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# Shape and ligand effect of palladium nanocrystals on furan hydrogenation

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**Abstract:** The Pd nanocrystals, including cube, octahedron and wire, were prepared by shape-controlled solution phase reduction. The shape-dependent effect of Pd, together with the effect of residual halogen ions and PVP, were investigated in selective hydrogenation of furan to tetrahydrofuran (THF). It was found that the residual halogen ions and PVP on the surface of Pd nanocrystals possibly reduced the hydrogenation activity in turn it prevented the further reaction such as ring opening, so high selectivity towards THF was achieved even at high temperature. The 5-fold twinned wire displayed poor activity in furan hydrogenation due to a large amount of strongly adsorbed iodide ion residues covering most of the Pd active sites. An appropriate PVP residue is necessary, which can effectively maintain the shape and size stability of Pd nanocube and octahedron, although the residual PVP partially block active Pd sites and reduce the activity for furan hydrogenation. The Pd nanocube enclosed by {100} facets exhibited about two times higher turnover frequency and lower apparent activation energy compared to the octahedron enclosed by {111} facets, suggesting a significant shape-dependent effect.

Key words: Palladium nanocrystal; Furan; Catalytic hydrogenation; Shape sensitivity; Ligand effect

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#### 1. Introduction

Extensive studies over the past few decades have demonstrated that the size and shape of a catalyst particle on the nanoscale profoundly affect its reaction performance. In particular, controlling the catalyst particle shape allows a selective exposure of the reactive facets with desirable surface coordination, on which the active sites can be enriched and tuned.<sup>1-5</sup> Zhou et al. reported that the CeO<sub>2</sub> nanorods with exposed {100} and {110} planes showed a higher CO oxidation activity than the {111}-exposed irregular nanoparticles.<sup>2</sup> Xie et al. demonstrated that the Co<sub>3</sub>O<sub>4</sub> nanorods with predominantly exposed {110} planes catalyzed CO oxidation at temperatures as low as -77 °C even in a moist feed gas.<sup>3</sup> In fact, besides the activity enhancement, exploring and understanding shape-dependent effect can also facilitate the catalytic selectivity improvement.<sup>4</sup> Bratlie et al. discovered that the exposed {100} surface on Pt cubic nanoparticles showed exclusive selectivity towards cyclohexane in benzene hydrogenation, whereas the {100} and {111} planes on cuboctahedral nanoparticles produced both cyclohexane and cyclohexene.<sup>5</sup>

Palladium is a common noble metal active component with a broad range of industrial applications in catalysis.<sup>6,7</sup> Therefore, investigating its shape-dependent effect is of great scientific importance and also of industrial interest.<sup>8</sup> Shuai et al. demonstrated that the catalytic reduction activity for waterborne contaminant removal varies with the Pd shape and size using nitrite, N-nitrosodimethylamine and diatrizoate hydrogenation as the probe reaction.<sup>9</sup> Recently, Choi et al. reported shape-dependent effect in formic acid oxidation reaction over a variety of Pd nanocrystals, including cubes, right bipyramids, octahedra, tetrahedra, decahedra, and icosahedra. They discovered that the Pd nanocrystals enclosed by {100} facets have higher specific activities than those enclosed by {111} facets and the twin defects can greatly enhance formic acid oxidation activities.<sup>10</sup> Nevertheless, till now, the research for shape-dependent effect of palladium is scarce in contrast to its extensive applications.

Furan and its derivatives can be massively obtained from biomass and therefore they are

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59 60 important platform molecules in hydrogenation and hydrodeoxygenation catalyzed by Pd, Pt, Ni, Cu-based catalysts to produce biofuels and chemicals.<sup>11-20</sup> Although furan and its derivatives hydrogenation over Pd-based catalysts has been extensively studied through experimental<sup>12-15</sup> and theoretic methods<sup>21-25</sup>, the shape-dependent effect of palladium has not been involved and discussed. Accordingly, in this work, we conducted shape-controlled synthesis of monodispersed Pd nanocrystals and tested their catalytic performance to gain insight into the shape-dependent effect of palladium nanocrystals on furan hydrogenation. On the other hand, the residual surfactants and other surface contamination originating from the nanocrystal synthesis process often affect the catalytic performance, even mask or mislead the shape effect. Thus the ligand-effect of palladium nanocrystals was also investigated.

# 2. Experimental

## 2.1. Pd nanocrystals preparation

The Pd nanocrystals, including cube, octahedron and wire, were prepared by solution phase reduction referenced to previous reports.<sup>26-28</sup> In a typical synthesis of Pd cubes, 5.5 mL of an aqueous solution containing polyvinylpyrrolidone (PVP, MW=55000, 105 mg), L-ascorbic acid (60 mg), KBr (75 mg) and KCl (141 mg) was pre-heated at 80 °C for 5 min, then 5.5 mL of Na<sub>2</sub>PdCl<sub>4</sub> aqueous solution (50 mM) was added. The mixture was heated at 80 °C under magnetic stirring for 3 h and cooled down to room temperature. The products were precipitated by acetone, separated via centrifugation at 12000 rpm, further purified by thorough washing with ethanol, water or ethanol-acetone mixture, vacuum desiccated, and finally collected. The procedure of Pd octahedra synthesis was similar to that of Pd cubes except that PVP (105 mg), citric acid monohydrate (197.5 mg) and Na<sub>2</sub>PdCl<sub>4</sub> (81 mg) were dissolved in a mixture solution containing 3 mL of ethanol and 8 mL of water. In the synthesis of Pd wires, 1.0 mL of aqueous solution containing PVP (388.5 mg), KI (332 mg), and 1.5 mL of NaOH aqueous solution (24 mM) and 2.0 mL of Na<sub>2</sub>PdCl<sub>4</sub>

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aqueous solution (50 mM) were added into a 20 mL Teflon-lined stainless-steel autoclave, heated at 200 °C for 2 h.

#### 2.2. Characterization

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 The Pd nanocrystals were characterized by TEM, HRTEM, XRD, FTIR, XPS, N<sub>2</sub> physisorption, CO pulse chemisorption and TPO techniques. The experimental details of characterization were shown in the ESI.

#### 2.3. Catalytic test

The liquid-phase selective hydrogenation of furan was carried out in a 100 ml autoclave equipped with a magnetic stirrer. The mass transfer limitation was eliminated when an agitating speed of 1000 rpm was used. In a typical reaction, 13.5 mmol of furan, 19.0 ml of ethanol, 0.18 g of n-tetradecane and 5 mg of Pd catalyst without any pretreatment were charged into the reactor, which was flushed with N<sub>2</sub> and further pressurized with H<sub>2</sub> to the desired pressure. Then the reaction temperature was raised to the desired value and agitation was started. After different reaction periods, the products were analyzed by an Agilent 7890B gas chromatograph equipped with a flame ionizing detector (FID) and a HP Innowax or PlotAl<sub>2</sub>O<sub>3</sub>/S capillary column. The conversion of furan and the selectivity of products were calculated on the basis of the mass balance of carbon using n-tetradecane as internal standard. In some kinetics measurements, the constant H<sub>2</sub> pressure was kept. All the experiments were conducted in triplicate for reproducibility of the data and the results were within an error of  $\pm 10$  %.

### 3. Results and discussion

3.1. Characterization of as-prepared Pd nanocrystals

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**Fig. 1** TEM images, 3D models and size distributions of the as-prepared Pd nanocubes (a), octahedra (b) and wires (c). The amplified inset of (b) shows that a small amount of tetrahedra and decahedra, exposing {111} planes as well, exist in octahedral synthetic system.

Fig. 1 shows the TEM images of as-prepared Pd nanocrystals. It could be found that monodispersed nanocubes (Fig. 1a) and wires (Fig. 1c) with uniform shape and size were synthesized. In the octahedral synthetic system (Fig. 1b), a small amount of tetrahedra and

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decahedra, exposing {111} planes as well, could be observed. The careful shape statistics demonstrates that proportion of octahedra is more than 80% (Fig. S1).



Fig. 2 HRTEM and FT images of Pd nanocubes (a, b), octahedra (c, d) and wires (e, f).

Fig. 2 shows the HRTEM images of as-prepared Pd nanocrystals. The fringes with lattice spacing of 0.22 and 0.19 nm could be indexed to the {111} and {200} planes of metal Pd. The detailed HRTEM analysis indicates that the cube and octahedron is Pd single crystal enclosed by six {100} facets or eight {111} facets, whereas the wire is 5-fold twinned crystal growing along <110> direction, exposing five {100} side planes.

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59 60 The size distributions of Pd nanocrystals are given in Fig. 1 a2, b2 and c2. Based on the shape and size statistics, the structural features of the Pd nanocrystals could be estimated and listed in Table 1.

 Table 1
 Structural features of the Pd nanocrystals derived from TEM statistics

Sample	Size (nm)	Calculated surface area $(m^2/g)$	Number of surface atoms (/g)
Cube	7.5 <sup>a</sup>	66.5	$8.79 \times 10^{20}$
Octahedron	8.1 <sup>a</sup>	76.4	$1.17 \times 10^{21}$
Wire	6.0 <sup>b</sup>	65.3	8.63×10 <sup>20</sup>

<sup>a</sup> Edge length of cube or octahedron. <sup>b</sup> Diameter of wire, the corresponding side length of pentagon cross section is 3.7 nm.

To further identify the structural features of the Pd nanocrystals, we tentatively conducted N2 physisorption and CO pulse chemisorption to measure BET surface area and metal surface area of the Pd nanocrystals. Unfortunately, all the results were not well reproducible, fluctuated from 1 to 10  $m^2/g$ . The surface areas derived from adsorption measurements are much smaller than the calculated values from TEM statistics, which is due to the impact of surface residues. The surface residue analysis (see later sections) show that PVP and halogen ions exist on the Pd surface. It is reasonable that microporous condensation for N<sub>2</sub> adsorption over aggregated samples was hindered by PVP, and halogen ions was responsible for surface poisoning for CO adsorption. The fluctuation of measured values is likely to be related to different degrees of aggregation caused by sample drying, and PVP on the surface of aggregated samples seems to have an uncertain effect on adsorption results. This limited us to obtain the specific surface area and active Pd surface area through adsorption measurements. However, the TEM analysis showed that the dried sample was easy to be re-dispersed into ethanol to monodisperse state. Considering the same solvent used in the catalytic test, thus in later sections the discussion of catalytic behavior and the calculation of TOF were based on the structural features of monodisperse

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# Pd nanocrystals, as shown in Table 1. The effect of surface residues will also be discussed.

Fig. 3 XRD patterns of Pd nanocubes (a), octahedra (b) and wires (c).

The XRD patterns of as-prepared Pd nanocrystals are depicted in Fig. 3. All the samples exhibited nearly identical diffraction peaks at 39.8, 46.3, 67.9, 81.9 and 86.3 degrees, which could be indexed to {111}, {200}, {220}, {311} and {222} diffractions of face-centered cubic Pd (PDF2 No.65-2867). No other diffraction peaks could be observed, suggesting almost complete reduction of Pd species.

Briefly, three metal Pd nanocrystals with different shapes were successfully prepared.

#### 3.2. Furan hydrogenation reaction

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 The liquid-phase selective hydrogenation of furan was conducted to test the as-prepared metal Pd nanocrystals. Generally, furan hydrogenation over metal catalysts proceeds along two pathways, ring hydrogenation to yield dihydrofuran (DHF) and then tetrahydrofuran (THF) or ring opening reaction to form butanol, butene, butane, propene, propane etc.<sup>11,19,24</sup> In all of our hydrogenation experiments operated at 25-150 °C, only two kinds of ring hydrogenation products formed, the major product THF and trace DHF. When the reaction temperature was raised, furan conversion increased and selectivity changed little. No ring opening products could be detected even at 150 °C. This product distribution was quite

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59 60 different from the previous observation over Pt single-crystal surfaces and Pt nanoparticles, where THF was dominant at low temperatures, butanol or propene was the main product at high temperatures.<sup>19</sup> The difference in catalytic performance between the two metals partially depends on their intrinsic properties. Compared with Pt catalysts, Pd shows a weak ability to break C-O and C-C bond, thus requiring higher temperatures to ring-opening hydrogenation. Another possible explanation is that the residual PVP or halogen ions on the surface of Pd nanocrystals reduced the hydrogenation activity in turn it prevented the further reaction such as ring opening. Considering the stability of Pd nanocrystals, no higher temperatures more than 150 °C was attempted in our tests.



**Fig. 4** Catalytic performance of different non-supported Pd nanocrystals for furan hydrogenation. Reaction conditions: furan, 13.5 mmol; ethanol, 19 ml; n-tetradecane, 0.18 g; catalyst loading, 5 mg; agitating speed, 1000rpm; H<sub>2</sub> pressure, 4.0 MPa; temperature, 80 °C; reaction period, 0.5 h.

Fig. 4 shows the catalytic performance of different Pd nanocrystals for furan hydrogenation at 80 °C under the H<sub>2</sub> pressure of 4.0 MPa. After 0.5 h reaction, the furan conversion over the nanocube, octahedron and wire was 100%, 61% and 11%, respectively. The cube enclosed by {100} facets is more active for furan hydrogenation than the octahedron enclosed by {111} facets. Similarly, the {100} facets of Pd nanocrystals were reported to be more active for the nitrite hydrogenation at low initial nitrite concentration<sup>9</sup>

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or for the formic acid oxidation<sup>10</sup> than the other terrace facets, such as {111}. For Pd wire, THF selectivity was 48% and no other product was detected. This carbon balance of far below 100% is due to the positive deviation of conversion caused by adsorbed furan on catalysts and volatilized furan in gas phase. This conversion deviation is significant at low furan conversion, while at high furan conversion it can be neglected and the carbon balance is close to 100%, as shown on the nanocube (98%) and octahedron (95%). Previous report<sup>10</sup> also indicated that twin defects of Pd nanocrystals can greatly enhance formic acid oxidation activities. However, the wire with twin defects displayed unexpected poor activity in furan hydrogenation, although the 5-fold twinned wire and nanocube both mainly expose {100} planes and have almost the same surface area (Table 1). It seems that the twin defects on the wire do not enhance furan hydrogenation activity, but lower it. Nevertheless, the presence of adsorbed species on the nanocrystal surface, which could block the active sites or affect the electronic structures, i.e., the ligand effect, should be considered.

#### 3.3. Effect of residual halogen ions

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**Fig. 5** Pd 3d and halogen XPS spectra of Pd nanocube (a, b), octahedron (c, d) and wire (e, f). The corresponding surface atom ratio: Br/Pd = 0.13 for nanocube, Cl/Pd = 0.07 for octahedron, I/Pd = 0.22 for wire.

Halogen ions can be adsorbed on the surface of Pd crystal. In our preparations, Br<sup>-</sup> was used for nanocube synthesis, I<sup>-</sup> was used for wire synthesis, and Cl<sup>-</sup> existed in all three synthetic raw materials. As reported in literature, the adsorption strength to Pd surface increases in the order of chloride < bromide < iodide.<sup>29</sup> Thus it is more likely that a large amount of strongly adsorbed iodide ion residues covering most of the Pd active sites is responsible for the poor activity of the Pd wire. The XPS analysis (Fig. 5) supports the above speculation. There is only one kind of halogen ion on the surface of each as-prepared sample, Cl<sup>-</sup> on octahedron, Br<sup>-</sup> on nanocube and I<sup>-</sup> on wire. The corresponding surface atom ratio is 0.07 (Cl/Pd) for octahedron, 0.13 (Br/Pd) for nanocube, and 0.22 (I/Pd) for wire, indicating the wire has the most halogen residues. This large amount of strongly adsorbed iodide ion residues and mask the intrinsic activity of the Pd wire. The nanocube and octahedron with a relatively small amount of halogen residues displayed high enough catalytic activity, therefore the subsequent discussion would focus on the nanocube and octahedron.

Considering that the residual bromide or chloride ions can also occupy the active sites, the intrinsic activities of the nanocube and octahedron should be higher than the displayed ones. Note, the surface Br/Pd ratio of the nanocube is larger than the Cl/Pd ratio of the octahedron, if the bromide and chloride ions are assumed to exert the same influence on Pd active sites, the activity decrease of the nanocube should be greater than that of the octahedron. Even so, the nanocube is more active than the octahedron, as shown in Fig. 4. Obviously, the nanocube has much higher intrinsic activity for furan hydrogenation than the octahedron.

3.4. Effect of residual PVP

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The shape and size stability of Pd nanocrystal catalysts is an essential prerequisite to investigate the shape effect. In our synthesis of Pd nanocrystals, PVP was used as stabilizers in colloidal synthesis to inhibit nanocrystal overgrowth and aggregation as well as to control the structural characteristics of the resulted nanocrystals. On the other hand, similar to the residual halogen ions, the residual PVP can modify the surface properties and impact catalytic behavior.<sup>30-34</sup> Thus it is necessary to explore the residual PVP.



Fig. 6 TPO-MS analysis of surface carbon over as-prepared Pd nanocube (a) and octahedron (b).

Based on TPO-MS results of the as-prepared Pd nanocube and octahedron (Fig. 6), the surface carbon amount, 3.81 mmol/g for cube and 0.93 mmol/g for octahedron, could be obtained from the sum of CO<sub>2</sub> and CO. Combined with the structural features of the Pd nanocrystals showing in table 1, the ratio of residual PVP monomer to surface Pd atom was estimated to be 0.43 for cube and 0.08 for octahedron. It seems that a considerable number of active sites were occupied although the as-prepared Pd nanocrystals were thoroughly

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59 60 washed, and the cube should loss more active sites. Nevertheless, the nanocube with more PVP residue displayed higher catalytic activity than the octahedron (shown in Fig. 4).



**Fig.** 7 FTIR spectra of the as-prepared Pd nanocubes (a), octahedra (b) and those subjected to NaBH<sub>4</sub> washing (c, d).

FTIR measurements were performed to further explore the residual PVP over Pd nanocrystals. As shown in Fig. 7 a and b, upon the as-prepared nanocube and octahedron, the band of PVP at around 1660 cm<sup>-1</sup> attributed to C=O stretch vibration, 1274, 1290, 1495 cm<sup>-1</sup> attributed to N-C stretch vibrations linking with different carbon atoms, and 1320-1463, 2850-2930 cm<sup>-1</sup> attributed to C-H vibrations can be distinctly distinguished. According to previous report, PVP molecule chemisorbs with its oxygen atom in the ring on the surface of fine Pd nanocrystals capped with a large number of PVP molecules, while PVP molecule chemisorbs with both the oxygen atom and nitrogen atom in the ring on the surface of large Pd nanocrystals capped by a small number of PVP molecules.<sup>35</sup> In our case, the presence of all three N-C stretch vibrations suggests that no nitrogen atom chemisorbs on the as-prepared Pd surface, and the red shift of the C=O stretch vibrational band can hardly be observed, implying that most of the oxygen atoms do not chemisorb, i.e., most of the PVP monomer just loosely deposit or suspend on Pd surface. Therefore, the actual coverage of PVP on the as-prepared Pd nanocrystal surface is not as high as the TPO-MS result, and the effect of residual PVP on Pd active sites is finite.

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**Fig. 8** TEM images of the Pd nanocubes and octahedra after catalytic test (a, c) and NaBH<sub>4</sub> washing (b, d). The inset of (a) and (c) shows the size distribution diagram.

Pd nanocrystals with clean surface are highly expected in the study of shape effect.<sup>31-34</sup> So an extra washing by NaBH<sub>4</sub> were operated to completely remove the residual PVP on the as-prepared Pd nanocrystals. As shown in Fig. 7 c and d, almost all the IR bands from PVP disappear after NaBH<sub>4</sub> washing. However, the PVP-free Pd nanocrystals are not stable and tend to deform and aggregate in ethanol solution, as shown in Fig. 8 b and d, thus cannot be used in catalytic test. This suggests that an appropriate PVP residue is necessary, which can effectively maintain the shape and size stability of Pd nanocube and octahedron, although it is possible that residual PVP partially block active Pd sites and reduce activity for furan hydrogenation. TEM images and the corresponding size distributions (Fig. 8 a, c and Fig. S2) further demonstrate that the nanocube and octahedron are stable enough, after catalytic reaction they still have almost the same shape and size as the as-prepared ones.

3.5. Kinetics test and shape-dependent effect

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**Fig. 9** Catalytic performance of Pd nanocube (a, c) and octahedron (b, d) for furan hydrogenation. (a, b), furan concentration vs. reaction time; (c, d),  $\ln(C_0/C)$  vs. reaction time. Reaction conditions: furan, 13.5 mmol; ethanol, 19 ml; n-tetradecane, 0.18 g; catalyst loading, 5 mg; agitating speed, 1000rpm; constant H<sub>2</sub> pressure, 4.0 MPa.

Fig. 9 shows the kinetics test result of furan hydrogenation over Pd nanocube and octahedron under the constant H<sub>2</sub> pressure of 4.0 MPa. In most cases, linear plots of  $\ln(C_0/C)$  versus time could be obtained, indicating that the reaction under the constant H<sub>2</sub> pressure follows pseudo first order kinetics for furan. The only exception was furan hydrogenation over Pd octahedron at 25 °C, where the furan concentration versus time displayed better linearity, showing a near zero order kinetics. Low temperatures resulted in the low surface reaction rate, and thus the Pd octahedron surface was saturated by adsorbed furan. The

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effect of hydrogen pressure was also investigated, as shown in Fig. S3. The reaction order with respect to hydrogen is 0.16 and 0.19 over cube and octahedron, respectively, which is far below the reaction order with respect to furan, indicating that furan hydrogenation reaction is more affected by the concentration of furan.

 Table 2
 Comparison of furan conversion, initial reaction rate, turnover frequency and apparent activation energy for Pd cube and octahedron

Sample	Conv.(%) <sup>a</sup>	$r_0 \ (mol \ g^{-1} \ h^{-1})^{b}$	TOF $(s^{-1})$	E <sub>a</sub> (kJ mol <sup>-1</sup> )
Cube	66	6.4	1.22	45.7
Octahedron	56	4.8	0.69	57.4

<sup>a</sup> Reaction conditions: furan, 13.5 mmol; ethanol, 19 ml; n-tetradecane, 0.18 g; catalyst loading, 5 mg; agitating speed, 1000rpm; H<sub>2</sub> pressure, 4.0 MPa; temperature, 50 °C; reaction period, 0.5 h.

 $^{\rm b}$  Initial reaction rates were derived from kinetics test at 50 °C.



Fig. 10 Arrhenius plots for furan hydrogenation over Pd nanocube and octahedron.

To verify the shape-dependent effect of Pd nanocrystals on furan hydrogenation, the intrinsic activity of Pd surface atom over nanocube and octahedron should be compared. As shown in Table 2, the initial reaction rate of Pd nanocube was 6.4 mol  $g^{-1}$  h<sup>-1</sup>, 33% higher than that of octahedron (4.8 mol  $g^{-1}$  h<sup>-1</sup>) under the selected reaction conditions. In fact, this activity difference was based on catalyst mass, contained the contribution of

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59 60 different numbers of active sites. So turnover frequency (TOF) was calculated to describe the activity of single active site. The TOF value of the nanocube was about two times higher than that of the octahedron, as shown in Table 2, suggesting a significant shape-dependent effect of Pd in furan hydrogenation. The Pd nanocube enclosed by {100} facets is more active for furan hydrogenation than the octahedron enclosed by {111} facets. Moreover, apparent activation energies for Pd nanocube and octahedron were estimated at a temperature range of 25-50 °C, and the corresponding Arrhenius plots were in Fig. 10. As expected, the highly active Pd nanocube presented a lower E<sub>a</sub>, 45.7 kJ mol<sup>-1</sup>, while the octahedron had a higher one, 57.4 kJ mol<sup>-1</sup>.

The above TOF calculations are based on the structural features of monodisperse Pd nanocrystals from TEM statistics, not on the number of active sites from chemisorption representing the effective atomic surface available in liquid phase reaction. As aforementioned, the residual PVP and halogen ions partially blocked Pd surface sites and reduced furan hydrogenation activity. Taking into account that more PVP and halogen ions present on the nanocube than those on the octahedron, so the decrease of active site number due to surface residues for nanocube should be more significant than that for octahedron, thus the presence of residual PVP and halogen ions does not influence the validity of the TOF comparison and the resulted shape-dependent effect. Compared to the Pd {111} facet, the {100} facet showing higher furan hydrogenation activity is probably related to the formation of stronger bonds with the reactants or intermediates, similar to the report in nitrite hydrogenation.<sup>9</sup>

#### 4. Conclusions

The Pd nanocrystals, including cube, octahedron and wire, were prepared by solution phase reduction to explore the shape-dependent effect of Pd on furan hydrogenation. It was found that an appropriate PVP residue is necessary, which can effectively maintain the shape and size stability of Pd nanocube and octahedron, although it is possible that residual PVP partially block active Pd sites and reduce activity for furan hydrogenation. The Pd

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nanocube enclosed by {100} facets exhibited much higher activity for furan hydrogenation than the octahedron enclosed by {111} facets, suggesting a significant shape-dependent effect. Considering the complex surface species on nanocube and octahedron, the electronic effects of residual PVP and halogen contributing to the difference in catalytic activity could not be completely excluded. The 5-fold twinned wire displayed poor activity in furan hydrogenation due to a large amount of strongly adsorbed iodide ion residues covering most of the Pd active sites.

## **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgments

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Shape and ligand effect of palladium nanocrystals on <sup>DGE: 10,1039/C8NJ05152F</sup> hydrogenation

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Nanocube enclosed by {100} facets is the most active, residual PVP and halogen ions occupy partial surface sites.