replacing DL-mandelic acid (150.0 mg) with benzoin (150.0 mg).

Synthesis of Pd NCs. In a typical preparation of Pd NCs, Na₂PdCl₄ (7.4 mg), PVP (100 mg), NaI (5 mg), and DMF (10 mL) were added to a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for approximately 10 min. The resulting homogeneous mixture was heated from room temperature to 120 °C for approximately 0.5 h and kept at 120 °C for 5 h in an oil bath. After cooling to room temperature, the colloidal products were collected by centrifugation and washed with an ethanol/acetone mixture three times.

Characterizations. The samples were prepared for characterization by dropping their cyclohexane or ethanol dispersions onto carbon-coated copper grids using pipettes. The grids were dried under ambient conditions. Low-magnification TEM was conducted on a HITACHI HT7700 transmission electron microscope at an acceleration voltage of 120 kV. High-magnification TEM and STEM were conducted on a FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. PXRD patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). The

concentration of catalyst was determined by ICP-AES (Varian 710-ES). All the X-ray photoelectron spectroscopy (XPS) measurements of these catalysts were collected with a Thermo Scientific, ESCALAB 250 XI system.

Hydrogenation measurements. The obtained PdCd_x NCs, PdCd_{0.82} NPs and Pd NCs were further loaded on carbon black (Vulcan XC72R carbon, C) with a total Pd content of 5 wt%, as determined by ICP-AES. All the hydrogenation runs were performed in a glass pressure vessel (volume: 48 mL, Chemical glass), to which solvent (10 mL, DMF), PdCd_x ($x = 0.53, 0.67, 0.82, 1.13$) (10 mg, 5 wt%) and substrate (0.68 mmol NPA/NBAD/NS) were added. When H₂ was the hydrogen source, the glass pressure vessel was sealed and purged three times with H₂ under stirring. The glass pressure vessel was then pressurized to 0.1 MPa using H₂ and heated to 60 °C under constant stirring. When HCOONH₄ was the hydrogen source, HCOONH₄ (1.5 mmol) was added to the glass pressure vessel. The glass pressure vessel was then sealed and heated to 60 °C under constant stirring. Samples were taken at fixed intervals by a sample tube. The samples were filtered and analyzed by a gas chromatograph (GC, Shanghai Yiyou, GC-7860, column: HP-5, 30 m × 0.32 mm × 0.25 μm) with a flame ionization detector (FID). All hydrogenation runs of PdCd_{0.82} NPs, Pd NCs and the commercial Pd/C were performed under the same conditions, changing PdCd_x NCs to PdCd_{0.82} NPs, Pd NCs and the commercial Pd/C. The turnover frequency numbers (TOF) based on Pd of these catalysts was calculated using the following equation.

$$\text{TOF}(\text{h}^{-1}) = \frac{n_{\text{substrate}}(\text{mmol}) \times \text{Conversion}}{n_{\text{Pd}}(\text{mmol}) \times t(\text{h})} = \frac{n_{\text{substrate}}(\text{mmol}) \times \text{Conversion}}{\frac{m_{\text{cat}}(\text{g}) \times \text{Pd wt \%}}{M_{\text{Pd}} \times 10^{-3}(\text{g mmol}^{-1})} \times t(\text{h})}$$

DFT models and calculations. All the calculations were performed with the “Vienna ab initio simulation package” (VASP5.4.4).²⁶⁻²⁹ The electron interactions were represented by the projector augmented wave (PAW) method and plane-wave basis functions with a kinetic energy cut-off of 400 eV.³⁰ The electronic interaction effect in the calculations was described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh (PBE) functional. Ground-state atomic geometries were obtained by minimizing the energy and force to 1.0×10^{-5} eV/atom and 0.05 eV/Å, respectively. To examine the effect of van der Waals interactions on reaction energetics, calculations were performed by using the DFT-D₃ functional.³¹ The vacuum spacing in the direction along the Z axis, with respect to the surface, was 15 Å between neighboring slab images, which is sufficient

to eliminate the interactions between the slabs. The climbing image nudged elastic band (CI-NEB) method was used to search the transition states and track minimum-energy paths for the reactions.^{32, 33}

The optimized lattice parameters for the primitive PdCd are 3.06, 3.06 and 3.76 Å. The PdCd [220] surface was modeled by a 3×3 supercell. All the slabs contained four atomic layers, and the top two layers were allowed to relax. For the calculation of the adsorption energy of small molecules on the slabs, we provide a definition for the calculation of the adsorption energy (E_{ad}) as:

$$E_{\text{ad}} = E_{\text{slab\&mol}} - (E_{\text{mol}} + E_{\text{slab}})$$

where $E_{\text{slab\&mol}}$, E_{mol} , and E_{slab} are the energies of the slabs with the adsorbed molecule, the single molecule and the slabs, respectively.

RESULTS AND DISCUSSION

A series of PdCd_x NCs were successfully prepared through a facile wet-chemical approach, where the compositions of PdCd_x NCs can be readily realized by tuning the amount of Cd precursor supplied while keeping the amount of Pd precursor constant (see **Experimental Section**). To achieve better control over the Pd-Cd nanostructure, a variety of synthetic parameters were optimized. We found that the proper amount of reducing agent and use of oleic acid (OA) are essential for the preparation of well-defined PdCd NCs (**figures S1-3**). The representative high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image shows that the PdCd_{0.82} NCs are fairly uniform in term of size and shape, with an average edge length of 10.8 nm (**Figure 1A**). The composition of the PdCd_{0.82} NCs was determined to be Pd:Cd = 55.1:44.9 by using an energy dispersive X-ray spectrophotometer (EDS), which is consistent with results from inductively coupled plasma atomic emission spectroscopy (ICP-AES, Pd:Cd = 55.4:44.6) (**figure S4**). As **Figure 1B** shows, all the peaks of the powder X-ray diffraction (PXRD) pattern can be indexed to a body-center unit cell, where the 2θ values of 39.1°, 42.5°, 50.4°, 61.7°, 68.0°, 75.6° and 83.2° can be indexed to the diffraction of the (111), (200), (002), (220), (202), (311) and (222) planes of PdCd alloy, respectively (JCPDS file no. 06-0570). The crystalline nature of the PdCd_{0.82} NCs was further confirmed by high-resolution HAADF-STEM (**Figure 1C**). The corresponding FFT pattern shows the crystal structure of PdCd_{0.82} NC, where the PdCd_{0.82} NC exposes the (220) crystal face along [001] zone axes (**Figure 1D**). **Figure 1E** exhibits enlarged HRTEM image from the area indicated by the white

dashed rectangle in **Figure 1D**. As shown in **Figure 1F**, the lattice spacing of crystal plane that parallel to the edge of cube is measured to be 0.154 nm, assigning to the (220) plane of PdCd (JCPDS 06-0570). The HAADF-STEM image and corresponding elemental mappings and the

line-scan analysis show that Pd and Cd are uniformly distributed throughout the whole NC (**Figures 1G and 1H**).

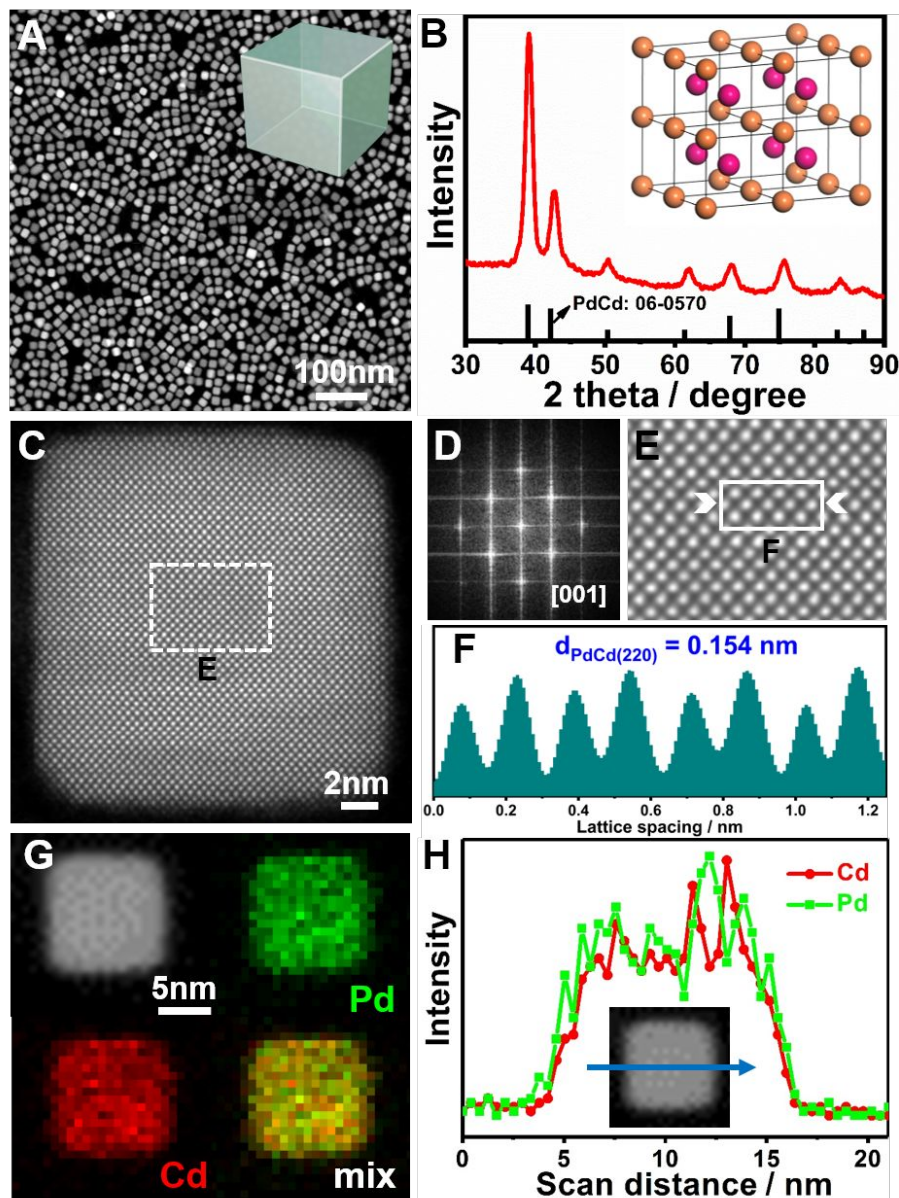


Figure 1. (A) HAADF-STEM image and (B) PXRD pattern of PdCd_{0.82} NCs. (C) High resolution HAADF-STEM image of PdCd_{0.82} NC. (D) Corresponding FFT image of (C). (E) Enlarged high resolution HAADF-STEM image from the selected area in (C). (F) Integrated pixel intensities of PdCd (taken from the white solid rectangle in (E)) along the arrow directions, which are perpendicular to the (220) facet. (G) HAADF-STEM image and corresponding elemental mappings and (H) line-scan analysis across the blue arrow. Inset in (A), cube model of Pd-Cd. Inset in (B), atomic model of Pd-Cd.

By simply changing the amount of Cd precursor supplied, with other conditions kept the same as the synthesis of the PdCd_{0.82} NCs, the PdCd_{0.53}, PdCd_{0.67} and PdCd_{1.13} NCs were readily obtained (see **Experimental**

Section). Typical STEM images of the PdCd_x NCs are displayed in **figures S5A, 5D and 5G**, where all the different PdCd_x NCs exhibit similar morphologies and sizes. Detailed characterizations were further carried out

to reveal the crystalline nature and elemental distributions of these PdCd_x NCs. The EDS results show that the atomic ratios of Pd/Cd in PdCd_{0.53}, PdCd_{0.67} and PdCd_{1.13} NCs are 64.9/35.1, 60.0/40.0 and 47.2/52.8, respectively, consistent with the ICP-AES results (**figure S4**). As more Cd is introduced, the PXRD peaks are shifted to smaller 2θ values assigned to the PdCd alloy phase, indicating the increased *d*-spacing and the dilation of the lattice-constant is due to the incorporation of Cd into the Pd *fcc* lattice (**Figure 2A**). This observation demonstrates that the PdCd alloy phase is maintained in these PdCd_x NCs, while the *d*-spacing can be tuned by controlling the Cd content, which ensures the potential control of their catalytic performance by readily optimizing Cd content. The crystalline nature of these PdCd_x NCs was further characterized by HRTEM (the insets of **figures S5A, 5D and 5G**). The lattice fringes are all approximately 0.15 nm, which can be assigned to the (220) plane of PdCd. The spatial distributions of Pd and Cd species in these PdCd_x NCs were then identified by HAADF-STEM, line-scan analysis and elemental

mappings, where Pd and Cd are distributed uniformly throughout the NCs (**figures S5B, 5C, 5E, 5F, 5H and 5I**). Precise surface control of PdCd_x NCs offer a potential for tuning their catalytic properties. X-ray photoelectron spectroscopy (XPS) was carried out to reveal the electronic interaction between the Pd and Cd of PdCd_x NCs (**Figures 2B and 2C**). The $3d_{3/2}$ and $3d_{5/2}$ peaks of Pd in PdCd_x NCs exhibit consecutive negative shifts with increasing Cd, suggesting that there is a slight electron transfer from Cd to Pd. The $3d_{3/2}$ and $3d_{5/2}$ peak positions of Cd in the PdCd_x NCs have no obvious shift, but the proportion of metallic Cd peaks are positively correlated with Cd peaks. The *d*-band of PdCd_x NCs further confirmed the electronic interaction between the Pd and Cd, where its center of gravity gradually shifted down with the increasing amounts of Cd (**Figure 2D**), indicating the variation of adsorption capability for PdCd_x NCs. Therefore, the PdCd_x nanostructures with different compositions exhibit tunable surface properties.

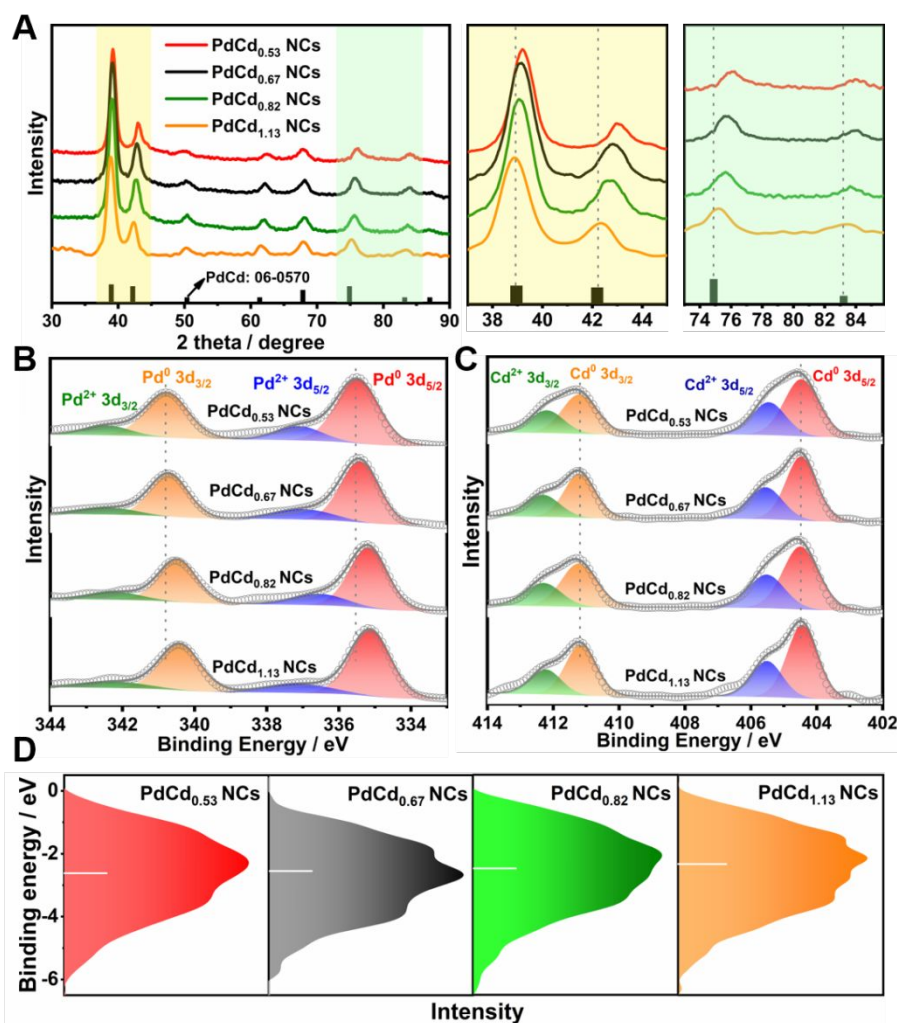
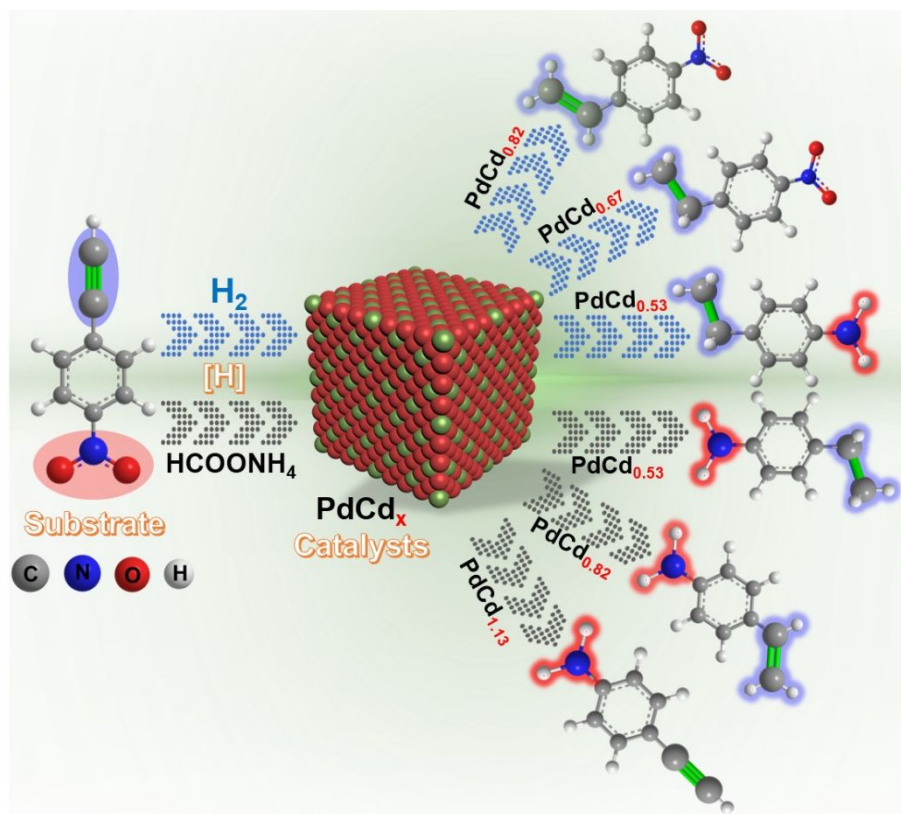


Figure 2. (A) PXRD patterns and enlarged PXRD patterns of PdCd_x NCs. XPS spectra of (B) Pd 3d and (C) Cd 3d of different PdCd_x NCs. (D) Surface valence band of PdCd_x NCs. All the spectra are background corrected. The white bar indicates the center of gravity.



Scheme 1. Schematic illustration showing different hydrogenation order of alkynyl and nitril over PdCd_x NCs using H₂ and HCOONH₄ as hydrogen sources.

Pd-based nanocatalysts have been widely used in hydrogenation reactions, and the quest for superior hydrogenation nanocatalysts that combine high activity, selectivity, and stability is state-of-the-art research.³⁴⁻³⁶ As a proof-of-concept application, the selective hydrogenation of NPA was first adopted as the model reaction to evaluate the performance of the PdCd_x NCs with different composition ratios. In this study, remarkable selectivity with a switchable feature for all five potential hydrogenation products was successfully realized, and the performance of PdCd_x NCs exhibits an obvious composition dependence as well as a distinct hydrogen source dependence (**Scheme 1**).

In detail, the selective hydrogenation of NPA into NS, 4-Nitroethylbenzene (NEY), 4-Ethylaniline (EA), 4-Aminophenylacetylene (APA) and 4-Aminostyrene (AS) has been readily achieved under optimal hydrogenation conditions (**Figure 3**). As a starting point, the PdCd_{0.82} NCs was applied to the hydrogenation of NPA using H₂ as

the hydrogen source under mild conditions (see Materials and Methods). As shown in **Figure 3A**, PdCd_{0.82} NCs exhibits a desirable conversion and selectivity to NS. The main product of NS (97.6 %) and trace NEY (2.4 %) were detected in a very short time period (0.5 h). The selectivity for NS (96.0 %) was maintained even after a 5 h reaction, indicating that PdCd_{0.82} is only able to reduce alkynyl to vinyl under this reaction condition. Inspired by this result, the hydrogenation properties of PdCd_{0.53}, PdCd_{0.67} and PdCd_{1.13} NCs were also tested under identical conditions. For PdCd_{1.13} NCs, the selectivity to NS was still obtained at a suitable level, while the hydrogenation conversion rate was decreased, revealing that an increased Cd content weakens the activity (**figure S6A**). In contrast, the high conversion rate of NPA still remained for PdCd_{0.67} and PdCd_{0.53} NCs, but the main hydrogenated product was converted to NEY and EA, respectively, indicating that an improved hydrogenation activity can be obtained by decreasing the ratio of Cd (**Figures 3B and 3C**). It is worth noting that the

intermediate products of NS and NEY were detected in the initial hydrogenation period over PdCd_{0.67} and PdCd_{0.53} NCs, respectively. Therefore, we can conclude that the product transformation path is from NPA to NEY and eventually to EA under H₂, where the hydrogenation trend of the functional groups is according to the order of alkyne > vinyl > nitril under this reaction condition. To confirm this conclusion, we further investigated the hydrogenation properties of these PdCd_x NCs by directly using NS or NEY as the substrate under identical reaction

conditions. As shown in **figure S7A**, the NS is hardly hydrogenated by PdCd_{1.13} and PdCd_{0.82} NCs, while a high conversion could be observed over PdCd_{0.67} and PdCd_{0.53} NCs. As expected, for NEY, only PdCd_{0.53} NCs exhibit a high conversion (**figure S7B**). Therefore, the satisfied selectivity to the specific products over PdCd_x NCs in NPA hydrogenation mainly results from the activity difference of PdCd_x NCs with different ratios of Cd.

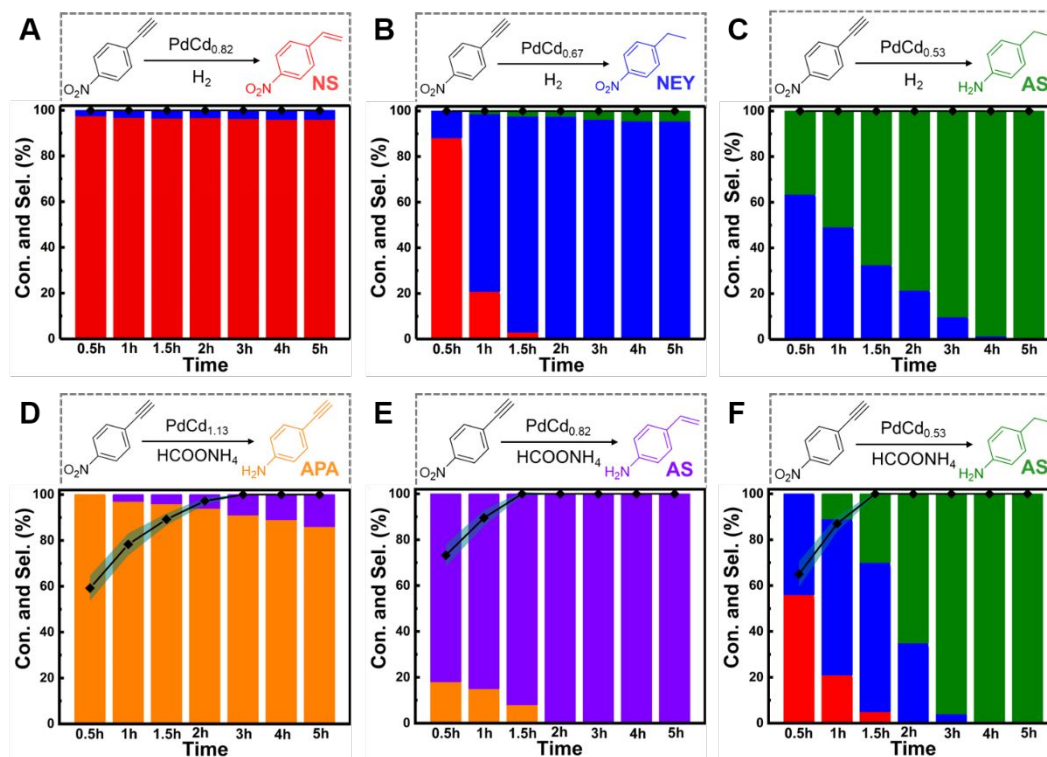


Figure 3. Hydrogenation of NPA over PdCd_x NCs. The conversion of NPA and selectivity to specific products vs. time using H₂ as the hydrogen source over (A) PdCd_{0.82} NCs, (B) PdCd_{0.67} NCs and (C) PdCd_{0.53} NCs. The conversion of NPA and selectivity to specific products vs. time using HCOONH₄ as the hydrogen source over (D) PdCd_{1.13} NCs, (E) PdCd_{0.82} NCs and (F) PdCd_{0.53} NCs. The light blue areas in (D, E, F) represent error bars of conversion.

The desired selectivity to NS, NEY and EA has thus been realized, and a distinct composition effect and hydrogenation trend (alkynyl > vinyl > nitril) have been observed. To further achieve the same level of selectivity to all hydrogenation products, the nitril must be initially reduced to yield APA and AS. Considering that metal-catalyzed reduction features various reducing agents other than molecular hydrogen,³⁷⁻³⁹ the use of different hydrogen sources might be an efficient approach to change the hydrogenation trend. As a hydrogen source, HCOONH₄ is an alternative, simple, and inexpensive reducing agent, which can offer eco-friendly reaction conditions and even enhance efficiency.³⁸ Therefore, we

were further motivated to explore the performance of PdCd_x NCs for selective NPA hydrogenation by using HCOONH₄. Significantly, a complete switch of selectivity to the products was achieved by changing the hydrogen source from H₂ to HCOONH₄. For PdCd_{1.13} NCs, the main hydrogenation product changed from NS to APA under the same hydrogenation conditions by replacing H₂ with HCOONH₄ (**Figures 3D and S6A**). Over the course of the hydrogenation reaction, it is clear that NPA was totally converted after 3 h, and the selectivity of APA reached 92.0 %. AS (8.0 %) was also detected in this process (**Figure 3D**). The hydrogenation properties of other PdCd_x NCs were also investigated. As shown in **Figure 3E**

PdCd_{0.82} NCs exhibit a higher hydrogenation conversion rate over PdCd_{1.13} NCs, while the main product is converted to AS (100 %). It is worth noting that the APA was also detected in the initial reaction period, indicating that the hydrogenation reaction proceeded on a different hydrogenation path by changing H₂ with HCOONH₄ as the hydrogen source. The PdCd_{0.67} NCs exhibits similar performance to PdCd_{0.82} NCs but are unable to maintain a high selectivity for AS and is further converted to EA after achieving a high conversion level (**figure S6B**). For the PdCd_{0.53} NCs, it is obvious that all of the NPA was converted into fully hydrogenated EA as the final reduction product (**Figure 3F**). It is worth emphasizing that the NS and NEY can be detected in short reaction time, indicating the same hydrogenation path over PdCd_{0.53} NCs whether using H₂ or HCOONH₄ as the hydrogen source, which demonstrates that the distinct hydrogen source effect can only be observed for the PdCd_x NCs with high Cd contents. Therefore, a distinct hydrogenation path was observed in the NPA hydrogenation by using HCOONH₄ as a hydrogen source, where the hydrogenation trend of functional groups is in the order of nitril > alkynyl > vinyl, in contrast with the hydrogenation reaction by using H₂ as the hydrogen source. In addition, to make a more precise comparison, the turnover frequency (TOF) of PdCd_x NCs based on Pd near the highest selectivity of the desired product was provided. As shown in **table S2**, the TOF of reactions using H₂ as a hydrogen source is generally higher than that of those using HCOONH₄ as a hydrogen source. Meanwhile, the Cd concentration has more effect on the TOF of reactions when using H₂ as the hydrogen source (**table S2**). Moreover, control experiments of the additional introduction of NH₃ in the presence of H₂ have been carried out. The results reveal that the hydrogenation rates or products are close to the cases only using H₂ as the hydrogen source (**Figure S8**), mostly because the excessive supply of H₂ blocks the action of NH₃ and prevents the hydrogenation trend as induced by HCOONH₄. This exactly proves the specific role of HCOONH₄ played in this reaction.

Pd NCs (**figures S9 and S10**) and PdCd_{0.82} NPs (**figure S11**) of a similar size were also prepared to better understand the roles of the composition and morphology of PdCd_x NCs in the highly selective hydrogenation reaction. As shown in **figure S12**, Pd NCs exhibit a much higher hydrogenation rate in the hydrogenation of NPA whether H₂ or HCOONH₄ is the hydrogen source, where NPA was fully hydrogenated into EA in a short time. The

performance of Pd NCs is very similar to that of the commercial Pd/C (**figure S13**), demonstrating that the hydrogenation rate is hard to control by pure Pd nanocatalysts and leads to a low selectivity for intermediate products in NPA hydrogenation. These results show that the introduction of Cd to Pd NCs is beneficial for a desirable selectivity for different hydrogenation products of NPA through precisely weakening the activity of Pd. In addition, PdCd_{0.82} NPs were also chosen as references to explore the shape/facet effect in the hydrogenation reaction. As shown in **figure S14**, PdCd_{0.82} NPs exhibits similar hydrogenation rates but shows a significantly reduced NS or AS selectivity compared with PdCd_{0.82} NCs, whether H₂ or HCOONH₄ is the hydrogen source. In other words, the systematic tuning of PdCd_x NCs is essential to achieve the desired competitive level of hydrogenation of NPA into NS, NEY, EA, APA and AS.

To understand the mechanism of two distinct hydrogenation paths over various PdCd_x NCs by using different hydrogen sources, a series of detailed experiments were further carried out. Considering that the surface properties of nanocatalysts largely affect the adsorption/desorption of the substrate and corresponding products, the PdCd_x NCs with different Cd contents can possess different surface properties for the adsorption/desorption of nitril and alkynyl. To make a direct comparison, experiments involving the hydrogenation of the physical mixture of phenylacetylene (PA) and nitrobenzene (NB) over PdCd_x NCs were conducted under different hydrogen sources. When H₂ is adopted as the hydrogen source, the hydrogenation rates of PA and NB decrease with the increased content of Cd, but the hydrogenation rate of PA is always much higher than that of NB in all the PdCd_x NC-catalyzed reactions (**figure S15**). In addition, while PdCd_{0.82} and PdCd_{1.13} NCs maintain a superior selectivity for styrene (SY) at different conversions, PdCd_{0.53} and PdCd_{0.67} NCs struggle to preserve the demanded selectivity for SY as the reaction proceeds. Significantly, a completely different catalytic behavior was observed for all PdCd_x NCs once HCOONH₄ was applied as the hydrogen source with other reaction conditions being the same. The hydrogenation rate of PA by using HCOONH₄ as the hydrogen source is slightly lower than that of H₂, while a much higher hydrogenation rate of NB was obtained, which is even higher than the hydrogenation rate of PA (**figure S16**). The contrary results of the hydrogenation rates for PA and NB with different hydrogen sources are consistent with the

different selectivity of NPA hydrogenation by using different hydrogen sources.

To illuminate the influence of the surfaces of PdCd_x NCs with different compositions on the catalytic performance, we used density functional theory (DFT) to investigate the catalytic processes. First, we constructed PdCd NCs with a (220) surface that matched with the experimental results. To simulate different compositions, we built the surface for pure Pd and PdCd_x NCs with ratios of Pd to Cd as 0.5, 0.8 and 1.25, respectively, on the top surface of the (220) plane (**figure S17**). As shown in **table S3**, the electron transferred from Cd to Pd increases

when the concentration of Cd increases and the trend matches well with XPS results. We further performed adsorption energy analysis for these established models. Since HCOONH₄ decomposes to HCOOH and NH₃, the HCOOH is the main reductive part as the hydrogen source in our simulations. As shown in **tables S1 and S4**, the adsorption of all the species (including the substrate, hydrogen sources, and possible products) decreases as the Cd concentration increases. Strong adsorption of the substrate and hydrogen sources implies high catalytic efficiency. Therefore, the activity of the PdCd_x NCs decreases with higher Cd concentrations.

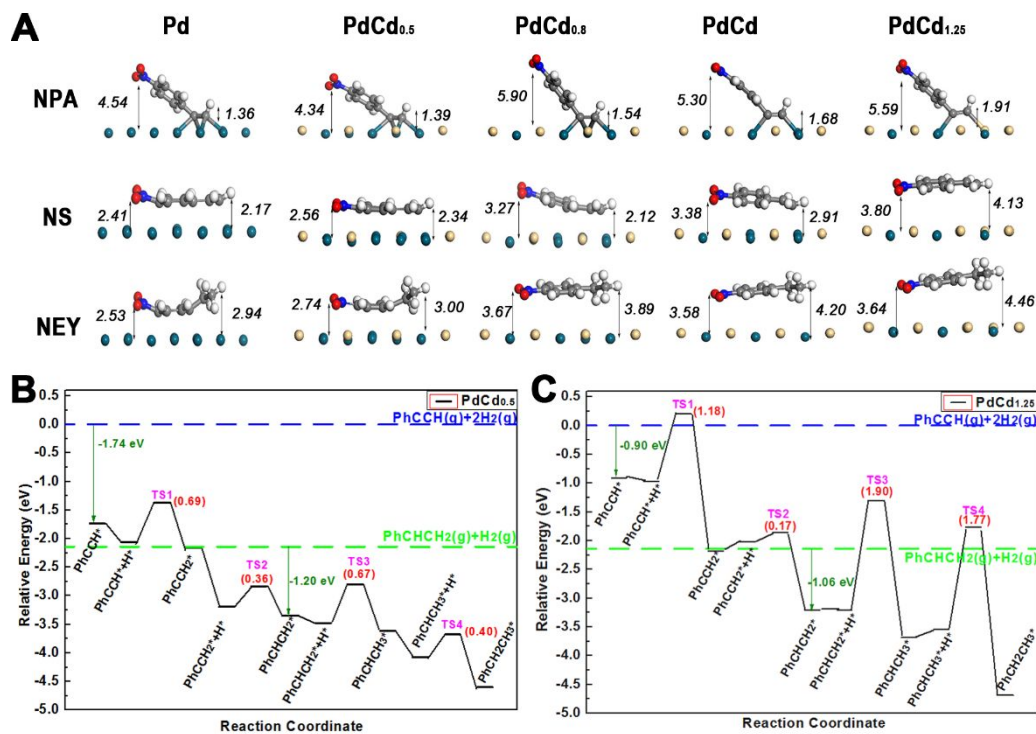


Figure 4. The adsorption configurations of adsorbates on pure Pd and PdCd_x NCs and reaction pathway for the hydrogenation of phenylacetylene on the PdCd_{0.5} (220) surface. (A) The different optimized configurations of NPA, NS and NEY adsorbed on the surface of pure Pd and PdCd_x NCs. The numbers represent the distances between the N atom (or C atom) and the surface (unit: Å). (B, C) Step-by-step hydrogenation mechanism of phenylacetylene to phenylethane on the (B) PdCd_{0.5} (220) surface and (C) PdCd_{1.25} (220) surface. Numbers in parentheses indicate the barriers of elementary steps. Cd, yellow; Pd, blue; C, gray; H, white.

The distinct hydrogen source (H₂ or HCOONH₄) dependence for PdCd_x NCs in hydrogenation reactions is also considered in this simulation. H₂ should be adsorbed on the metal surface first and then be activated to hydrogenate the substrates. **Figure 4A** shows the optimized configurations of NPA, NS and NEY adsorbed on the surface of pure Pd and PdCd_x NCs. Notably, Pd or Cd is in the coordinated environment that displays

stronger bindings with alkynyl and vinyl groups than nitril groups on the surface of Pd and PdCd_x NCs, so that alkynyl and vinyl groups would be hydrogenated preferentially, which is in agreement with the reductive order (alkynyl > vinyl > nitril) observed experimentally. HCOONH₄ can be ionized into HCOO⁻, NH₃ and H⁺ in solutions. HCOO⁻ can provide a negatively charged H⁻ anion that is highly reductive and nucleophilic, where the

H⁻ anion prefers to attack N atoms with positive charges in nitril groups; when the reduction reaction starts, the proton H⁺ would attack the O atom with a negative charge in a nitril group (**figure S18**).⁴⁰⁻⁴² The reduction of nitril groups occur more preferentially than the hydrogenation of alkynyl and vinyl groups, mainly because nitril can directly react with HCOO⁻ (or H⁺).

Whether H₂ or HCOONH₄ is used as a source of hydrogen, the selectivity has been tuned with the increase of Cd concentration. As shown in **Figures 4B and 4C**, we studied the mechanisms of hydrogenation of phenylacetylene to phenylethane on the PdCd_{0.5} (220) surface and PdCd_{1.25} (220) surface by the transition state (TS) search and the related structures can be seen in **figure S19**. It is noticed that on the PdCd_{0.5}(220) surface, the adsorption energies of phenylacetylene and styrene are -1.74 eV and -1.20 eV, respectively, which are much larger than the activation barriers, thus leading to the final product being phenylethane. However, on the PdCd_{1.25}(220) surface, the activated barriers of the first and third reaction steps reach 1.18 eV and 1.90 eV, which are much higher than the adsorption energies of phenylacetylene and styrene. These data indicate that on the PdCd_{1.25} (220) surface, it is not easy for the reaction to occur and the catalytic activity is low. When the concentration of Cd doping increases, on the one hand, the adsorption of reactants (phenylacetylene, styrene) has weakening effects, on the other hand, the activation barriers of reactions on PdCd_{1.25} surfaces are higher than that on PdCd_{0.5} surfaces. Both results show that PdCd_{1.25} is less effective than PdCd_{0.5} for the reaction of the hydrogenation of phenylacetylene to occur. This is consistent with the phenomena observed in the experiment: the increase of Cd concentration weakens the catalytic effect on the hydrogenation of phenylacetylene. Therefore, the adsorption energies of the substrates are significantly reduced as the Cd concentration increases. That is, the decreases of the adsorption energies can protect intermediates from further hydrogenation and lead to the final product since it will be more easily desorbed from the surface. Based on this rule, we could determine the final product in different situations. For example, for PdCd_{0.5} with H₂ as the hydrogen source, EA will be the final product because its adsorption energy of -1.32 eV is lower than that of NS and NEY. For PdCd_{0.8}, the adsorption configuration shows that NEY is parallel to the surface and does not bind to the metal surface, indicating the physical adsorption of NEY on the PdCd_{0.8} surface rather than the chemical bindings. Additionally, NEY has

the minimum adsorption energy of -0.98 eV (**table S4**); thus, NEY would desorb most easily and become the final product. The case of PdCd has a similar trend to that of PdCd_{0.8}. Finally, NS will be the final product on the PdCd_{1.25} surface due to its lowest adsorption energy of -0.87 eV. This trend is fully in line with the experimental data. When HCOONH₄ is the hydrogen source, in which case EA, AS, and APA are the possible products, we could also determine the final product based on the minimum adsorption energy rule from **table S4**, and the trend is also consistent with the experimental data. Furthermore, the differences between the adsorption energies of NPA and NS (NS and NEY, APA and AS, AS and EA) decrease with increasing Cd concentrations, indicating that the adsorption energy of the reactants and the corresponding reduction products are getting closer. Thus, the reactant tends to be desorbed more easily, broadly agreeing with the experimental results.

Encouraged by these efficient hydrogenation results, hydrogenation reactions with other similar substrates (NBAD and NS) over PdCd_x NCs were also carried out. As expected, a desirable level of conversion for NBAD and a competitive NS selectivity for all potential hydrogenation products have been achieved under the optimized hydrogenation conditions (**table S5 and table S6**), which also exhibits an obvious composition dependence and a distinct hydrogen source dependence. From the comparison of catalysts performance in our work with some benchmark catalysts in others' works, it is apparent that most previous studies solely focused on achieving a high selectivity of one desired hydrogenated product. In contrast, the realization of high selectivity for all potential hydrogenation products under one catalysis system is the most striking feature of our work (**table S2**).

A practically relevant hydrogenation catalyst should exhibit both high performance (activity and selectivity) and excellent stability. We have also evaluated the stability of PdCd_x NCs by consecutive reactions, where constant amounts of substrate were added in each run. As shown in **Figures 5 and S20**, after being reused six times, a superior conversion level was maintained for all PdCd_x NCs, with no obvious deactivation of the PdCd_x NCs in the consecutive reactions. A slightly decreased selectivity to different hydrogenation products of NPA was observed. The detailed characterizations for the catalysts after recycling experiments were carried out. It is clear to see that there are no obvious morphology/composition changes after hydrogenation in these cases (**figure S21**).

Uniform elemental distributions have been also confirmed by the elemental mappings and the line-scan analysis (figure S22). Further XPS studies reveal that there are no obvious differences of Pd and Cd for catalysts (figure S23). Considering the largely maintained structure of PdCd_x NCs after recycles (figure S21-S23), it

is reasonable to infer that the decreased selectivity is mainly attributed to the subtle surface change of chemical states under the reducing conditions and the adsorption of reaction species.

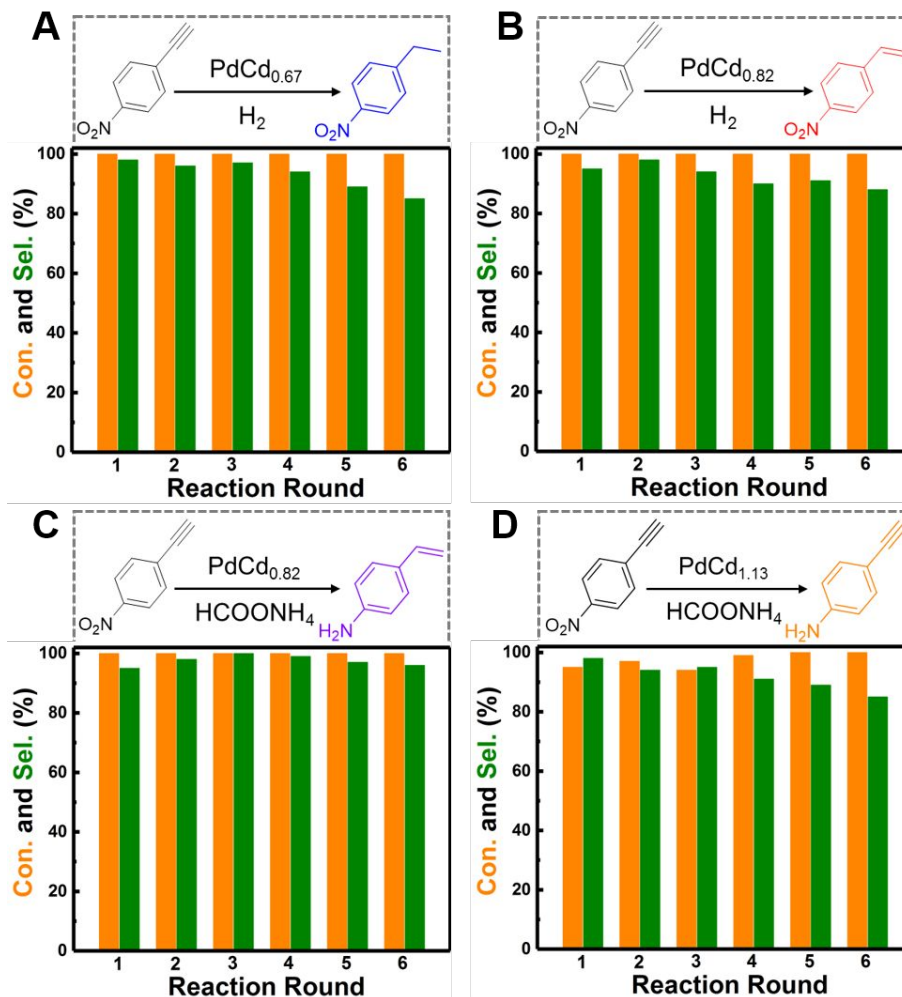


Figure 5. The reusability of PdCd_x NCs. The consecutive hydrogenation reactions of NPA over (A) PdCd_{0.67} NCs and (B) PdCd_{0.82} NCs using H₂ as the hydrogen source. The consecutive hydrogenation reactions of NPA over (C) PdCd_{0.82} NCs and (D) PdCd_{1.13} NCs using HCOONH₄ as the hydrogen source. The reaction time is 2 h for each run.

CONCLUSIONS

In summary, we have presented a wet-chemical strategy for a series of well-defined and nanocubic PdCd_x nanocatalysts with a tunable composition for the flexible selectivity control of NPA hydrogenation for all potential hydrogenation products. The performance of the PdCd_x NCs exhibited strong dependence of both composition tuning and hydrogen source selections, where the

irreplaceable role of Cd and uniform nanocube morphology in the remarkable selective hydrogenation has been identified. DFT calculations have been performed to elucidate the origin underlying the exceptional selectivity of PdCd_x NCs, in which the tuning of adsorption energy of hydrogenation products by precise modulation of Cd play a key role in boosting the selectivity. The PdCd_x NCs also exhibit excellent reusability with negligible activity/selectivity decay and

structure/composition changes after consecutive reactions. The generality of the outstanding hydrogenation performance of PdCd_x can be readily applied to other similar substrates (e.g., NBAD and NS). The present finding opens promising opportunities towards the rational design of practically relevant hydrogenation nanocatalysts with extremely high selectivity for broad applications such as fine chemical production and beyond.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website site.

Detailed information for characterizations, DFT calculations and hydrogenation performances, including Figures S1- S23 and Tables S1-S6.

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Notes

The authors declare no competing financial interests.

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