Pd Cluster Nanowires as Highly Efficient Catalysts for Selective Hydrogenation Reactions

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Abstract: Palladium is a key catalyst invaluable to many industrial processes and fine-chemical synthesis. Although recent progress has allowed the synthesis of Pd nanoparticles with various shapes by using different techniques, the facile synthesis of Pd nanocrystals and turning them into a highly active, selective, and stable catalyst systems still remain challenging. Herein, we report the highly selective one-pot synthesis of monodisperse Pd cluster nanowires in aqueous solution; these consist of interconnected nanoparticles and may serve as highly active catalysts because of the enrichment of high index facets on the surface, including

Keywords: butadiene · cinnamaldehyde · nanostructures · palladium · selective hydrogenation {443}, {331}, and {221} steps. For the first time, carbon nanotube and γ -Al₂O₃ immobilized Pd cluster nanowires showed highly enhanced catalytic performance in the liquid-phase selective hydrogenation of cinnamaldehyde and gas-phase hydrogenation of 1,3-butadiene relative to immobilized Pd icosahedra and nanocubes, as well as commercial Pd catalysts.

Introduction

The synthesis of noble-metal nanocrystals with controllable morphologies has attracted enormous interest due to the fascinating size- and shape-dependent properties of the nanocrystals and invaluable applications in catalysis, electronics, biotechnology, and magnetism.^[1] It is documented that the specific crystal facets and sizes of the noble-metal structures have great influences on their chemisorption properties and catalytic performance.^[2] Hence, special nanostructures with uniform sizes and well-defined shapes are highly desired to regulate their performance for various catalytic applications. To date, palladium nanocrystals with a large variety of shapes, including polyhedra, plates, wires, rods, bars, and tripods, have previously been synthesized by using a number of different methods.^[3] More recently, the structure dependence of oxygen reduction reaction (ORR) activity for shape-controlled Pd nanocrystals has been reported, which demonstrated that Pd nanocubes enclosed by

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{100} facets were one order of magnitude more active than Pd octahedra enclosed by {111} facets for ORR activity and comparable to that of the state-of-the-art Pt catalyst.^[4] Herein, we report a new type of Pd cluster nanowires, which were assembled from Pd clusters and showed excellent reactivity and selectivity in both liquid- and gas-phase selective hydrogenation reactions.

It is known that defects, including atomic steps, edges, and kinks, usually serve as active sites, and thus, exhibit a high chemical reactivity and catalytic activity for most structuresensitive reactions.^[5] Herein, we have synthesized Pd nanocrystals in a variety of shapes, including cluster nanowires, icosahedra, and nanocubes, through a facile aqueous solution method. The current one-pot synthesis of Pd nanoparticles with different shapes in aqueous solution should then be extremely catalytically interesting due to the highly selected well-defined morphologies (>95%), in comparison with the low selectivity of Pd morphologies described in previous works.^[6] It is noted that the cluster nanowires consisted of interconnected nanoparticles, which may lead to exposure of a large number of Pd atoms at defects, especially at the junctions and/or contact perimeters between Pd nanoparticles, and thus, may serve as highly active catalysts. Herein, we show for the first time that Pd cluster nanowires are the most active for the hydrogenation of cinnamaldehyde (CAL). By immobilization of the Pd nanoparticles on carbon nanotubes (CNTs) and γ -Al₂O₃, the catalytic activity and stability of the Pd nanoparticles was greatly enhanced in the liquid-phase hydrogenation of CAL and gas-phase hydrogenation of 1,3-butadiene. Specifically, the turnover frequencies (TOFs) and reaction rates of the immobilized Pd cluster nanowires were about two orders of magnitude higher than those of the Pd nanocubes. The TOFs and rea-

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ction rates of γ -Al₂O₃-immobilized Pd cluster nanowires were about 20 times that of the referenced commercial Pd/C catalyst with spherical Pd nanoparticles with average diameter of 4.0 nm in 1,3-butadiene hydrogenation.

Results and Discussion

Pd cluster nanowires were synthesized by the reduction of PdCl₂ in the presence of poly(vinyl pyrrolidone) (PVP), NaF, and sodium dodecyl sulfate (SDS). Here, PdCl₂ and PVP act as the Pd precursor and reducing agent, respectively. NaF, together with SDS, is responsible for both shape and size control. The cluster nanowire is made of nodes (heavy dark dots) and smaller stems, and has a larger overall size than the individual nanoparticle, but still retains a higher surface area than conventional three-dimensional spherical aggregations. Figure 1A shows representative TEM images of as-synthesized Pd cluster nanowires. For a single nanowire, it consists of interconnected nanoparticles (top right inset in Figure 1A). Grain boundaries can be clearly observed. The lattice fringes are not continuous and their orientations vary (Figure 1C and D), demonstrating that the interconnected Pd nanowire is polycrystalline. This is further confirmed by the FFT pattern in the inset of Figure 1 C. The average cross-sectional diameter of the Pd nanowires was (4.0 ± 0.7) nm, as determined by random measurements of 450 cross-sections. The length of such ultrathin nanowires is in the domain of about 50 nm and can reach up to 200 nm. Aberration-corrected HRTEM images of Pd cluster nanowires are shown in Figure 1B-G, in which the border atoms are clearly resolved. The crystal orientation is along the <110> zone axis. As shown in Figure 1B, Pd cluster nanowires possess a high density of low-coordinate atomic steps, such as {110}, {443}, {331}, and {221} steps, that can be identified on the border atoms (detailed assignments of step sites are given in Figure S1 in the Supporting Information). As depicted in Figure 1E-G (marked by lines), the interfacial dislocation, intragranular dislocation, and microtwin can be clearly observed, respectively. These defects, apart from the above-mentioned atomic steps, could make great contributions to excellent catalytic performance. A key role was demonstrated for NaF, together with SDS, in controlling the morphology, due to the formation of mixed morphologies, including nanowires, short rods, and irregular particles without them (see Figure S2A and B in the Supporting Information). Furthermore, with the reaction time shortened to 2 h, a typical intermediate of bent rods was captured by TEM (Figure 1H and I), which shows a strong growth orientation tendency toward a 1D structure through linking the ends of particle and/or rods. On the basis of our previous works,^[7] we deduced that the formation mechanism of the cluster nanowires proceeded as follows: In the first step, Pd nucleated and grew to form Pd particles. Then the rest of Pd ions were reduced by autocatalytic process and anisotropically grew to form short rods. Finally, the rods were one-dimensionally assembled into wires by oriented at-



Figure 1. A) TEM image of as-synthesized Pd cluster nanowires, the inset in the top right is the high-magnification TEM image of a single Pd cluster nanowire (scale bar: 10 nm) and the inset in the bottom left is the distribution of cross-sectional diameters of the Pd cluster nanowires. B)– G) Aberration-corrected high-resolution (HR) TEM images of Pd cluster nanowires oriented along the <110> zone axis, the atomic steps (B), interfacial dislocation (E), intragranular dislocation (F), and microtwin (G) can be clearly observed; the insets in B) and C) are the corresponding fast Fourier transform (FFT) patterns. H) Low- and I) high-magnification TEM images of the product collected from the reactions with the same conditions as those used in the synthesis of Pd cluster nanowires, but with a shorter reaction time of 2 h.

tachment at the ends of each short rod. The coexistence of irregular particles, short rods, and nanowires in the product synthesized during a shorter reaction time or in the absence of SDS and NaF provided indirect evidence of this route.

Fortunately the current route for the synthesis of cluster nanowires is effective in the selective synthesis of Pd icosahedra and nanocubes, which provides the possibility of systematically investigating the effect of structure on catalytic performance under similar conditions. Recent studies have shown that nanocrystals exposing high index or specific facets may show better stability and performance in catalytic reactions.^[4,5,8] However, in many cases, the capping ligands, the metal precursors, and synthetic conditions were quite

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different for nanocrystals with different shapes, which may bring uncertainties and complicate the structure-function relationship study because the catalytic process is usually sensitive to surface properties. Pd icosahedra were synthesized by reducing PdCl₂ with PVP in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA·2Na). Here, EDTA·2Na is used as morphology-controlled reagent, whereas PVP serves as both a reducing agent and a stabilizing agent. Furthermore, we found that Pd nanocubes can be highly selectively obtained by only introducing I⁻ ions into the initial aqueous solution for producing Pd icosahedra. This suggests that I⁻ can serve as a capping agent in this system to promote the formation of {100}.

As illustrated in Figure 2A, the as-synthesized Pd icosahedra were uniform with average edge lengths of (14.5 ± 1.1) nm, as determined by random measurements of 300 edge lengths and selectivity to icosahedra over 95%. High-

resolution scanning electron microscopy (HRSEM; Figure S3A in the Supporting Information) and high-angle annular dark-field scanning TEM (HAADF-STEM; Figure S3B in the Supporting Information) analyses showed that these Pd nanocrystals had regular icosahedral structures. Figure 2B shows a typical HRTEM image of a single Pd icosahedron. Clearly, multiply twinned structures can be observed on the surfaces of the Pd icosahedra and different growth directions can be identified for the two planes adjoining the boundary. The spots of the corresponding FFT pattern are shown in the inset of Figure 2B, in which the six distinct spots with hexagonal symmetry, corresponding to the planes of crystalline Pd, can be clearly seen. The lattice spacing of one of the faces of the icosahedron was 0.225 nm, which could be indexed as the {111} plane of Pd. The phase purity and high crystallinity of the Pd icosahedra were also supported by powder XRD (Figure S4 in the Supporting In-



Figure 2. TEM (A) and HRTEM (B) images of as-synthesized Pd icosahedra; the inset in the bottom left of B corresponds to the FFT pattern and the inset in the top right in B is the geometric model of an individual Pd icosahedron. C) TEM image of as-synthesized Pd nanocubes; the insets show the HRTEM image of a single nanocube (top right) and the corresponding selected-area FFT pattern. TEM images of CNT-immobilized Pd nanocrystals with shapes of cluster nanowires (D), icosahedra (E), and nanocubes (F). TEM images of γ -Al₂O₃-immobilized Pd nanocrystals with shapes of cluster nanowires (G), icosahedra (H), and nanocubes (I). The insets in the bottom left of D) and G) are size distributions of cross-sectional diameters of Pd cluster nanowires. The insets in the bottom left of A), E), and H) are size distributions of Pd nanocubes by edge lengths.

formation). Furthermore, it should be stressed that, by using the as-synthesized Pd icosahedral nanoparticles as seeds, larger icosahedral nanoparticles with a size of (26.7 ± 2.3) nm for the edge lengths could be obtained (Figure S5 in the Supporting Information). As shown in Figure 2C, well-defined Pd nanocubes were formed with a narrow size distribution of (16.7 ± 1.7) nm, as determined by random measurements of 580 edge lengths, and with >95% selectivity. The fringes in the HRTEM image are separated by 0.194 nm, close to {200} lattice spacing of face centered cubic (fcc) palladium (top right inset in Figure 2C). The corresponding selected-area FFT pattern (bottom-right inset in Figure 2C) shows square symmetry for the spots, indicating the Pd nanocubes have a fcc structure, which is in agreement with the XRD pattern of the as-synthesized products (Figure S6 in the Supporting Information). In addition, interestingly, when we did not add EDTA-2Na to the initial aqueous solution for producing Pd nanocubes, Pd nanocrystals with an abnormal shape were observed (Figure S7 in the Supporting Information).

When considering that the direct use of a colloidal Pd cat-

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alyst could be unfavorable in practical applications (e.g., separation and reuse of the catalyst after reaction), the Pd nanocrystals were immobilized on CNT and γ -Al₂O₃ supports, which are generally employed as metal supports in catalysis, and the former were much more chemically inert than the latter. The representative TEM images of immobilized Pd catalysts are also included in Figure 2D–I. Clearly, the morphologies and size distributions of these immobilized Pd nanocrystals were essentially the same as those of the corresponding unsupported Pd nanocrystals, except for difficulties in distinguishing the morphology of the Pd cluster nanowires masked by CNTs; however, it could be discerned with the aid of HADDF-STEM and energy-dispersive X-ray spectroscopy (EDS) analyses (Figure S8 in the Supporting Information).

In view of the industrial importance of the products of selective hydrogenation of α,β -unsaturated aldehydes (e.g., CAL) and butadiene (Figure S9 in the Supporting Information), the design and development of more efficient and selective catalysts remains as a challenging task.^[9] Figure 3



Figure 3. Hydrogenation of CAL over Pd cluster nanowires (\Box) , icosahedra (\bullet), and nanocubes (Δ) at 50°C with an initial H₂ pressure of 5.0 atm.

shows the kinetic curves for Pd nanocrystals shaped as cluster nanowires, icosahedra, and nanocubes for the selective hydrogenation of CAL at 50 °C. In the initial 20 min, the CAL conversion was 53, 39,

and 1% for Pd cluster nanowires, icosahedra, and nanocubes, respectively. Total consumption of CAL was found for Pd cluster nanowires within 289 min, in comparison with a maximum conversion of 56% within 722 min over Pd nanocubes. The morphologies of the Pd cluster nanowires and icosahedra were maintained after one cycle of the catalytic reaction, as revealed by TEM images (Figure S10A and B in the Supporting Information); however, the product yield decreased by around 20% for the first cycle of hydrogenation. The high dispersion property of Pd nanocrystals in water resulted in the loss of a small portion of Pd nanocrystals when removing the supernatant during washing with deionized water and centrifugation. To overcome the problem of catalyst recycling and reuse, the Pd nanocrystals were immobilized on CNTs and y-Al₂O₃ as mentioned previously. It was found that the specific reaction rates and TOFs of CNT-immobilized Pd cluster nanowires and icosahedra were about twice as high as those of unsupported Pd nanocrystals (Table S1 in the Supporting Information). Specifically, the TOF of CNT-immobilized cluster nanowires was up to 3.3 s⁻¹, which was one order of magnitude higher than that of commercial Pd/Al₂O₃ (0.30 s⁻¹) at 60°C with 10 bar H₂.^[10] Likewise, the morphologies of the immobilized Pd cluster nanowires and icosahedra were also maintained after one cycle of the catalytic reaction (Figure S10C and D in the Supporting Information). Furthermore, after three successive cycles with intermediate washing with water, the catalytic activity of CNT-immobilized Pd cluster nanowires was essentially unchanged. All Pd catalysts formed hydrocinnamaldehyde as the main product, except for the most active CNT-immobilized Pd cluster nanowires, which formed 3-phenyl-1-propanol as the main product after complete consumption of CAL. The selectivity to cinnamyl alcohol over Pd icosahedra could be up to 37.4%, while a trivial amount of cinnamyl alcohol was found for Pd cluster nanowires and nanocubes. This observation is in good agreement with a theoretical study that the {111} orientation of palladium favors the formation of cinnamyl alcohol.[11]

Table 1 shows a summary of the reaction rates and TOFs for CNT- and γ -Al₂O₃-immobilized Pd nanocrystals in the selective hydrogenation of 1,3-butadiene at 24 °C. The order of catalytic activity in terms of the reaction rates and TOFs on both CNT and γ -Al₂O₃ supports was as follows: Pd cluster nanowires >Pd icosahedra >Pd nanocubes. Specifically, the catalytic activity of the immobilized Pd cluster nanowires was two orders of magnitude higher than that of Pd nanocubes. Notably, although the loadings of Pd nanocrystals on γ -Al₂O₃ were much less than those of CNTs, the re-

Table 1. Catalytic performance and hydrogen temperature programmed desorption (H_2 -TPD) results of CNTand γ -Al₂O₃-immobilized Pd nanocrystals for 1,3-butadiene hydrogenation.

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Catalyst ^[a]	Pd loading [wt %]	Pd size [nm]	Pd dis- persion ^{[b}]	T _{max} ^[c] [°C]	H ₂ /Pd ^[c] [mmol]	Conv. ^[d]	Rate ^[e]	TOF ^[f] [s ⁻¹]
CNT-Pd ICH	0.74	14.5	0.06	95	0.31 (0.19)	57.0	2.5	1.16
CNT-Pd CUB	0.96	16.7	0.07	111 (285)	0.091 (0.12)	1.0	0.04	0.015
Pd/C	3.0	4.0	0.29	73 (431)	0.30 (0.67)	90	7.7	0.78
Al ₂ O ₃ -Pd CLW	0.05	4.0	0.20	62 (506)	2.12 (19.59)	83.6	142.4	20.96
Al ₂ O ₃ -Pd ICH	0.06	14.5	0.06	105 (506)	2.00 (1.03)	22.7	32.2	14.92
Al ₂ O ₃ –Pd CUB	0.25	16.7	0.07	64	0.18	20.9	1.8	0.76

[a] CLW=cluster nanowires, ICH=icosahedra, and CUB=nanocubes. [b] Calculated on the basis of the morphologies and sizes of the Pd nanocrystals (see the Supporting Information). [c] The numbers in parentheses are associated with the higher temperature desorption peak. [d] The stable conversion of 1,3-butadiene in 6 h of time-on-stream (TOS). [e] The unit is molh⁻¹ per g of Pd. [f] Calculated on the basis of exposed Pd atoms.

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action rates and TOFs on γ -Al₂O₃ were one order of magnitude higher than those on CNTs. The activity of γ -Al₂O₃-immobilized Pd cluster nanowires was more than 18 times that of commercial Pd/C, with spherical Pd nanoparticles with an average diameter of 4.0 nm (Figure S11 in the Supporting Information), under the same reaction conditions. Interestingly, the hydrogenation of 1,3-butadiene over the immobilized Pd catalysts had more than 98% selectivity for butenes; less than 2.0% butane was detected over the CNTstabilized Pd cluster nanowires at high conversions of 1,3-butadiene (94%; Figure S12 in the Supporting Information). The major component of the product butenes was 1butene (40-60%) and the trans/cis ratio (4.5-8.2) of 2butene on y-Al₂O₃-immobilized Pd nanocrystals was higher than that of CNT-immobilized Pd nanocrystals (1.3-3.0). The stability of y-Al₂O₃-immobilized Pd catalysts was further examined by recycling the catalyst. The high conversion of 1,3-butadiene (82%) and the high selectivity (99%) for butenes in TOS of 6 h were found on γ -Al₂O₃-immobilized Pd cluster nanowires. The morphology of cluster nanowires remained intact after the hydrogenation reaction (Figure S13 in the Supporting Information).

 H_2 -TPD experiments were carried out on these immobilized Pd nanocrystals and commercial Pd/C catalysts to gain information about H_2 activation/dissociation. The H_2 -TPD profiles shown in Figure 4 feature two hydrogen desorption



Figure 4. H₂-TPD curves after the chemisorption of H₂ at 60 °C over CNT- (A) and γ -Al₂O₃-immobilized (B) Pd nanocrystals of a) cluster nanowires, b) icosahedra, c) nanocubes, and d) commercial Pd/C catalyst. TCD = thermal conductivity detector.

peaks: one at low (≈ 200 °C) and another at high temperatures (200–400 °C on CNTs, 400–570 °C on γ -Al₂O₃). The low-temperature H₂ desorption peak should comprise of the chemisorbed hydrogen and decomposition of hydride species associated with Pd.^[12] The higher temperature peak could be ascribed to the desorption of hydrogen spillover from Pd to the support.^[12,13] The desorption temperature (T_{max}) and the ratio of H₂/Pd are also included in Table 1. It should be noted that the amount of hydrogen chemisorption over the immobilized Pd cluster nanowires was the highest, whereas the T_{max} was the lowest for the immobilized cluster nanowires, icosahedra, nanocubes, and the commercial Pd/C catalyst. Specifically, the y-Al2O3-immobilized Pd cluster nanowires showed that H₂/Pd ratios up to 2.12; this is in excess of the unwarranted (but widely adopted) assumption of an exclusive H₂/Pd adsorption stoichiometry of 1:2.^[14a,b,c] When considering that the adsorption stoichiometry is only applicable when Pd hydride formation is circumvented, however, the hydride species associated with Pd formed in our case because pure H₂ adsorption was employed. Furthermore, this assumption is in question because evidence from adsorption stoichiometry is dependent on Pd particle size/dispersion.^[14c,d,e] Guil and co-workers found that the adsorption stoichiometry on Ir/Al₂O₃ and Ir/SiO₂ varied from 1.1 to 2.4, depending on the support and particle size/ shape.^[15] However, we could find no evidence in the literature on the influence of Pd morphology on adsorption stoichiometry; therefore, we consider that this is the first reported instance of this effect. These results indicated that H2 dissociation/activation occurred more facilely and the amount of activated H was most abundant on the immobilized Pd cluster nanowires. Furthermore, the amount of hydrogen desorption associated with spillover hydrogen atoms from Pd to γ -Al₂O₃ and the greater T_{max} value than those of CNT-immobilized Pd nanocrystals indicates an enhanced interface/ interaction between Pd and y-Al₂O₃.

The above results have clearly shown that immobilized Pd cluster nanowires with mainly exposed {110}, {443}, {331}, and {221} facets are more advantageous in the hydrogenation reactions of CAL and 1,3-butadiene than those of icosahedra enclosed with {111} facets and nanocubes with mainly {100} facets. The higher catalytic activities of immobilized Pd cluster nanowires in comparison with icosahedra and nanocubes could partly be due to the exposure of a larger number of Pd atoms at steps and dislocations, especially the enrichment of defects at the interface of integrated Pd nanoparticles, as demonstrated by aberration-corrected HRTEM (Figure 1). Currently, it is difficult to decouple the two effects of Pd morphology and size on hydrogenation activity, although it has been well documented that hydrogenation of 1,3-butadiene and/or alkenes is generally structure sensitive.^[16,17] Studies by the groups of Boitiaux and Tardy have shown that TOFs decreased with a decrease in Pd particle size (i.e., an increase of Pd dispersion) in the hydrogenation of 1,3-butadiene over supported Pd catalysts.^[16b,17] Zaera et al. recently reported that the selectivity of isomerization to *trans/cis* olefins could be tuned by controlling Pt shape.^[18] The highest TOFs for the immobilized Pd cluster nanowires with the highest dispersions indicated that morphology or other factors could outweigh the size effect of Pd particles. Taking into account that the activation/dissociation of H₂ was generally regarded as a rate-determining step in the hydrogenation of CAL and 1,3-butadiene, the highest capability of H₂ dissociation/activation on the immobilized Pd cluster nanowires agreed well with the highest catalytic activity on the catalyst.

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Conclusion

We have demonstrated the highly selective synthesis of Pd nanocrystals with three different shapes (cluster nanowires, icosahedra, and nanocubes) in an environmentally benign solvent using one-pot method. In particular, the cluster nanowire was synthesized for the first time. By immobilization of Pd nanocrystals on CNTs and γ -Al₂O₃, the catalytic activity and stability of Pd nanocrystals was greatly enhanced in the liquid-phase hydrogenation of CAL and gasphase hydrogenation of 1,3-butadiene. The TOFs and reaction rates of the immobilized Pd cluster nanowires were about two orders of magnitude higher than those of the Pd nanocubes and one order of magnitude higher than those of commercial Pd/C and/or Pd/ γ -Al₂O₃ catalysts in both reactions.

Experimental Section

Chemicals: PdCl₂, PVP (MW=30000), CAL, isopropanol, and ethanol were analysis reagent (A.R.) grade and purchased from the Beijing Chemical Reagent Company. NaF, NaI, ethylenediaminetetraacetic acid disodium salt (EDTA·2Na), and sodium dodecyl sulfate (SDS) were A.R. grade and purchased from the Beijing Research Institute for Nonferrous Metals. The reactant gases 1,3-butadiene, N2, and H2 were purchased from the Beijing AP Beifen Gases Industry Company. CNTs (inner diameter 5-8 nm and outer diameter 8-15 nm; BET surface area 185 m²g⁻¹) supplied by Tsinghua University were heated at reflux in a concentrated sulfuric acid (98%)/nitric acid (68%) mixture (3:1 v/v) under vigorous stirring for 3 h at 80 °C. Pd/C with 3.0 wt % Pd was purchased from Aldrich. $\gamma\text{-}Al_2O_3$ (BET surface area $170\,m^2g^{-1})$ was purchased from Merck. All reagents were used as received without further purification. Deionized water was used for the synthesis of nanocrystals. Synthesis of Pd cluster nanowires: PdCl₂ solution (1 mL, 90 mM), NaF (21 mg), SDS (289 mg), and PVP (300 mg) were added to deionized water (7.0 mL) and stirred for 10 min at room temperature. The resulting homogeneous brown solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 220 °C for 6 h before it was cooled to room temperature. The products were separated by centrifugation at 11000 rpm for 20 min and further purified twice with deionized water.

Synthesis of Pd icosahedra: A solution of $PdCl_2$ in water (1 mL, 90 mM), EDTA-2Na (372 mg), and PVP (60 mg) were added to deionized water (7.0 mL) and stirred for 10 min at room temperature. The resulting homogeneous brown solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 160 °C for 6 h before it was cooled to room temperature. The products were separated by centrifugation at 11000 rpm for 20 min and further purified twice with deionized water.

Synthesis of Pd nanocubes: A solution of $PdCl_2$ in water (1 mL, 90 mM), EDTA-2Na (372 mg), PVP (60 mg), and NaI (75 mg) were added to deionized water (7.0 mL) and stirred for 10 min at room temperature. The resulting homogeneous brown solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 160 °C for 6 h before it was cooled to room temperature. The products were separated by centrifugation at 11000 rpm for 20 min and further purified twice with deionized water.

Preparation of supported Pd catalysts: CNT- and γ -Al₂O₃-immobilized Pd nanocrystals were prepared by combining a solution containing a certain amount of Pd colloids dispersed in water with a suspension of CNTs or γ -Al₂O₃ in ethanol. The mixture was sonicated for 40 min and stirred for 6 h. After being left overnight, the precipitate was suction filtered

and then washed with deionized water three times. The final solid was dried at $60\,^{\circ}C$ and ground with a mortar and pestle.

Typical procedure for selective hydrogenation of CAL: The liquid-phase hydrogenation of CAL was carried out in a glass batch reactor (2.0 mL, SUPELCO) closed with a Teflon septum and equipped with a pressure gauge and a side arm with an on-off lock. A microsyringe was able to inject and withdraw liquid or gas through the lock. Typically, the reactor with CNT-immobilized Pd nanocrystals (10 mg) or Pd colloids (0.1 g; deionized water as the solvent, containing 0.051 mg cluster wires, 1.0 mg icosahedra, and 0.096 mg nanocubes) and CAL (50.0 mg, 0.5 mmol) in isopropanol (1.0 mL) was purged with hydrogen for three times and then hydrogen was introduced (5 bar). The reaction was assumed to start when the reactor was introduced into the oil bath at 50 °C and vigorously stirred (ca. 1000 rpm). At a desired reaction time, the reaction mixtures (20 µL) were taken through the microsyringe and analyzed with a HP gas chromatography equipped with a flame ionization detector (FID) and a FFAP column. n-Nonane was used as an internal standard to calibrate the reaction products.

Typical procedure for selective hydrogenation of 1,3-butadiene: 1,3-Butadiene hydrogenation was performed in a continuous-flow quartz tube microreactor (i.d.=6 mm) at room temperature (23°C) and atmospheric pressure. CNT-immobilized Pd nanocrystals (10 mg; 15 mg for y-Al2O3, 5 mg for commercial Pd/C) were used in a powder form as-prepared and diluted with quartz sand (440 mg, $>\!100$ mesh). The immobilized Pd and commercial Pd/C catalysts were ground and screened in sizes of 100-120 mesh. The reactant gas, containing a mixture of 1,3-butadiene, H₂, and N_2 with a volume ratio of 1:49:97, was passed through the CNT-immobilized icosahedra, nanocubes, and y-Al2O3-immobilized nanocubes at the rate of 18.8 mLmin⁻¹. In a series of pre-experiments at a fixed reactant flow rate of 18.8 mLmin⁻¹, we found that the CNT- and γ -Al₂O₃-immobilized Pd icosahedra and nanocubes exhibited 1.3-butadiene conversions ranging from 1 to 57%. Specifically the reaction rate of CNT-immobilized Pd icosahedra (2.50 molh⁻¹ per g of Pd) was not affected by changing the flow rate of the reaction feed and by using various catalyst pellet sizes (140-160 mesh). However, 100% conversion was found on CNT- and γ -Al₂O₃-immobilized Pd cluster nanowires and commercial carbon-supported Pd catalyst at room temperature (23°C) and atmospheric pressure. Therefore, the flow rate of the reaction feed was increased from 18.8 to 76.9 mL min $^{-1}$ for the CNT- and $\gamma\text{-Al}_2\text{O}_3\text{-immobi-}$ lized Pd cluster nanowires, and commercial carbon-supported Pd catalyst. In this case, we found that the reaction rate of CNT-immobilized Pd cluster nanowires (22.0 molh⁻¹ per g of Pd) was not significantly affected (<20%) by further changing the flow rate of the reaction feed and by using various catalyst pellet sizes (140-160 mesh). The reactor effluent was analyzed online by using a SP-6890 (FID, GDX-501 as an adsorbent) gas chromatograph.

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