

The Structure Sensitivity of Alkynol Hydrogenation on Shape- and Size-Controlled Pd Nanocrystals: Which Sites Are Most Active and Selective?

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ABSTRACT

The activity and selectivity of structure-sensitive reactions are strongly correlated with the shape and size of the nanocrystals present in a catalyst. This correlation can be exploited for *rational catalyst design*, especially if each type of surface atom displays a different behavior, to attain the highest activity and selectivity. In this work, uniform Pd nanocrystals with cubic (in two different sizes), octahedral, and cubo-octahedral shapes were synthesized through a solution-phase method with poly(vinyl pyrrolidone) (PVP) serving as a stabilizer and then tested in the hydrogenation of 2-methyl-3-butyn-2-ol (MBY). The observed activity and selectivity suggested that two types of active sites were involved in the catalysis - those on the planes and at edges, which differ in their coordination numbers. Specifically, semi-hydrogenation of MBY to 2-methyl-3-buten-2-ol (MBE) occurred preferentially at the plane sites regardless of their crystallographic orientation, Pd₍₁₁₁₎ and/or Pd₍₁₀₀₎, whereas over-hydrogenation occurred mainly at the edge sites. The experimental data can be fit with a kinetic modeling based on a two-site Langmuir-Hinshelwood mechanism. By considering surface statistics for nanocrystals with different shapes and sizes, the optimal catalyst in terms of productivity of the target product MBE, was predicted to be cubes of roughly 3 nm in edge length. This study is an attempt to close the material and pressure gaps between model single crystal surfaces, tested under ultra high vacuum conditions, and real catalytic systems, providing a powerful tool for *rational catalyst design*.

INTRODUCTION

The structure sensitivity of reactions catalyzed by metal nanocrystals has attracted considerable attention over the past decades.¹ The activity and selectivity of structure-sensitive reactions are strongly affected by both the size and shape of the nanocrystals in a catalyst. The ratio between surface atom types (e.g., vertex, edge, and plane) changes substantially when varying the size of a nanocrystal (Figure S1, Supporting Information). The fraction of atoms located on (111) and/or (100) crystallographic planes increases with size at the expense of edge and vertex atoms. This change leads to a *size effect*, which manifests itself with an increase (antipathetic structure-sensitivity) or decrease (sympathetic structure-sensitivity) of the turnover frequency (TOF) as a function of particle size.² In addition, shape variation can result in important morphological differences: for example, cubes only display (100) plane atoms on the surface while octahedra only present (111) plane atoms and cubo-octahedra have a mixture of both.^{3,4} This difference contributes to a *shape effect*, especially when each type of surface atom possesses a different reactivity. For structure-sensitive reactions, such shape and size effects could be used to perform a *rational catalyst design* to achieve a superior catalyst in terms of activity and/or selectivity.

Many recent studies have been carried out to investigate the catalytic behaviors of different crystal planes on model catalysts⁵⁻⁷. Most of these studies were performed in ultra-high vacuum using single metal crystals exhibiting definite crystallographic planes. However, these model catalysts are far away from the real catalytic systems. These *material and pressure gaps* are believed to be overcome using stable nanostructures with desirable crystallographic orientations such as nanowires,⁸ cubes,⁹ tetrahedra,^{10,11} and cubo-octahedra.^{12,13} Indeed, synthesis of nanocrystals with different shapes has been achieved through colloidal methods for a wide variety of different metals.¹⁴⁻¹⁶ These nanocrystals with well-defined shapes can be used as prepared as catalysts to explore the facet sensitivity of liquid-phase reactions. Recent reviews gather the results of the catalytic behavior of colloidal nanocrystals in cross-coupling, electron transfer, hydrogenation and oxidation reactions.^{14,17}

Among structure-sensitive reactions, Pd-catalyzed alkyne hydrogenations are of special interest due to their importance in bulk and fine chemical production. The size effect for this type of reaction was first reported by Boitiaux and co-workers.¹⁸ Recently, it was shown that the dependence of TOF on the particle size disappeared when only one type of surface atom, namely Pd₍₁₁₁₎, was taken into account,^{19,20} suggesting that these atoms were the active sites involved in the catalysis. Using this approach, atoms located on Pd₍₁₁₁₎ have been identified as the active sites in the hydrogenation of 1,3-butadiene^{6,7} and 2-methyl-3-butyn-2-ol (MBY).^{21,22} However, the nanocrystals used in these size-dependence studies only presented a very low percentage of Pd₍₁₀₀₎ atoms on the surface,^{6,7,21-24} implying that their influence, although measurable, might be easily overlooked. Furthermore, the existence of two or more different kinds of active sites responsible for observed size effects has not been thoroughly discussed in the literature.²⁵

In this work, poly(vinyl pyrrolidone) (PVP)-stabilized Pd nanocrystals with well-defined shapes were synthesized and tested *per se* (without any catalytic support) in the water-assisted selective hydrogenation of MBY in order to compare the activity and selectivity of plane surface atoms, namely Pd₍₁₀₀₎ and Pd₍₁₁₁₎, with edge surface atoms, Pd_{edge}. Specifically, we examined Pd nanocubes of two different sizes (6 nm and 18 nm in edge length), Pd octahedra of 31 nm in edge length, and Pd cubo-octahedra of 5.5 nm in size. A simple model involving two different types of active sites, Pd_{plane} and Pd_{edge}, was used to successfully describe the differences observed in activity and selectivity between the samples. The kinetic modeling was performed using a two-site Langmuir-Hinshelwood mechanism, with one single set of kinetic and adsorption constants specific to the reaction path or adsorption equilibrium of a compound on a given active site. The results of modeling were consistent with our observations, which, in turn, allowed optimizing the Pd catalyst's size and shape.

METHODS

Nanocrystal synthesis. Both the Pd nanocubes and cubo-octahedra were synthesized according to our

previously published protocols.^{26,27} For the Pd octahedra, they were prepared as follows: 3 mL of an aqueous Na₂PdCl₄ solution (9.5 mg/mL) was added into an aqueous solution (8 mL) containing 105 mg of PVP, 100 μ L of CH₃CHO, and 0.3 mL of the Pd nanocubes (1.8 mg/mL, 18 nm in edge length) at 60 °C under magnetic stirring. The final products were collected by centrifugation and washed with ethanol and water to remove excess PVP.

Characterization. The shape and size of the nanocrystals were analyzed by transmission electron microscopy (TEM), using a Philips CM20 microscope operated at 200 kV. High-resolution TEM images were recorded with a CM300 FEG (Philips/FEI) microscope operated at 300 kV.

To determine the amount of Pd loaded in each catalytic run, an aliquot of the nanocrystal suspension was analyzed by atomic absorption spectroscopy (AAS) using a Shimadzu AA-6650 spectrometer. The specific wavelength used for Pd²⁺ was 475 nm.

X-ray photoelectron spectroscopy (XPS) data were collected using an Axis Ultra instrument (Kratos analytical, Manchester, UK) under ultra-high vacuum condition (<10⁻⁸ Torr) and with a monochromatic Al K α X-ray source (1486.6 eV). The adventitious carbon 1s peak was calibrated at 284.5 eV and used as an internal standard to compensate for any charging effects.

Hydrogenation reactions. The reactions were carried out in a baffled semi-batch stainless steel reactor (250 mL autoclave, Büchi AG, Switzerland) equipped with a heating jacket and a hydrogen supply system. An 8-blade disk turbine impeller was used as the stirrer. The molar ratio between MBY and surface Pd atoms was kept at a constant of ~140,000 in all cases. An appropriate amount of the Pd nanocrystals and 1 g of MBY were diluted with water up to 200 mL and sonicated for 5 min before introducing them into the reactor. After the reactor had been charged, it was flushed with N₂ and set to 60 °C. Subsequently, it was flushed with H₂ and pressurized to 0.3 MPa. Samples were periodically withdrawn from the reactor and analyzed by gas chromatography (GC). The accuracy of the analysis was found to be of 0.1 wt.% for all products.

RESULTS AND DISCUSSION

Synthesis and characterization of the Pd nanocrystals with controlled shapes and sizes. We synthesized Pd nanocubes, octahedra, and cuboctahedra to investigate the effect of shape on catalytic properties. We also prepared Pd nanocubes with two different sizes using a bromide-assisted method described previously (Figure 1A and B).²⁷ Figure 1 shows TEM images of the Pd nanocrystals, where the Pd octahedra were obtained by reducing a Pd precursor with CH₃CHO in the presence of the 18 nm Pd nanocubes as seeds (Figure 1C) and the Pd cuboctahedra were synthesized by reducing a Pd precursor with L-ascorbic acid in the presence of PVP (Figure 1D). HRTEM imaging of each sample showed the nanocrystals to be monocrystalline and bounded by the expected crystallographic planes as seen in Figure S2 in the Supporting Information. Furthermore, particle counting allowed determining the average particle size of each sample in which more than 95% of the nanocrystals corresponded to the expected shapes (Figure S3, Supporting Information).

Despite the extensive cleaning procedures to which the nanocrystals are subjected, it is common to find traces of the stabilizing agent in the samples, which can modify the behavior of the catalyst.^{13,28,29} Therefore, during this study, all samples were prepared with the same stabilizer, namely PVP. Furthermore, XPS analyses did not detect Br⁻ or Cl⁻ on the surface of the nanocrystals after cleaning, as shown in Figure S4 of the Supporting Information for CUB6. The XPS spectra of the other samples were analogous to the former.

The statistics of surface atoms⁴ for ideal face-centered cubic (*fcc*) nanocrystals allow one to determine the relative numbers of different types of surface atoms on a nanocrystal with a particular size and shape (see Figure S1, Supporting Information). Concern has been expressed regarding the utilization of idealistic models to characterize the surface of nanocrystals.²⁵ Therefore, a non-ideal model was employed in the present work,⁴ where an incomplete extra layer of atoms was added to the surface of the nanocrystal. Table 1 summarizes this information for the Pd nanocrystals used in this work. TEM imaging was used to obtain the mean particle diameter.

Structure-sensitivity of MBY hydrogenation. The reaction network for MBY hydrogenation is depicted in [Scheme 1](#).^{21,22,30,31} MBY can be either semi-hydrogenated to 2-methyl-3-buten-2-ol (MBE) through *path a*, directly hydrogenated to 2-methyl-3-butan-2-ol (MBA) through *path c* or oligomerized into C-10 species through *path d*. Furthermore, MBE can be over-hydrogenated to MBA through *path b*. In this work *path d* was not observed, and was thus eliminated from the network for simplicity. In our previous study,²² the hydrogenation of MBY showed an antipathetic structure-sensitivity, suggesting at a first glance that only plane surface atoms were responsible for the catalytic activity of Pd nanocrystals, since their relative amount increases with particle size (see [Figure S1](#), Supporting Information).

The Pd nanocrystals shown in [Figure 1](#) were tested as unsupported catalysts for the water-assisted hydrogenation of MBY. In order to confirm the morphological stability of the catalysts during the reaction, cubic nanocrystals were subjected to the reaction conditions for 2.5 h and were observed with TEM immediately after. The nanocrystals maintained their shape ([Figure S5](#), Supporting Information) and, being the least favourable shape, the result could be extrapolated to the other nanocrystals.

All nanocrystals were active, thus confirming that Pd₍₁₀₀₎ present on cubes could indeed catalyze the hydrogenation of MBY. The values for MBY transformation rate and TOF are summarized in [Table 2](#). In order to evaluate the specific activities of the various types of surface atoms, two models describing the observed TOF were applied. The first activity model (A) is based on the assumption that the observed activity (TOF_{obs}) depends linearly on the fraction of each plane atom (x_i) and their specific activity (TOF_i):

$$\text{A: } TOF_{obs} = TOF_{111} \cdot x_{111} + TOF_{100} \cdot x_{100} \quad (1)$$

Edge atoms were considered to be inactive, following the results published in literature.^{6,7,19-22} As a result, the observed *size and/or shape dependence* of the nanocrystals would actually be due to the change of the relative amount of surface atoms.

Model A was first applied to CUB18 and OCT, the two samples with the highest fraction of plane atoms. [Equation \(1\)](#), together with the statistics of surface atoms from [Table 1](#), was used to estimate

TOF_{111} and TOF_{100} . From these calculations, $Pd_{(100)}$ and $Pd_{(111)}$ plane atoms were found to be almost equally active in MBY hydrogenation. The model was, however, unable to predict the observed values of TOF for CUB6 and COT. These results, together with the fact that CUB6 and COT samples present 15% and 30% of low-coordination (edge) atoms on their surfaces, suggest that a model including the latter would be able to describe the system more accurately. Since $Pd_{(100)}$ and $Pd_{(111)}$ plane atoms were found to show a similar activity, then model B was suggested as follows:

$$\text{B: } TOF_{obs} = TOF_{plane} \cdot x_{plane} + TOF_{edge} \cdot x_{edge} \quad (2)$$

The application of model B (see Table 2) simultaneously to all four samples allowed the estimation of the specific plane and edge TOFs, which were found to be $19.3 \pm 2.4 \text{ s}^{-1}$ and $4.7 \pm 0.8 \text{ s}^{-1}$, respectively. This result suggests that MBY adsorbs on all types of surface atoms, but its reactivity depends on the coordination number of the active site. Indeed, strong adsorption strengths of the electron rich alkyne on low-coordination atoms, such as edge atoms, led to a decrease in activity in the hydrogenation of 1-butyne.^{32,33} It is worth noting that model B can account for the antipathetic structure sensitivity shown in MBY hydrogenation, since an increase in size will still imply an increase in TOF_{obs} .

Selectivity towards the target product, MBE, also pointed towards the existence of two types of active sites, namely plane and edge atoms. Figure 2 shows the selectivity at 50% and 95% conversion of each sample as a function of the fraction of edge atoms on their surfaces. It can be appreciated that at 50% conversion selectivity is independent of both the size and shape of the nanocrystal. This is in line with the thermodynamic selectivity shown in alkyne hydrogenations: as long as the coverage of the alkyne is high enough, it will “block” the active sites due to its higher adsorption strength as compared to the olefinic compound.³ This observation implies that both the plane and edge sites selectively semi-hydrogenate towards MBE, only that the rate over the latter is 4-fold lower than the rate over the former.

When approaching full conversion, however, there seems to be a clear correlation between over-hydrogenation and the amount of edge atoms (Figure 2). For a given metal, the adsorption strength of the substrate varies in the same order: aromatic < olefin < diolefin < alkyne. A plot depicting the activity

of the metal as a function of the adsorption strength thus gives rise to the known “volcano” curve with the maximum located between olefins and diolefins.³³ This observation implies that an increase in the adsorption strength of the alkyne, such as adsorbing on an edge atom rather than on a plane atom, would reduce the activity, whereas an opposite trend would be observed for the olefin. Therefore, at high conversion, when the coverage of MBY becomes insufficient to ensure the blocking of all active sites, MBE can adsorb and over-hydrogenate towards MBA. The rate for over-hydrogenation of MBE should then be higher on edge sites than on plane sites. This was indeed observed at 95% conversion on CUB18 and OCT samples, which contained very few edge sites and demonstrated the lowest selectivity to MBA. These results are in line with the literature where at high dispersions, i.e., small particle size, 1-butene hydrogenation was fast, whereas hydrogenation of 1-butyne decreased sharply.³² Furthermore, the edge sites were recently suggested as possible active sites for the hydrogenation of MBE to MBA over Pd.³⁴

Figure 3 shows schematically the active sites present on each type of nanocrystal used in this work, where Pd₍₁₁₁₎ and Pd₍₁₀₀₎ plane atoms were considered as a single site (σ_1) and edge atoms were considered as another type of active site (σ_2). The reaction network for MBY hydrogenation shown in Scheme 1 can then be modified to include the observations gathered experimentally (see Scheme 2). The semi-hydrogenation of MBY proceeds through both σ_1 and σ_2 sites. The direct hydrogenation of MBY to MBA, observed even at low conversion, takes place exclusively on σ_1 sites. The over-hydrogenation of MBE to MBA, on the other hand, is catalyzed solely by σ_2 sites. Equation (2) can now be rewritten as:

$$TOF_{obs} = TOF_{\sigma_1} \cdot x_{\sigma_1} + TOF_{\sigma_2} \cdot x_{\sigma_2} \quad (3)$$

Kinetic modeling. In order to model the reaction kinetics, a Langmuir-Hinshelwood mechanism assuming two types of active sites as well as dissociative hydrogen adsorption³⁵ and bimolecular reactions between the adsorbed species was applied. The detailed derivation of the reaction rate expressions can be found in the Supporting Information. The full kinetic expressions obtained are

shown below:

$$r_1 = \frac{k_{1,\sigma_1} K_{Y,\sigma_1}^* K_{H_2,\sigma_1} C_{H_2} K_{Y,\sigma_1} C_Y}{\left(1 + K_{Y,\sigma_1} C_Y + K_{E,\sigma_1} C_E + K_{A,\sigma_1} C_A + \sqrt{K_{H_2,\sigma_1} C_{H_2}}\right)^2} \quad (4)$$

$$r_2 = \frac{k_{2,\sigma_1} K_{Y,\sigma_1}^{***} K_{Y,\sigma_1}^{**} K_{Y,\sigma_1}^* K_{H_2,\sigma_1}^2 C_{H_2}^2 K_{Y,\sigma_1} C_Y}{\left(1 + K_{Y,\sigma_1} C_Y + K_{E,\sigma_1} C_E + K_{A,\sigma_1} C_A + \sqrt{K_{H_2,\sigma_1} C_{H_2}}\right)^2} \quad (5)$$

$$r_3 = \frac{k_{3,\sigma_2} K_{Y,\sigma_2}^* K_{H_2,\sigma_2} C_{H_2} K_{Y,\sigma_2} C_Y}{\left(1 + K_{Y,\sigma_2} C_Y + K_{E,\sigma_2} C_E + K_{A,\sigma_2} C_A + \sqrt{K_{H_2,\sigma_2} C_{H_2}}\right)^2} \quad (6)$$

$$r_4 = \frac{k_{4,\sigma_2} K_{E,\sigma_2}^* K_{H_2,\sigma_2} C_{H_2} K_{Y,\sigma_2} C_Y}{\left(1 + K_{Y,\sigma_2} C_Y + K_{E,\sigma_2} C_E + K_{A,\sigma_2} C_A + \sqrt{K_{H_2,\sigma_2} C_{H_2}}\right)^2} \quad (7)$$

Equations (4-7) can be simplified by partly grouping the constants in the numerator as well as by neglecting the coverage by hydrogen³⁵ and the alkane. This diminishes the number of degrees of freedom of the system by reducing the number of adjustable parameters:

$$r_1 = \frac{k_{1,\sigma_1}^* K_{Y,\sigma_1} C_Y}{\left(1 + K_{Y,\sigma_1} C_Y + K_{E,\sigma_1} C_E\right)^2} \quad (8)$$

$$r_2 = \frac{k_{2,\sigma_1}^* K_{Y,\sigma_1} C_Y}{\left(1 + K_{Y,\sigma_1} C_Y + K_{E,\sigma_1} C_E\right)^2} \quad (9)$$

$$r_3 = \frac{k_{3,\sigma_2}^* K_{Y,\sigma_2} C_Y}{\left(1 + K_{Y,\sigma_2} C_Y + K_{E,\sigma_2} C_E\right)^2} \quad (10)$$

$$r_4 = \frac{k_{4,\sigma_2}^* K_{E,\sigma_2} C_E}{\left(1 + K_{Y,\sigma_2} C_Y + K_{E,\sigma_2} C_E\right)^2} \quad (11)$$

The mass balance for MBY, MBE and MBA are given by the following equations:

$$\frac{dC_Y}{dt} = \frac{n_{Pd}}{V} (-r_1 - r_2 - r_3) \quad (12)$$

$$\frac{dC_E}{dt} = \frac{n_{Pd}}{V} (r_1 + r_3 - r_4) \quad (13)$$

$$\frac{dC_A}{dt} = \frac{n_{Pd}}{V} (r_2 + r_4) \quad (14)$$

Equations (8-14) were solved simultaneously using Berkeley's Madonna³⁶ software with Runge-Kutta's method for differential equations. Subscripts Y, E and A refer to the alkyne, alkene and alkane, respectively. The adsorption constants K_{Y,σ_1} , K_{Y,σ_2} , K_{E,σ_1} and K_{E,σ_2} were set to be equal for all samples since the main premise of the study is that the MBY molecules interact specifically with each type of site, regardless of the size or shape of the nanocrystal. The kinetic constants, however, were varied from sample to sample (Table S2, Supporting Information). The quality of the fitting to the experimental points obtained was satisfactory in all cases, as it can be appreciated in Figure S6 in the Supporting Information.

Since it was observed that activity could be correlated to the relative amounts of plane and edge sites (Table 2), the model was pushed one step further by assuming that the kinetic constants should follow the same principle. They were thus rendered independent of the size and shape of the Pd nanocrystals by expressing them in terms of mols of surface atom of Pd (equation 15).

$$k_{j,k}^{**} = \frac{k_{j,k}^*}{D} \left[\frac{\text{mol}}{\text{mol}_{\text{surfPdS}}} \right] \quad (15)$$

where the subscripts j and k correspond to reaction path and site type, respectively, and D refers to the dispersion of the nanocrystal (see Table 1). The constant shown in equation (15) is thus expressed by total amount of surface Pd atoms, but it is not yet specific to one of the two types of sites used in this work. A further normalization with respect to the fraction of each type of site is then necessary:

$$k_{j,k}^{***} = \frac{k_{j,k}^{**}}{x_k} \left[\frac{\text{mol}}{\text{mol}_{\text{surfPdS}}} \right] \quad (16)$$

The constants obtained in this way are specific to a reaction path and active site type, but independent of the size and shape of the nanocrystals. Four specific kinetic constants were estimated and then found to satisfy all samples through equations (8-16) with errors lower than 20% (see Table 3). These values

suggest that plane sites are 3.5 times more active in the selective hydrogenation of MBY to MBE, but that this reaction can indeed take place over the edge sites as well. Furthermore, it can be seen that the consecutive hydrogenation of MBE to MBA on edge sites is kinetically favored.

The kinetics obtained for all samples were successfully modeled using this set of constants. It can be seen (Figure 4) that the fitting remains accurate despite the experimental errors and the simplifications made. The conjugation of equations (8-16) with the set of empirically obtained constants (Table 3) provides a powerful tool that allows for a full kinetic description of a Pd nanocrystal regardless of its size and shape, as long as the statistics of surface atoms can be estimated.

Optimization of size and shape for the Pd nanocrystals. Size and shape optimization is often performed by only considering *activity* as the optimization criterion.³⁴ If this approach is applied, then equation (3) can be combined with the statistics of surface for common nanocrystal shapes to yield the graph presented in Figure 5A. As expected, *shape* does not exert a considerable effect on TOF for MBY transformation since both (111) and (100) planes behave similarly. Cubo-octahedra, however, are slightly disfavored due to the larger fraction of edge atoms (or σ_2 sites), which are considerably less active in the hydrogenation of MBY relative to plane atoms (or σ_1 sites). The most significant *size effect* is observed in the 3-20 nm range, after which the reaction becomes size and shape independent with respect to TOF. Nanocrystals smaller than 3 nm in size start to lose their bulk properties^{2,25} and, consequently, the catalytic behavior may not follow the prediction. This region is depicted with dotted lines.

If, on the other hand, MBY transformation rate is referred to the total amount of Pd, then both size and shape effects change substantially (Figure 5B). While there would be no difference between cubic or octahedral nanocrystals, cubo-octahedra will be significantly less active due to their low dispersions. This difference, however, can be neglected for particles larger than 15 nm in size, after which the reaction becomes again size and shape independent. Therefore, if the activity of a catalyst is used as the only optimization criterion, either cubes or octahedra of roughly ~5 nm in size should be the best choice

for the catalyst.

Selectivity is a very, if not the most, important catalytic property for most applications. Therefore, a dual *selectivity-activity criterion* for optimization seems to be well-justified. To achieve this, we had to combine equations (8-16) with the set of empirically obtained constants (Table 3) and the statistics of surface atoms for the nanocrystals in study. This allowed us to obtain simulation curves analogous to those shown in Figures S6 and 4 for cubic, octahedral and cubo-octahedral nanocrystals with sizes in the range of 3-50 nm (Figure S7, Supporting Information). From such simulations, the selectivity towards MBE at 95% conversion can be estimated for all different nanocrystals:

$$S_E = \frac{C_E}{C_Y^0 - C_Y} \quad (17)$$

Figure 5C shows the results of the simulations. Selectivity towards MBE increases monotonically with particle size in the order cubes > octahedra > cubo-octahedra. Figure 5B and C, can be combined (Figure 5D) to simultaneously optimize selectivity and activity, showing that the reaction is indeed structure sensitive in the size range studied. In this case, the productivity of the target product is plotted against particle size for all three shapes. As a result, two optimal nanocrystals can be proposed. If the productivity of MBE is to be maximized, then cubic nanocrystals of approximately 3 nm would be the best choice. If, on the other hand, a pure selectivity criterion is judged as more appropriate, then larger cubic nanocrystals should be chosen. In this case, a compromise between productivity and selectivity must be reached.

The structure-sensitivity of a chemical reaction is specific for each catalytic system.²⁵ Therefore, such modeling-simulation approach combined with the experimental kinetic data obtained from uniform, well-defined metal nanocrystals, gives a powerful tool for *rational catalyst design* for a given chemical reaction.

CONCLUSIONS

We have studied the structure sensitivity of the water-assisted selective hydrogenation of MBY over uniform, unsupported Pd nanocrystals with different sizes and shapes. The Pd nanocrystals were prepared with cubic, octahedral, and cubo-octahedral shapes using a solution-phase method, with PVP serving as a stabilizing agent. The observed activity and selectivity suggested that two types of active sites were involved in the catalysis, which differ in coordination numbers and are located on planes and edges, respectively. A two-site Langmuir-Hinshelwood kinetic model allowed for an accurate description of the experimentally observed activity and selectivity. Semi-hydrogenation to MBE was found to occur on both types of sites, but the reactivity depended on the coordination number of the atoms. Edge atoms were 4-fold less active in the semi-hydrogenation as compared to the plane atoms. Over-hydrogenation to MBA occurred solely on the edge atoms presumably due to increased adsorption strength of the alkene. Selectivity was then linked to the fraction of edge sites on each type of nanocrystal. Kinetic simulations pointed towards ~3 nm cubic nanocrystals as an optimal catalyst for the highest productivity of MBE.

Metal nanocrystals with tuned sizes and shapes prepared via colloidal techniques can be considered as a *new generation of model catalysts*, which allow overcoming the material and pressure gaps in catalysis and complementing single crystal studies, which inherently lack the complexity of industrial catalysis. The approach shown in this work provides a powerful tool for *rational catalyst design* for industrially relevant chemical reactions under real conditions.

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ASSOCIATED CONTENT

Supporting Information Available. Statistics of surface atoms for common *fcc* crystal shapes, HRTEM imaging and particle size distribution of the nanocrystals, XPS spectra of CUB6 sample, TEM image of cubic nanoparticles after the reaction, complete Langmuir-Hinshelwood mechanism for the hydrogenation of 2-methyl-3-butyn-2-ol, kinetic modeling with one set of adsorption constants and kinetic simulations results to estimate the productivity of the target product MBE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

FIGURE CAPTIONS

Figure 1. TEM images of the PVP-stabilized Pd nanocrystals used in this work. A) 6 nm cubes, B) 18 nm cubes, C) 31 nm octahedra, and D) 5.5 nm cubo-octahedra.

Figure 2. Selectivity towards the target product, 2-methyl-3-buten-2-ol (MBE), at 50% (●) and 95% (■) conversion of MBY as a function of the amount of edge atoms.

Figure 3. Schematic illustrations of the two types of active sites involved in the hydrogenation of 2-methyl-3-butyn-2-ol (MBY). Atoms on the planes, regardless of their crystallographic orientations, constitute the first type of active site, σ_1 . Low-coordination atoms, or atoms at the edges, represent the second type of active site, σ_2 .

Figure 4. Experimental data points for 2-methyl-3-butyn-2-ol (MBY, ●), 2-methyl-3-buten-2-ol (MBE, ■), and 2-methyl-3-butan-2-ol (MBA, ▲) and the prediction curves obtained with a single set of adsorption and kinetic constants for A) CUB6, B) CUB18, C) OCT and D) COT samples. Reaction conditions: 1 g of MBY, $\text{MBY}:\text{Pd}_{\text{surf}}=140000$, 200 mL of H_2O , 60 °C, 0.3 MPa of H_2 .

Figure 5. Optimization of Pd nanocrystal size and shape based on A) TOF, B) MBY transformation rate, C) selectivity towards 2-methyl-3-buten-2-ol (MBE) at 95% conversion, and D) transformation rate, or productivity of MBE.

SCHEME TITLES

Scheme 1. General reaction network for the hydrogenation of 2-methyl-3-butyn-2-ol (MBY).

Scheme 2. Modified reaction network for the hydrogenation of 2-methyl-3-butyn-2-ol (MBY), showing the active sites involved in each path.

TABLES

Table 1. The statistics of surface atoms⁴ for the nanocrystals used in this work.

Sample	d_p [nm]	Surface statistics			
		D^a [%]	x_{111}^b [%]	x_{100}^b [%]	x_{edge}^b [%]
CUB6	6	16.7	-	72.1	15.8
CUB18	18	6.0	-	90.0	6.0
OCT	31	3.6	93.2	-	5.5
COT	5.5	18.3	43.7	5.6	30.3

^a Dispersion (%), defined as the ratio of the number of surface atoms (N_S) to the total number of atoms (N_T).

^b Fraction of surface atoms of a given type, $x_i = N_i/N_S$

Table 2. Activity^a models A and B as applied to the catalytic responses of differently shaped Pd nanocrystals to account for the structure-sensitivity of the reaction.

Sample	$-R_{\text{MBY}}$ [mol·mol _{Pd} ⁻¹ ·s ⁻¹]	TOF _{obs} [s ⁻¹]	Model A ^b			Model B ^c	
			TOF ₁₁₁ [s ⁻¹]	TOF ₁₀₀ [s ⁻¹]	TOF _{est} [s ⁻¹]	TOF _{plane} [s ⁻¹]	TOF _{edge} [s ⁻¹]
CUB6	2.55	15.3	-	19.2	13.8		
CUB18	1.05	17.5	-	19.2	17.5	19.3±2.4	4.7±0.8
OCT	0.53	14.6	15.6	-	14.6		
COT	2.25	12.3	18.4	19.2	9.1		

^a Reaction conditions: 1 g of MBY, MBY:Pd_{surf}=140000, 200 mL of H₂O, 60 °C, 0.3 MPa of H₂.

^b In this model, TOF₁₁₁ and TOF₁₀₀ were first estimated from OCT and CUB18, respectively, and then applied to CUB6 and COT samples.

^c All samples were fitted simultaneously.

Table 3. A set of constants used to model all samples simultaneously.^a

Adsorption constants [L mol ⁻¹]				Kinetic constants [mol mol ⁻¹ _{surf Pd} s ⁻¹]			
K _{Y,σ1}	K _{Y,σ2}	K _{E,σ1}	K _{E,σ2}	k ^{***} _{1,σ1}	k ^{***} _{2,σ1}	k ^{***} _{3,σ2}	k ^{***} _{4,σ2}
20.5	56.5	0.2	2.7	83.8	2.3	24.0	428.2

^a Reaction conditions: 1 g of MBY, MBY:Pd_{surf}=140000, 200 mL of H₂O, 60 °C, 0.3 MPa of H₂.

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FIGURES

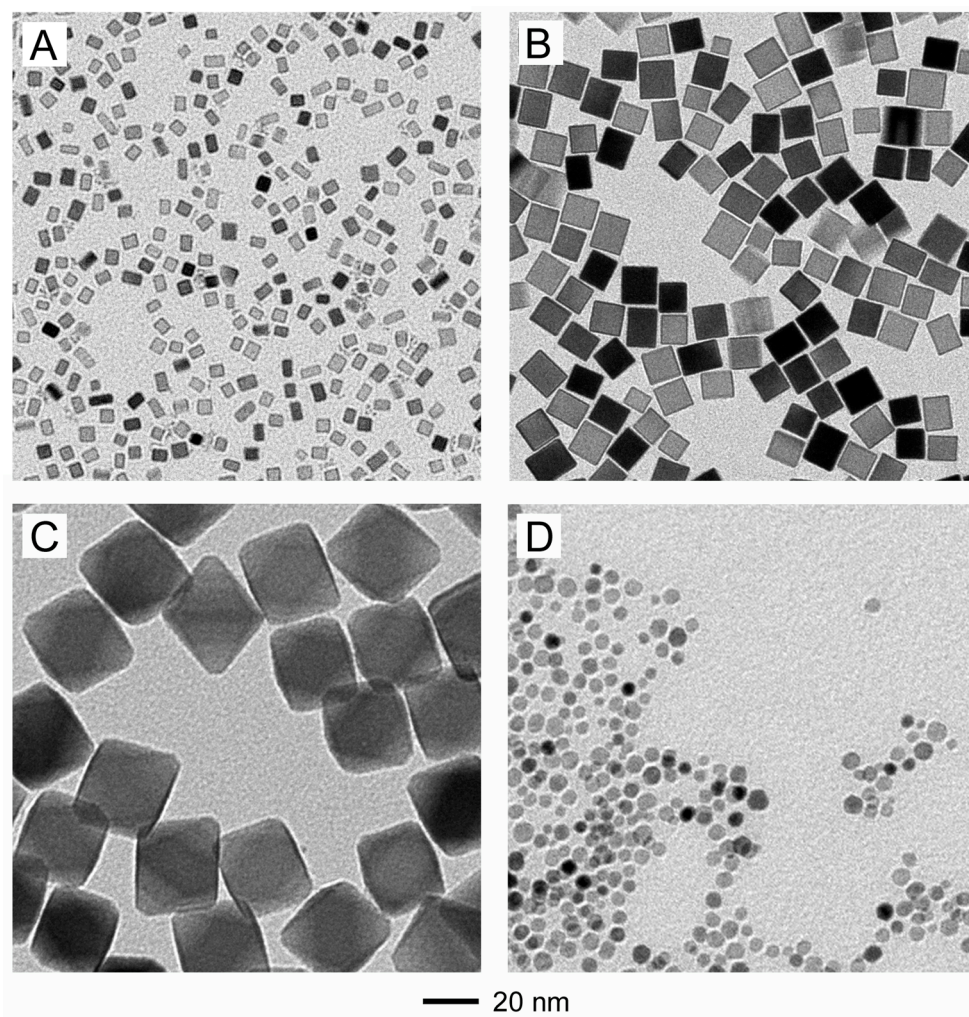


Figure 1. TEM images of the PVP-stabilized Pd nanocrystals used in this work. A) 6 nm cubes, B) 18 nm cubes, C) 31 nm octahedra, and D) 5.5 nm cubo-octahedra.

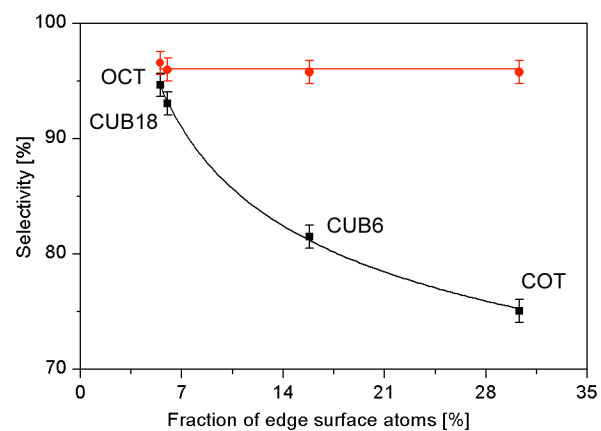


Figure 2. Selectivity towards the target product, 2-methyl-3-buten-2-ol (MBE), at 50% (●) and 95% (■) conversion of MBY as a function of the amount of edge atoms.

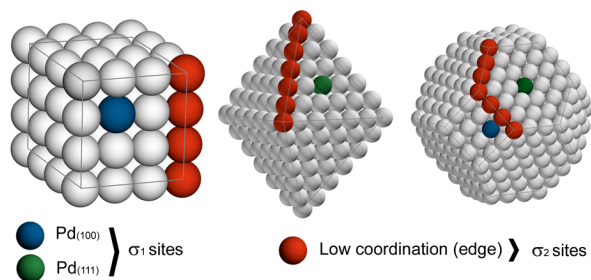


Figure 3. Schematic illustrations of the two types of active sites involved in the hydrogenation of 2-methyl-3-butyn-2-ol (MBY). Atoms on the planes, regardless of their crystallographic orientations, constitute the first type of active site, σ_1 . Low-coordination atoms, or atoms at the edges, represent the second type of active site, σ_2 .

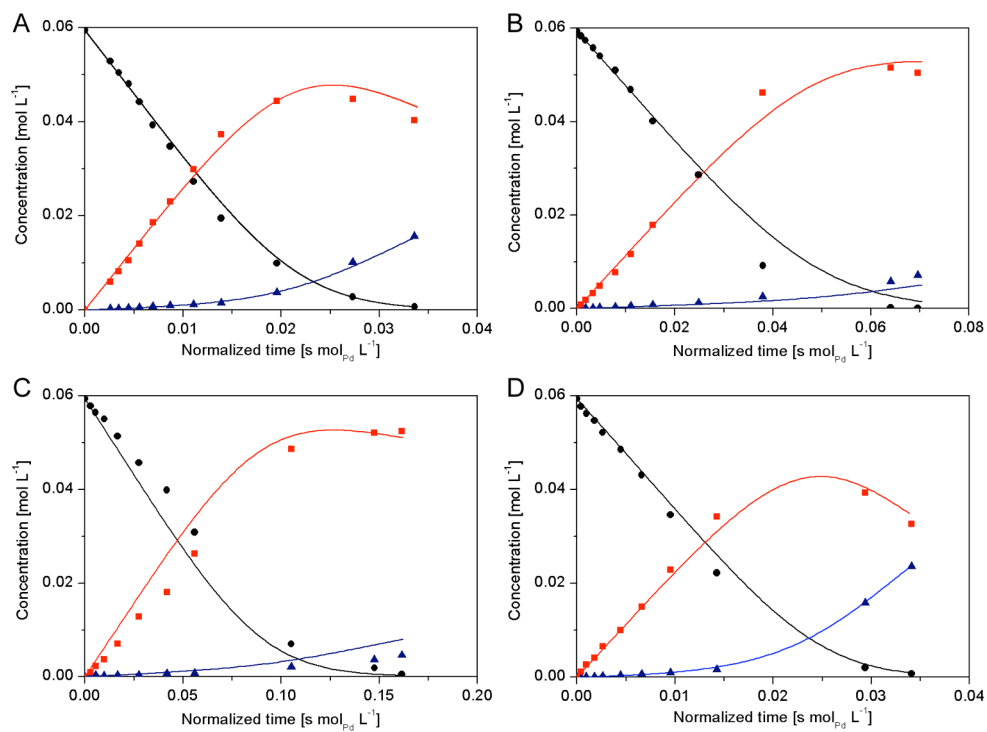


Figure 4. Experimental data points for 2-methyl-3-butyn-2-ol (MBY, ●), 2-methyl-3-buten-2-ol (MBE, ■), and 2-methyl-3-butan-2-ol (MBA, ▲) and the prediction curves obtained with a single set of adsorption and kinetic constants for A) CUB6, B) CUB18, C) OCT and D) COT samples. Reaction conditions: 1 g of MBY, $\text{MBY}:\text{Pd}_{\text{surf}}=140000$, 200 mL of H₂O, 60 °C, 0.3 MPa of H₂.

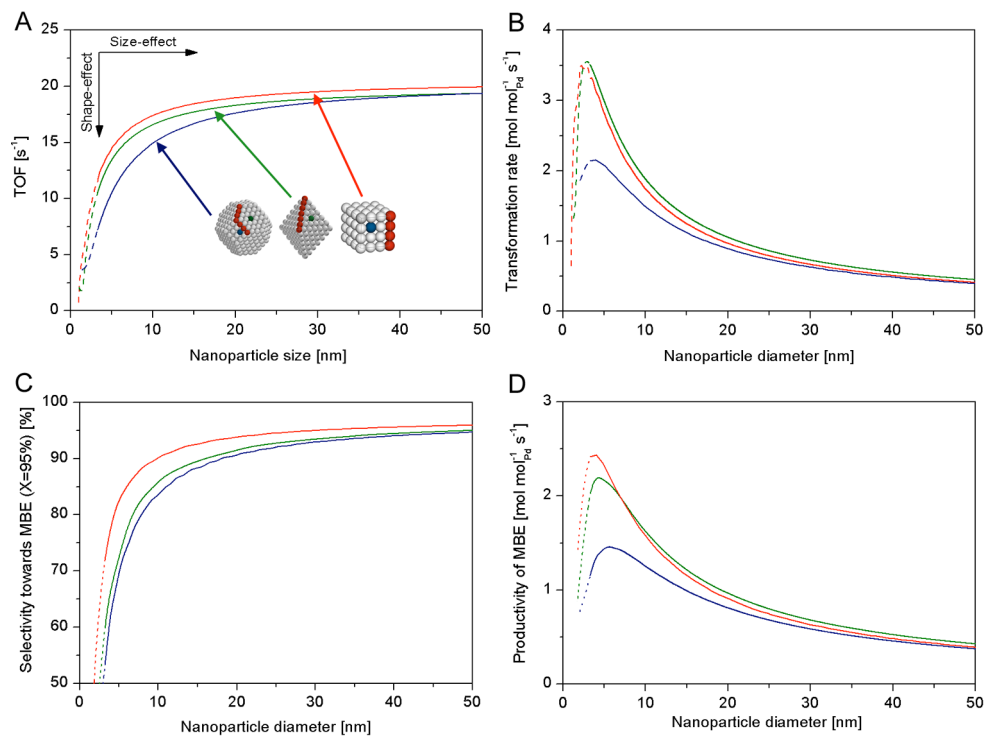
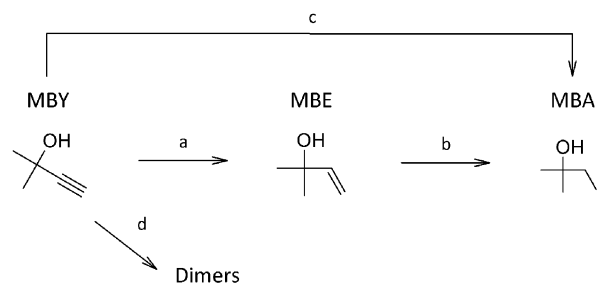
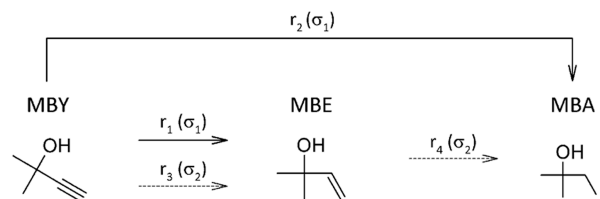


Figure 5. Optimization of Pd nanocrystal size and shape based on A) TOF, B) MBY transformation rate, C) selectivity towards 2-methyl-3-buten-2-ol (MBE) at 95% conversion, and D) transformation rate, or productivity, of MBE.

SCHEMES



Scheme 1. General reaction network for the hydrogenation of 2-methyl-3-butyn-2-ol (MBY).



Scheme 2. Modified reaction network for the hydrogenation of 2-methyl-3-butyn-2-ol (MBY), showing the active sites involved in each path.

SYNOPSIS TOC

