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Performance of facet-controlled Pd nanocrystals in 2-ethylanthraquinone hydrogenation[†]

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In this study, single-crystal Pd nanocrystals with exposed (100) and (111) facets were prepared and their catalytic performance were compared in 2-ethylanthraquinone hydrogenation reaction through immobilization on γ -Al₂O₃ as catalyst. Our experimental results combined with density functional theory calculations showed that the Pd (100) facet was more active than Pd (111) in C==O hydrogenation but less active in saturation of aromatic rings. Directed by this result, a high-performance Pd/ γ -Al₂O₃ nanocatalyst was successfully prepared using a one-step synthesis method, which could not only control the exposure of the Pd (100) facet but also increase the stability of Pd components. This catalyst exhibited superior catalytic performance with a hydrogenation efficiency of up to 15.0 g L⁻¹ and a selectivity of 99.1% under mild reaction conditions (0.2 MPa, 50 °C, 15 min), which was superior to that of the catalyst prepared by an impregnation method.

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1. Introduction

Hydrogen peroxide (H_2O_2) is a popular oxidizing agent widely used in the industry of electronics, pharmaceutical, papermaking, wastewater treatment and so on, because of its efficient oxidizing properties and its significant environmental friendliness as the by-product of its oxidation reactions is water.^{1,2} The main industrial synthesis method for H₂O₂ is the anthraquinone process.³ In this method, 2-ethylanthraquinone (EAQ) is hydrogenated to 2-ethylanthrahydroquinone (EAQH₂) in the presence of a catalyst, and then EAQH₂ is oxidized by O₂ to yield H₂O₂ with regeneration of the starting EAQ. In the hydrogenation process, the target product EAQH₂ undergoes further hydrogenation to give various products through two reaction pathways. The first reaction route is the successive saturation of aromatic rings to generate 2-ethyl-5,6,7,8-tetrahydroanthracene-9,10-diol $(H_4 EAQH_2)$ and 2-ethyl-1,2,3,4,5,6,7,8-octahydroanthracene-9,10-diol (H₈EAQH₂). The second route is the hydrogenolysis of C-O bonds to give 2-ethylanthrone (EAN) as the main product. Among them, only H₄EAQH₂ can be oxidized by O₂ to generate H₂O₂ and its corresponding 2-ethyl-5,6,7,8-tetrahydroanthraquinone (H₄EAQ) can also be used in the production cycle of H₂O₂. Thus EAQ and H₄EAQ are called as "active quinones" and other hydrogenation products are considered as "degradation products".⁴⁻⁶ The formation of degradation products substantially reduces the amount of active quinones.⁷ Therefore, the development of a highly active catalyst with high selectivity to active quinones is one of the priority issues of process improvement, since an excellent catalyst will possibly lead to a reaction process with higher safety and lower cost.

Drelinkiewicz et al. carried out pioneering work to investigate high-performance catalysts for EAQ hydrogenation.4,5,8-14 They reported that modification of the adsorption properties of the Al₂O₃ or SiO₂ support surface towards EAQ molecules using Na₂SiO₃,⁹ polyaniline¹² or alkali modifiers (Li, Na, K, Cs)¹⁴ could reduce the rate of reactions in the "deep hydrogenation" stage. Li et al.^{15,16} improved the preparation methods of the Al₂O₃ support used in EAQ hydrogenation. They prepared spherical Al₂O₃ and SiO₂-Al₂O₃ using the conventional oil-drop (OD) method and Al₂O₃ using the separate nucleation and aging step (SNAS) method. The order of average hydrogenation efficiency and selectivity to active quinones was Pd/Al_2O_3 (SNAS) (10.9 g L⁻¹, 97%) > $Pd/SiO_2-Al_2O_3$ (OD) $(10.3 \text{ g L}^{-1}) > \text{Pd/Al}_2\text{O}_3 \text{ (OD)} (8.6 \text{ g L}^{-1}, 93\%)$. The improved performance can be ascribed to the modified pore structure of the support, which can increase the dispersion of Pd and decrease the diffusion resistance. Luo et al.¹⁷ treated glass beads with subcritical water and used them as supports to prepare a novel kind of Pd catalyst with an egg-shell structure and high dispersion. The conversion of EAQ reached as much as 60% in less than 2 s with a hydrogenation efficiency of 11.2 g L^{-1} .

These research studies mainly focused on the modification of supports. Few attempts have been made to prepare high-performance catalysts used in the anthraquinone process

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by controlling the catalytic chemistry of Pd based on catalyst design principles. The Pd catalysts currently used in the anthraquinone process are mainly prepared by an impregnation method, which is poor in controlling sizes and shapes. The obtained Pd particles did not present a uniform, well-defined atomic structure on the surface. A potential method to improve their catalytic performance is to replace these particles with single-crystal nanoparticles enclosed by specific highly active facets.¹⁸ A wide variety of nanocrystals enclosed by different facets have been prepared by carefully control-ling reaction conditions, which provide an opportunity to understand the relationship between crystal facets and reactivity.¹⁹⁻²³

Herein, we prepared Pd cubes, cuboctahedra and octahedra with exposed (100) and (111) facets. They were supported on γ -Al₂O₃ as catalysts and used for EAQ hydrogenation reaction in order to compare the catalytic performance of different facets. Meanwhile, density functional theory (DFT) calculations were applied in an attempt to establish a relationship between the reaction mechanism and different facets. On the basis of these results, we prepared a high-performance supported Pd nanocrystal catalyst with high stability of Pd components by using a one-step synthesis method.

2. Experimental

2.1 Chemicals

Na₂PdCl₄ (AR; Energy Chemical, China); poly(vinylpyrrolidone) (PVP; molecular weight 58 000 g mol⁻¹; AR; J&K Chemical, China); KBr, KCl, L-ascorbic acid and formaldehyde solution (40%) (AR, Guangfu Chemical, China); γ -Al₂O₃ (AR, CNOOC Tianjin Chemical Research Institute, China); EAQ, trioctyl phosphate and trimethylbenzene (AR, TCI, Japan). All chemicals were used as received.

2.2 Synthesis of Pd nanocrystals and then loading on $\gamma\text{-Al}_2O_3$ support

The detailed procedures of the synthesis of Pd nanocrystals were described as follows: a) synthesis of Pd cubes:²⁴ 12 mL of aqueous Na₂PdCl₄ solution (63.8 mM) was introduced into 32 mL of an aqueous solution containing 0.378 mmol of PVP, 1.36 mmol of L-ascorbic acid and 10 mmol of KBr or a mixture of 0.2 mmol of KBr and 9.8 mmol of KCl at 80 °C. The solution was stirred for 3 h. b) Synthesis of Pd cuboctahedra and octahedra:18 they were prepared using the prepared Pd nanocubes (using a mixture of KBr and KCl as a capping agent) as seeds. 0.7 mL or 1.0 mL of the prepared Pd cube slurry was mixed with acetone and then centrifuged. The collected cubes were washed several times with deionized water and then re-dispersed in 1 mL of deionized water. 32 mL of aqueous solution containing 0.378 mmol of PVP and 400 μ L of formaldehyde solution was added. The obtained solution was stirred for 0.5 h and heated to 60 °C. Then 12 mL of aqueous Na₂PdCl₄ solution (39.6 mM) was introduced with stirring and allowed to react for 3 h at 60 °C.

All Pd nanocrystals were collected by centrifugation with acetone and washed with deionized water. After that, 30 mg of Pd cubes (using KBr as capping agent), cuboctahedra and octahedra were dispersed in 20 mL of deionized water. Then 10 g of γ -Al₂O₃ was added into the Pd slurry with magnetic stirring. The material was vigorously mixed for 2 h and was left to stand at 45 °C for 12 h. The obtained samples were filtered, washed with deionized water and dried at 120 °C under vacuum. The obtained catalysts were named as Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃, respectively.

2.3 One-step synthesis of Pd/Al₂O₃

In order to enhance the stability of Pd nanocrystals on the γ -Al₂O₃ support, we developed a one-step synthesis method to prepare the Pd/Al₂O₃ catalyst. The detailed procedures were as follows: 10 g of γ -Al₂O₃ was dispersed in 36 mL of aqueous solution containing 3.7 mmol of KBr, 0.14 mmol of PVP and 0.5 mmol of L-ascorbic acid. The slurry was heated to 80 °C. Then 4 mL of aqueous Na₂PdCl₄ solution (70.5 mM) was introduced and stirred for 3 h. The obtained sample was filtered, washed with deionized water, and dried at 120 °C under vacuum. The obtained catalyst was denoted as Pd-Situ/Al₂O₃.

For comparison, a supported Pd catalyst was prepared by the traditional impregnation method and named as Pd-Im/Al₂O₃. 10 g of γ -Al₂O₃ was dispersed in 20 mL of aqueous Na₂PdCl₄ solution (28.2 mmol). Then, the material was vigorously mixed for 2 h and was left to stand at 45 °C for 12 h. The obtained sample was filtered, washed with deionized water, dried at 120 °C and calcined in static air at 500 °C.

2.4. Catalyst characterization

 N_2 adsorption-desorption isotherms were determined at -196 °C using an ASAP 2000 analyzer (Micromeritics, USA). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out using an Iris advantage device (Thermo Jarrel Ash, USA). Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) analysis were carried out using a JEOL JEM2010 microscope under an accelerating voltage of 200 kV (JEOL, Japan). An AMI-200ip was used to perform pulse chemisorption to determine the CO uptake (Thermo Jarrel Ash, USA). The catalysts were reduced at 300 °C respectively for 1 h and then cooled to room temperature in He. Pulse CO chemisorption was performed using a 500 µL pulse of CO in a He carrier gas. A 1:1 CO/Pd ratio was assumed to determine the Pd surface content of the catalysts.

2.5 Catalytic performance test

The hydrogenation experiment was carried out in an autoclave at 0.2 MPa and 50 °C. The working solution was prepared by dissolving 120 g of solid EAQ in 1 L of a mixed solvent composed of trioctyl phosphate and trimethylbenzene with a volume ratio of 1:1. Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃, Pd-Octa/Al₂O₃ and Pd-Situ/Al₂O₃ were pretreated at 300 °C in

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10% H₂/Ar for 2 h before reaction. Pd-Im/Al₂O₃ was pretreated at 500 °C in 10% H₂/Ar for 2 h. Then 60 mL of the working solution was mixed with 1.2 g of catalyst, and then the mixture was hydrogenated in a H₂ atmosphere for 15 min. After the hydrogenation reaction, the solution was instantaneously centrifugally separated with a rotating speed of 3000 rpm for 15 min to remove the solid catalyst. Then, 2 mL of the catalyst-free solution was placed into 20 mL of deionized water, and the mixture was oxidized by oxygen at room temperature for 30 min in a separating funnel. 2 mL of dilute phosphorous acid was added to the deionized water to prevent H₂O₂ decomposition during the oxidation reaction. After the oxidation reaction, a H₂O₂ aqueous solution was obtained from the sublayer solution of the separating funnel. The H₂O₂ content was analyzed by titration with a KMnO₄ solution. Prior to titration, 5 mL of a 20 wt.% sulfuric acid solution was added to the H₂O₂ solution. The catalytic activity is expressed by the following simplified equation:15

$$B = \frac{C \times V_0 \times 0.017 \times 1000}{V} \tag{1}$$

where *B* is the hydrogenation efficiency, *C* is the KMnO₄ solution concentration (mol L^{-1}), *V*₀ is the KMnO₄ solution volume (mL) and *V* is the H₂O₂ solution volume (mL).

A high performance liquid chromatograph (HPLC) equipped with a C18 separation column and a UV detector was used to analyze the concentrations of EAQ and H₄EAQ in the re-oxidized working solution, which were denoted as $n^{t}(\text{EAQ})$ and $n^{t}(\text{H}_{4}\text{EAQ})$, respectively. The mobile phase was a mixture of methanol and water with a volume ratio of 80:20. The wavelength of the ultraviolet radiation was 245 nm. The sum of the EAQ and H₄EAQ concentrations in the solution was smaller than the initial concentration of EAQ (*i.e.*, $n^{0}(\text{EAQ})$). This difference was assumed as cumulative of the degradation products (n_{D}) given by the mass balance:^{4,12}

$$n_{\rm D} = n^0({\rm EAQ}) - n^{\rm t}({\rm EAQ}) - n^{\rm t}({\rm H}_4{\rm EAQ})$$
(2)

The selectivity toward active quinones can be calculated by the equation: 16

$$S = \frac{n^{t}(\text{EAQ}) + n^{t}(\text{H}_{4}\text{EAQ})}{n^{0}(\text{EAQ})} \times 100\%$$
(3)

2.6 Computational methods

All of the calculations were performed based on DFT as implemented in MS CASTEP software (Accelrys Inc.).²⁵ The nonlocal exchange and correlation energies were calculated with the Perdew-Wang (PW91) functional²⁶ of the generalized gradient approximation (GGA). Calculations including spin polarization have been performed for all structures presented here.

A supercell includes a (3×2) unit in the surface plane and a vacuum region of ~20 Å. The Pd (111) and Pd (100) slabs include four layers. In all calculations, the atoms in the lowest layer were fixed at their bulk positions.^{27,28} The atoms in the top three layers of the slab together with the adsorbed EAQ were allowed to relax. The sampling of the surface Brillouin zone was restricted to a (2×3) Monkhorst–Pack grid.

Adsorption energies, bond lengths and Mulliken charges were further analyzed to aid in elucidating the relationship between the structural and electronic properties of the catalysts with different crystal facets and their catalytic performance.

3. Results and discussion

3.1 The properties of Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃ and their catalytic performance

Fig. 1 presents the TEM images and edge length distributions of the Pd cubes. When a mixture of KBr and KCl was used as a capping agent, the nanocrystals showed homogeneous edge length distribution (5-10 nm) with an average edge length of ca. 7.4 nm (Fig. 1a). When only KBr was used as a capping agent, the average edge length was 9.9 nm (Fig. 1b). The added halide ions formed ligand complexes with Pd²⁺ and slowed down the reduction rate of the Pd precursor. Cl⁻ coordinated more weakly than Br⁻ to Pd²⁺, so when the mixture of KBr and KCl was used as a capping agent, the precursor reduction rate increased, and the number of seeds in the nucleation step increased, which led to the formation of smaller nanocrystals.²⁹ An HRTEM image and the corresponding FFT pattern taken from an individual cube suggested that it was a piece of single crystal. The obtained interplanar spacing of 0.195 nm from the fringes of the lattice was in agreement with the (100) lattice spacing of the face-centered cubic (fcc) Pd (0.195 nm), suggesting that the nanocrystal surface was enclosed by the (100) facet.24

Fig. 2a and b present the TEM images of Pd particles prepared by the seed-mediated growth of Pd cubes with an average edge length of 7.4 nm. The additional Pd atoms deposited on the (100) facets, leading to the formation of (111) facets. The Pd cube grows in the order of cube \rightarrow cuboctahedron \rightarrow truncated octahedron \rightarrow octahedron.¹⁸ When a volume of the Pd-cube slurry (1.0 mL) was used, the shape of the cubes transformed to cuboctahedra (Fig. 2a). The newly formed hexagonal surfaces were enclosed by (111) facets, but the remaining square surfaces were enclosed by (100) facets. When the volume of the slurry decreased to 0.7 mL, Pd octahedra with sharp corners were mainly synthesized (Fig. 2b). These particles were fully enclosed by (111) facets.

Pd-Cube/Al₂O₃ (using 9.9 nm cubes), Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃ were prepared by dispersing the as-prepared Pd nanocrystals on the Al₂O₃ support surface and were also characterized by TEM. As shown in Fig. 3a–c, the morphologies and dimensions of the Pd nanocrystals remained unchanged during the supporting process.



Fig. 1 TEM and the corresponding HRTEM images of Pd cubes synthesized using different capping agents: (a) a mixture of KBr and KCl, (b) only KBr. The insets show the edge length distribution, structural diagram and FFT pattern.

The concentration of surface active Pd was measured by CO chemisorption. As shown in Table 1, the surface Pd concentrations of Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃ were similar. The ratio of surface atoms in a single Pd nanocrystal was also calculated using a mathematical method based on the hypothesis that the nanocrystals consisted of fcc crystals and were free of surface defects.³⁰ These results were similar to those of the CO chemisorption tests. The number of Pd atoms at the corner and edge sites was minor, which only accounted for 3.8%, 6.5% and 6.4% of the Pd atoms on the cube, cuboctahedron and octahedron surface, respectively.

The catalytic performance of the catalysts for EAQ hydrogenation is shown in Fig. 4. The EAQ hydrogenation process includes the main hydrogenation reaction (EAQ \rightarrow EAQH₂) and two excessive hydrogenation reactions, which formed H₄EAQH₂ and degradation products, such as aromatic rings, fully saturated products (H₈EAQH₂) and hydrogenolysisderived products (EAN). The formation of H₈EAQH₂ was observed only after the complete transformation of EAQ to EAQH₂.^{4,11,31} So we assumed that H₈EAQH₂ was not generated in our system. The degradation products consisted of hydrogenolysis-derived products. The activity of the Pd catalysts in the main hydrogenation reaction (Fig. 4a), namely, hydrogenation of C=O, increased in the order: $Pd-Cube/Al_2O_3 > Pd-Cuboct/Al_2O_3 > Pd-Octa/Al_2O_3$. The turnover frequency (TOF) of the main hydrogenation reaction was also calculated. The TOF of Pd-Cube/Al₂O₃ (9.9 s⁻¹) was higher than that of Pd-Cuboct/Al₂O₃ (7.3 s⁻¹) and Pd-Octa/Al₂O₃ (5.3 s⁻¹). The TOF of Pd/Al₂O₃ prepared by an impregnation method measured by Li et al.¹⁶ in a fixed bed reactor was about 0.2 s⁻¹. The activity of the Pd catalysts in the first excessive hydrogenation reaction (Fig. 4b), namely, hydrogenation of aromatic rings, increased in the order: Pd- $Octa/Al_2O_3 > Pd-Cuboct/Al_2O_3 > Pd-Cube/Al_2O_3$. The three Pd catalysts showed similar activity in the second excessive hydrogenation reaction (Fig. 4c), namely, hydrogenolysis of C-O bonds. Considering that the main difference between Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃ lies in their exposed facets (the size-effect of the Pd nanocrystals on the EAQ hydrogenation activity is not obvious, the related analysis is listed in the ESI[†]), it is supposed that the Pd exposed facets play a vital role in the EAQ hydrogenation reaction.

3.2 Catalytic mechanism of Pd (100) and Pd (111) in the EAQ hydrogenation reaction

It has been demonstrated that the facets on the surface of Pd nanocrystals have a strong influence on catalytic



Fig. 2 TEM and the corresponding HRTEM images of Pd nanocrystals: (a) cuboctahedra, (b) octahedra. The insets show the edge length distribution, structural diagram and FFT pattern.

properties.^{18,29,32–37} For Pd nanocrystals, the (111) facet was more active than the (100) facet in CO oxidative coupling to dimethyl oxalate³⁶ and direct synthesis of hydrogen peroxide from hydrogen and oxygen;³⁴ whereas in some other reactions, such as formic acid oxidation,¹⁸ CO oxidation²⁹ and oxygen reduction reaction,³⁷ the (100) facet showed a higher activity than the (111) facet. These results indicated that the surface crystal facets of Pd exhibited different catalytic mechanisms in various reactions. The catalytic mechanism in the EAQ hydrogenation reaction primarily involves two steps: activation of H₂ molecules and activation of C==O in EAQ. The results from many theoretical studies have indicated that the more open crystal facet Pd (100) was generally more active than the dense highly coordinated facet Pd (111) in the adsorption and activation of H₂ molecules.^{38–41}

However, there are no reports regarding the performance of different Pd facets in the activation of EAQ. Therefore, based on our experimental results, the ability of Pd (100) and Pd (111) to activate C=O in EAQ has been studied here. The optimized structures of EAQ adsorbed on the Pd (100) and Pd (111) facets are shown in Fig. 5. The distance between the C or O atom in C=O of EAQ and the nearest Pd atom and the change in the C=O bond length in EAQ (Table 2) indicated that the ability of the catalyst to activate the C=O bond was as follows: Pd (100) > Pd (111).

In order to further understand the mechanism of the excessive hydrogenation reactions, the abilities of Pd (100) and Pd (111) to activate C-O and C=C in EAQH₂ have also been studied here. The optimized structures of EAQH2 adsorbed on the Pd (100) and Pd (111) facets are shown in Fig. 6a-b and the changes in C-O and C=C bond lengths are shown in Fig. 6c. On the (100) facet, the bond lengths of two C-O changed from 1.34 to 1.46 and 1.42 Å, respectively. On the (111) facet, the bond lengths of two C-O changed from 1.34 to 1.45 and 1.41 Å, respectively. The changes in the C-O bond length in EAQH₂ between the two facets were similar, which indicated that there was little difference between their abilities to activate the C-O bond in EAQH₂; whereas, the changes in each corresponding C=C bond length in aromatic rings demonstrated that (111) was more favored than (100) in the activation of the C=C bond in EAQH₂. In general, based on our experimental results and DFT calculations, it is supposed that the (100) facet is more favored than (111) in C=O hydrogenation reactions but less active in saturation of aromatic rings. Their abilities in C-O hydrogenolysis reactions are almost the same.



Fig. 3 TEM and the corresponding HRTEM images of (a) Pd-Cube/Al₂O₃, (b) Pd-Cuboct/Al₂O₃ and (c) Pd-Octa/Al₂O₃.

3.3 The properties of Pd-Situ/Al₂O₃ via one-step synthesis and its catalytic performance

Although the nanocrystal catalysts showed superior catalytic performance because of their well-defined sizes, shapes and facets, the loaded metal nanocrystals on the support were unstable and easily lost during catalytic reactions as a result of the weak interactions between the metal nanocrystals and the support. Pd-Cube/Al₂O₃ lost approximately 20 wt.% Pd during the first reaction cycle (Table 4). In order to overcome this problem, we prepared Pd-Situ/Al₂O₃ using a one-step method. The TEM image of Pd-Situ/Al₂O₃ is presented in Fig. 7a. Most of these Pd nanocrystals were cubic and a small portion (<14%) was found to be irregularly shaped by counting 50 particles. The HRTEM image of the cubes revealed that the lattice spacing was 0.195 nm (Fig. 7b), indicating that the Pd nanocrystals were enclosed by (100) facets. It was coincident with common knowledge that Pd nanocrystals with cubic shape are mainly enclosed by (100) facets. The surfaces of these irregularly shaped particles were still enclosed by (100) facets (Fig. S3c in the ESI[†]). The standard errors to the mean particle sizes of Pd particles through TEM measurement were also calculated. The mean edge length and standard error of the nanocrystals were found to be as follows: cubes (d = 9.9 nm, $\delta = 1.4$ nm), cuboctahedra (d =8.7 nm, δ = 2.0 nm), octahedra (*d* = 14.1 nm, δ = 1.8 nm). The mean particle size and standard error of Pd-Situ/Al₂O₃ were d = 8.6 nm, $\delta = 2.1$ nm, respectively. The degree of uniformity in size of the nanoparticles in Pd-Situ/Al₂O₃ was similar to that of the prepared single-crystal Pd nanoparticles. These results indicated that the Pd cubic nanocrystals enclosed by (100) facets were synthesized and evenly supported on the Al₂O₃ surface using the one-step method. In comparison with Pd-Situ/Al₂O₃, Pd-Im/Al₂O₃ showed monodispersity, with particle sizes ranging from 2 to 7 nm, and some Pd aggregations could also be seen (Fig. 7c). The obtained interplanar spacings of 0.198 and 0.227 nm from the fringes of the lattice shown in Fig. 7d were in agreement with the (100) and (111) lattice spacings of crystalline Pd, respectively, which demonstrated that the exposed facets of the Pd particles were (100) and (111) facets. This indicated that the impregnation method was poor in controlling sizes and shapes.

The chemical compositions and textural properties of the prepared catalysts are summarized in Table 3. The bare γ -Al₂O₃ exhibited a mesoporous structure with S_{BET} = 161 m² g⁻¹, V_{p} = 0.52 cm³ g⁻¹, and D_{p} = 12.9 nm. For samples Pd-Im/Al₂O₃ and

Table 1	Concentration of sur	face Pd calculated	using different methods

Sample	Surface Pd content ^{<i>a</i>} $(\mu mol g^{-1})$	Dispersion ^b (%)	$\frac{\text{Terrace atom ratios}^{c}(\%)}{(100)}$ (111)		Corner/edge atom ratio ^d (%)	
Pd-Cube/Al ₂ O ₃	2.65	14.1	10.5		3.8	
Pd-Cuboct/Al ₂ O ₃ Pd-Octa/Al ₂ O ₃	2.48 2.73	13.2 14.5	7.3	3.4 10.3	6.5 6.4	

^{*a*} From CO chemisorption. ^{*b*} Mole ratio of CO/Pd_{total}. ^{*c*} Number of terrace atoms on the surface/total number of atoms in a single particle, calculated using a mathematical method. ^{*d*} Number of corner/edge atoms/number of atoms on the surface, calculated using a mathematical method.



Fig. 4 Hydrogenation of EAQ on Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃: (a) EAQ conversion, (b) concentration of generated H_4EAQH_2 , and (c) concentration of degradation products.

Pd-Situ/Al₂O₃, their surface areas and total pore volumes decreased to $S_{\text{BET}} = 151 \text{ m}^2 \text{ g}^{-1}$, $155 \text{ m}^2 \text{ g}^{-1}$ and $V_{\text{p}} = 0.49 \text{ cm}^3 \text{ g}^{-1}$, 0.49 cm³ g⁻¹, respectively. This was caused by some Pd particles distributed inside the pores that partially blocked the micropores. Compared with the Al₂O₃ support, the S_{BET} , V_{p} and D_{p} of Pd-Cube/Al₂O₃, Pd-Cuboct/Al₂O₃ and Pd-Octa/Al₂O₃



Fig. 5 Optimized structures of EAQ adsorbed on the (a) Pd (100) and (b) Pd (111) surfaces (): Pd; (): C; (): C); (): H).

Table 2 Adsorption energies, C=O bond length in EAQ, total Mulliken charges of EAQ after adsorption and the distance between C or O and the nearest Pd

Catalyst	Pd (100) facet	Pd (111) facet
E_{ads}^{a} (eV)	2.16	1.57
C=O bond length ^b (Å)	1.30	1.26
	1.29	1.25
Mulliken charge (e)	-2.99	-2.85
C–Pd distance ^{c} (Å)	2.19	2.29
O–Pd distance ^c (Å)	2.18	2.85

 ${}^{a}E_{ads} = -(E_{total} - E_{EAQ} - E_{catalyst})$. ${}^{b}As$ a reference, the length of the C=O bond in EAQ prior to activation by the catalyst is 1.24 Å. c Refers to the distance between the C or O atom in C=O of EAQ and the nearest Pd atom at the catalyst surface.

changed a little. Thus, taking into account that the average pore diameter of Al_2O_3 was 12.9 nm and the particle size of Pd nanocrystals were in the range of 8–17 nm, it was obvious that these particles were less likely to penetrate into the pores and to be distributed at the external surface of the support.

When Pd-Situ/Al₂O₃ was used to catalyze EAQ hydrogenation, it showed obvious higher hydrogenation efficiency and selectivity than Pd-Im/Al₂O₃ (shown in Table 4). The exposed (100) facets were responsible for its high performance in this reaction. The higher hydrogenation efficiency of Pd-Situ/Al₂O₃ than that of Pd-Cube/Al₂O₃ was ascribed to its smaller particle size, which led to a higher concentration of surface active Pd. For Pd-Situ/Al₂O₃ and Pd-Im/Al₂O₃, negligible Pd loss was found in the used catalyst by ICP analysis. The stability of the Pd component in these catalysts was tested. The working solution containing catalysts was stirred at high speed (1000 rpm) under normal temperature and normal pressure in a nitrogen environment. It was found that Pd-Situ/Al₂O₃ could achieve a hydrogenation efficiency of 14.0 g L⁻¹ after vigorous stirring for 70 h. The hydrogenation



Fig. 6 Optimized structures of EAQH₂ adsorbed on the (a) Pd (100) and (b) Pd (111) surfaces (\bigcirc : Pd; \bigcirc : C; \bigcirc : O; \bigcirc : H) and (c) the change in C-O and C=C bond lengths. The unit of distance is Å.



Fig. 7 TEM and the corresponding HRTEM images of (a, b) Pd-Situ/Al₂O₃ and (c, d) Pd-Im/Al₂O₃.

efficiency of Pd-Im/Al₂O₃ also declined from 12.4 to 10.8 g $\rm L^{-1}.$ After easy separation and pretreatment, it was found that

 $Pd\text{-}Situ/Al_2O_3$ lost approximately 15 wt.% Pd. A similar amount of Pd loss was also detected for $Pd\text{-}Im/Al_2O_3.$ The

Table 3 Chemical compositions and textural properties of the catalysts and bare supports

Sample	Pd^{a} (wt.%)	$S_{\rm BET}^{\ \ b} ({ m m}^2 { m g}^{-1})$	$V_{\rm p}^{\ b} ({\rm cm}^3 {\rm g}^{-1})$	$D_{\mathrm{p}}^{b}(\mathrm{nm})$
Pd-Cube/Al ₂ O ₃	0.20	159	0.51	12.9
Pd-Cuboct/Al ₂ O ₃	0.21	161	0.52	12.8
Pd-Octa/Al ₂ O ₃	0.19	160	0.52	12.9
Pd-Situ/Al ₂ O ₃	0.20	153	0.49	12.7
Pd-Im/Al ₂ O ₃	0.21	151	0.49	12.7
Al ₂ O ₃	_	161	0.52	12.9

^{*a*} As determined by ICP. ^{*b*} The BET surface area, total pore volume (V_p) and average pore diameter (D_p) were measured from the N₂ adsorptiondesorption isotherms.

Table 4 The stability test of Pd-Cube/Al_2O_3, Pd-Situ/Al_2O_3 and Pd-Im/Al_2O_3

	Catalytic performance				Pd (wt.%)		
	Initial		70 h				
Sample	$B(g L^{-1})$	S (%)	$B(g L^{-1})$	S (%)	Fresh	Once	70 h
Pd-Cube/Al ₂ O ₃	13.9	99.1	8.5	99.3	0.20	0.16	0.12
Pd-Situ/Al ₂ O ₃	15.0	98.9	14.0	99.0	0.20	0.19	0.17
$Pd-Im/Al_2O_3$	12.4	98.3	10.8	98.5	0.21	0.21	0.19

violent collisions between the catalyst particles and between the catalyst particle and reactor's wall under vigorous stirring led to the loss of Pd. Consequently, the one-step method enhanced interactions between the metal nanocrystals and the support. Meanwhile, we also noticed that some Pd particles of Pd-Situ/Al₂O₃ grew within the Al₂O₃ pores and this kind of structure protected these Pd particles from violent collisions. These results indicated that the one-step synthesis method improved the stability of the Pd component to a great extent.

4. Conclusion

In summary, we have prepared Pd cubes, cuboctahedra and octahedra by controlling the growth of cubic seeds. Then, we immobilized them on the γ -Al₂O₃ support and studied their catalytic performance for EAQ hydrogenation reaction. After comparing the catalytic activities of these nanocrystals and the DFT calculation results, we concluded that Pd (100) was more active than Pd (111) in C=O hydrogenation but less active in saturation of aromatic rings. Their abilities in C-O hydrogenolysis reactions were almost the same. Nanocrystals enclosed by (100) facets exhibited the highest activity with high selectivity to active quinones under mild reaction conditions (0.2 MPa, 50 °C), which was apparently superior to those of the catalysts prepared by the impregnation method. The one-step synthesis of Pd nanocrystals/Al₂O₃ greatly increased the interactions between the nanocrystals and the support, thus the stability of the Pd component was greatly enhanced. The ultrahigh activity, as well as its novel structure with controllable exposed facets, makes this catalyst very attractive for both fundamental research and practical applications.

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References

- 1 H. Shang, H. J. Zhou, Z. H. Zhu and W. H. Zhang, J. Ind. Eng. Chem., 2012, 18, 1851.
- 2 J. Tan, J. S. Zhang, Y. C. Lu, J. H. Xu and G. S. Luo, *AIChE J.*, 2012, **58**, 1326.
- 3 J. Garcia-Serna, T. Moreno, P. Biasi, M. J. Cocero, J. P. Mikkola and T. O. Salmi, *Green Chem.*, 2014, 16, 2320–2343.
- 4 A. Drelinkiewicz and A. Waksmundzka-Gora, J. Mol. Catal. A: Chem., 2006, 246, 167.
- 5 R. Kosydar, A. Drelinkiewicz and J. P. Ganhy, *Catal. Lett.*, 2010, 139, 105.
- 6 T. Nishimi, T. Kamachi, K. Kato, T. Kato and K. Yoshizawa, *Eur. J. Org. Chem.*, 2011, 4113.
- 7 Q. L. Chen, Chem. Eng. Process., 2008, 47, 787.
- 8 A. Drelinkiewicz and M. Hasik, J. Mol. Catal. A: Chem., 2001, 177, 149.
- 9 A. Drelinkiewicz, R. Kangas, R. Laitinen, A. Pukkinen and J. Pursiainen, *Appl. Catal.*, *A*, 2004, 263, 71.
- 10 A. Drelinkiewicz, A. Pukkinen, R. Kangas and R. Laitinen, *Catal. Lett.*, 2004, 94, 157.
- 11 A. Drelinkiewicz and A. Waksmundzka-Gora, *J. Mol. Catal. A: Chem.*, 2006, **258**, 1.
- 12 A. Drelinkiewicz, A. Waksmundzka-Gora, W. Makowski and J. Stejskal, *Catal. Commun.*, 2005, **6**, 347.
- 13 A. Drelinkiewicz, A. Waksmundzka-Gora, J. W. Sobczak and J. Stejskal, *Appl. Catal.*, *A*, 2007, 333, 219.
- 14 R. Kosydar, A. Drelinkiewicz, E. Lalik and J. Gurgul, Appl. Catal., A, 2011, 402, 121.
- 15 J. T. Feng, H. Y. Wang, D. G. Evans, X. Duan and D. Q. Li, *Appl. Catal.*, *A*, 2010, 382, 240.
- 16 P. G. Tang, Y. Y. Chai, J. T. Feng, Y. J. Feng, Y. Li and D. Q. Li, *Appl. Catal.*, A, 2014, 469, 312.
- 17 C. Shen, Y. J. Wang, J. H. Xu, Y. C. Lu and G. S. Luo, *Chem. Eng. J.*, 2011, 173, 226.

- 18 M. S. Jin, H. Zhang, Z. X. Xie and Y. N. Xia, *Energy Environ. Sci.*, 2012, 5, 6352.
- 19 B. Lim, M. J. Jiang, J. Tao, P. H. C. Camargo, Y. M. Zhu and Y. N. Xia, *Adv. Funct. Mater.*, 2009, **19**, 189.
- 20 M. Chen, B. H. Wu, J. Yang and N. F. Zheng, Adv. Mater., 2012, 24, 862.
- 21 Y. N. Xia, Y. J. Xiong, B. Lim and S. E. Skrabalak, Angew. Chem., Int. Ed., 2009, 48, 60.
- 22 A. R. Tao, S. Habas and P. D. Yang, Small, 2008, 4, 310.
- 23 C. J. Jia and F. Schuth, Phys. Chem. Chem. Phys., 2011, 13, 2457.
- 24 S. Kim, D. W. Lee and K. Y. Lee, J. Mol. Catal. A: Chem., 2014, 383, 64.
- 25 Accelrys webpage, http://accelrys.com/mstudio/.
- 26 N. Luiggi and O. Febres, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 1992.
- 27 L. Y. Gan, Y. X. Zhang and Y. J. Zhao, J. Phys. Chem. C, 2010, 114, 996.
- 28 A. Maiti, R. Gee, R. Maxwell and A. Saab, *J. Phys. Chem. B*, 2006, **110**, 3499.
- 29 M. S. Jin, H. Y. Liu, H. Zhang, Z. X. Xie, J. Y. Liu and Y. N. Xia, *Nano Res.*, 2011, 4, 83.
- 30 R. Van Hardeveld and F. Hartog, Surf. Sci., 1969, 15, 189.

- 31 E. Santacesaria, M. Di Serio, R. Velotti and U. Leone, J. Mol. Catal., 1994, 94, 37.
- 32 R. Xu, D. S. Wang, J. T. Zhang and Y. D. Li, *Chem. Asian J.*, 2006, 1, 888.
- 33 R. Narayanan and M. A. El-Sayed, Nano Lett., 2004, 4, 1343.
- 34 S. Kim, D. W. Lee and K. Y. Lee, J. Mol. Catal. A: Chem., 2014, 391, 48.
- 35 K. M. Bratlie, H. Lee, K. Komvopoulos, P. D. Yang and G. A. Somorjai, *Nano Lett.*, 2007, 7, 3097.
- 36 Z. N. Xu, J. Sun, C. S. Lin, X. M. Jiang, Q. S. Chen, S. Y. Peng, M. S. Wang and G. C. Guo, ACS Catal., 2013, 3, 118.
- 37 M. H. Shao, T. Yu, J. H. Odell, M. S. Jin and Y. N. Xia, *Chem. Commun.*, 2011, 47, 6566.
- 38 S. Wilke, D. Hennig, R. Löber, M. Methfessel and M. Scheffler, *Surf. Sci.*, 1994, 307–309, 76, Part A, .
- 39 G. W. Watson, R. P. K. Wells, D. J. Willock and G. J. Hutchings, *J. Phys. Chem. B*, 2001, **105**, 4889.
- 40 X. Q. Qi, Z. D. Wei, L. Li, M. B. Ji, L. L. Li, Q. Zhang, M. R. Xia, S. G. Chen and L. J. Yang, *Comput. Theor. Chem.*, 2012, 979, 96.
- 41 P. Ferrin, S. Kandoi, A. U. Nilekar and M. Mavrikakis, *Surf. Sci.*, 2012, **606**, 679.