Abstract: We use a coordination-based kinetics model to look at the kinetics of the turnover frequency (TOF) for the oxygen reduction reaction (ORR) for platinum nanoclusters. Clusters of octahedral, cuboctahedral, cubic, and icosahedral shape and size demonstrate the validity of the coordination-based approach. The Gibbs adsorption energy is computed using an empirical energy model based on density functional theory (DFT), statistical mechanics, and thermodynamics. We calculate the coordination and size dependence of the Gibbs adsorption energy and apply it to the analysis of the TOF. The platinum ORR follows a Langmuir–Hinshelwood mechanism, and we model the kinetics using a thermodynamic approach. Our modeling indicates that the coordination, shape, and the Gibbs energy of adsorption all are important factors in replicating an experimental TOF. We investigate the effects of size and shape of some platinum polyhedra on the oxygen reduction reaction (ORR) and the effect on the mass activity. The data are modeled quantitatively using lognormal distributions. We provide guidance on how to account for the effects of different distributions due to shape when determining the TOF.

Keywords: catalysis; reaction kinetics; coordination; nanoclusters; platinum

1. Introduction

There is a long history of speculation that catalytic reactions depend on structure and shape, and thus the coordination of the catalyst [1]. Indeed, in 1985, Falicov and Somorjai proposed that coordination-sensitive edge and kink sites would be most likely to be active for structure-sensitive reactions [2]. Nanocluster synthesis has reached the stage where narrow particle size distributions of desired shapes of many elements and alloys may be achieved [3]. This allows experimentalists to fine-tune catalytic reactions so that specific shapes, sizes, and thus the coordination of the catalyst is known. We model the kinetics (turnover frequency (TOF)) of surface sites showing that they strongly depend on the shape and structure of nanoclusters.

The oxygen reduction reaction (ORR) has much application to fuel cell technology. There is previous work on the size dependence of the ORR. Shao et al. showed experimentally in 2011 that platinum nanoparticles have a maximum in the mass activity around 2.2 nm [4]. Likewise, there have been modeling efforts by Nesselberger et al. [5], Tritsaris et al. [6], and Tripkovic, et al. [7]. Somewhat more recently, Rück, et al. have determined the platinum ORR size dependence via density functional theory (DFT) [8]. Furthermore, DFT has been combined with kinetic Monte Carlo methods to look at the TOF on platinum nanoclusters [9]. We calculate the Gibbs energy using an established procedure [10] for the ORR reactions and incorporate it into the mass activity of the ORR via the TOF. This may lend insight into experimental needs of cluster morphology and its impact on the TOF.
Recently, we have determined coordination specific magic formulas for the surface sites of 19 different nanoclusters [11]. These magic formulas can assist our understanding of the coordination and size-dependent surface behavior of clusters. In the size dimension of the mesoscale, neither the atomic nor bulk apply, and much activity relies on the surface coordination of the specific cluster being studied. While the exact dimensions of the mesoscale are ambiguous, a good approximation is clusters with diameter $D \approx 5–100$ nm. DFT studies on the surface states of nanoclusters show that for $D \approx 3$ nm for gold [12], and $D \approx 2$ nm, for platinum [13], the transition from the atomic to bulk has occurred. In addition, Hoover, et al. calculate that the difference in entropy between the thermodynamic prediction and the exact entropy is less than $k_B$ (Boltzmann’s constant) when the number of atoms, $N > 400$ for classical close packed harmonic cubes [14]. This shows that quite small clusters may be modeled with thermodynamics. Similarly, an estimate of $D$ as a lower limit of the mesoscale can be made from thermal fluctuations [15]. For a cube of dimension $D$ and volume $D^3$, with $\rho_n$ atoms per unit volume, the thermal fluctuations are about $\delta T/T \approx (\rho_n D^3)^{-1/2}$. For solids and liquids, $\rho_n \approx 50/nm^3$. If we accept fluctuations of $10^{-2}$, this gives $D \approx 5$ nm.

The Gibbs adsorption energy has been calculated by a few authors using a DFT approach [16,17]. Unfortunately, the size range of interest for the TOF is rather large for DFT, and a range of sizes is required. We provide a coordination approach using an empirical energy model combined with DFT, and add statistical mechanics along with thermodynamics to complete the Gibbs adsorption energy calculation. This enables us to determine the Gibbs adsorption energy, $\Delta G$, as a function of size and coordination. By modeling clusters using a coordination approach, we are able to avoid the need for supercomputer calculations, as the computational demands are modest (only desktop models required). This is a different approach to calculating the Gibbs energy.

2. Methods

We define $G$ as the Gibbs energy of the cluster (which depends on the size), then, because of adatoms being bonded to the outer shell atoms, there is an increase in $G$ that is called the adsorption energy and is denoted as $\Delta G$. This can be split up over different coordination types of the atoms on the outer shell bonding to adatoms. We suppose a kink atom adds to the adsorption energy with an amount $\Delta G_k$. Similarly an edge atom adds $\Delta G_e$, while a facet atom contributes $\Delta G_f$ then [18]

$$\Delta G = \sum_{o \in \{f,e,k\}} \Delta G_o N_o$$  \hspace{1cm} (1)

where $N_o$ is the number of atoms in the outer shell of the indicated type. If $N_S = N_f + N_e + N_k$ is the total number of atoms in the outer shell bonded to adatoms, then this can be rewritten as

$$\Delta G = \Delta G_f \cdot (1 - f_e - f_k) + \Delta G_e \cdot f_e + \Delta G_k \cdot f_k$$ \hspace{1cm} (2)

where the edge and kink sites which have explicit coordinations for specific structures (see Table 1). Note that Equation (2) applies to adsorption to on-top sites; otherwise, not all adatoms will be bonded to atoms in the outer shell.

We have a fundamental relationship for the Gibbs energy and adsorption constant, $K_a$:

$$K_a = \exp \left( -\frac{\Delta G}{RT} \right)$$ \hspace{1cm} (3)

where $R$ is the gas constant and $T$ is the temperature in Kelvin. Bronsted–Evans–Polanyi relationships are widely used in homogeneous and heterogeneous catalysis [18,19], using a relationship for reaction constants $k$ and equilibrium constants $K$ as follows,

$$k = gK^\alpha, \hspace{1cm} 0 < \alpha < 1$$ \hspace{1cm} (4)
where \( g \) and \( \alpha \) (Polanyi parameter) are constants. The Polanyi parameter is unitless and a proper fraction, as given originally by Brønsted [20]. We then have

\[
k_a = k'_a \exp \left( -\alpha \left( f_n^e \cdot \chi_e(D_n) + f_k^k \cdot \chi_k(D_n) \right) \right),
\]

(5)

where

\[
\chi_e(D) = \frac{\Delta G_e(D) - \Delta G_f(D)}{RT}, \quad \chi_k(D) = \frac{\Delta G_k(D) - \Delta G_f(D)}{RT},
\]

(6)

and

\[
k'_a = g \exp \left( -\frac{\Delta G_f}{RT} \right).
\]

(7)

We now proceed with the explanation of the method to calculate \( \Delta G \).

In the early 1990s, DFT studies on metal clusters gave \( E(cn_i) \), the bonding energy of atom \( i \), as a function of its coordination \( cn_i \), and that led to the following empirical relationship [21],

\[
E(cn_i) = E_0 - A \cdot \sqrt{cn_i} + B \cdot (cn_i),
\]

(8)

where \( E_0 \), \( A \), and \( B \) are constants of the fit [10], see Table 2. By definition, we then have the bond energies, \( E_{ij} \), as a function of coordination:

\[
E_{ij} = \frac{1}{2 \cdot cn_B} \left( E(cn_i) + E(cn_j) \right),
\]

(9)

where \( cn_B \) is the bulk coordination, or 12 for fcc metals. For details on this model, we refer the reader to reference [10].

**Table 1.** Formulas for nanocluster shapes [11]. The variable \( n \) refers to the number of shells in the cluster, \( cn \) to standard coordination number, fcc to face centered cubic, \( N_S \) the number of surface atoms, and \( N_T \) the total number of atoms.

| \( cn \) | fcc Truncated Cube | \( cn \) | fcc Octahedron |
|---------|-------------------|---------|---------------|
| 5       | 12\( n - 12 \)    | 4       | 6             |
| 7       | 24                | 7       | 12\( n - 12 \)|
| 8       | 12\( n^2 - 12n - 18 \) | 8       | 4\( n^2 - 12n + 8 \) |
| \( N_S \) | 12\( n^2 - 6 \) | \( N_S \) | 4\( n^2 + 2 \) |
| \( N_T \) | 4\( n^3 + 3n^2 + 3n - 7 \) | \( N_T \) | \( \frac{2}{5}n^3 + 2n^2 + \frac{7}{5}n + 1 \) |
| \( cn \) | Icosahedron       | \( cn \) | fcc Cuboctahedron |
| 6       | 12                | 5       | 12            |
| 8       | 30\( n - 30 \)    | 7       | 24\( n - 24 \) |
| 9       | 10\( n^2 - 30n + 20 \) | 8,9    | 6\( n^2 - 12n + 6,4n^2 - 12n + 8 \) |
| \( N_S \) | 10\( n^2 + 2 \) | \( N_S \) | 10\( n^2 + 2 \) |
| \( N_T \) | \( \frac{10}{3}n^3 - 5n^2 + \frac{11}{3}n - 1 \) | \( N_T \) | \( \frac{10}{3}n^3 - 5n^2 + \frac{11}{3}n - 1 \) |

**Table 2.** Bond strength parameters for platinum, where \( R^2 \) is the least squares regression.

| Element | \( E_0 \) | \( A \) | \( B \) | \( R^2 \) |
|---------|-----------|--------|--------|----------|
| Pt      | 0.0       | 1.7898 | 0.0501 | 0.987    |

To allow for small deviations from the average bond length, we define \( i \) and \( j \) as nearest neighbors, and separate them from the rest by requiring that \( r_{ij} < r_c \), where \( r_c \) is a threshold value, appropriate for the nanocluster. The value for \( r_c \) must be less than the distance for second nearest neighbors and
varies with the crystal structure. For fcc crystals, \( r_c < 1.41 \cdot r_{\text{min}} \), where \( r_{\text{min}} \) is the smallest bond length [11]. Thus,

\[
A(i,j) = \begin{cases} 
1, & \text{if } r_{ij} < r_c \text{ and } i \neq j \\
0, & \text{otherwise}
\end{cases}
\]  

(10)
describes the adjacency matrix for the cluster, and

\[
E(i,j) = \begin{cases} 
 r_{ij}, & \text{if } r_{ij} < r_c \text{ and } i \neq j \\
0, & \text{otherwise}
\end{cases}
\]  

(11)
describes the Euclidean matrix for the cluster. We use an adjacency matrix and Euclidean matrix to determine the diameter, \( D \), of the nanoclusters [11], where the bond length in the clusters depends on the average coordination [22]:

\[
r(cn) = \frac{2r_B}{1 + \exp \left( \frac{12 - \langle cn \rangle_c}{8 \cdot (cn)_c} \right)}. 
\]  

(12)
Here, \( r_B \) is the bulk bond length and \( \langle cn \rangle_c \) is the average coordination of the cluster. We find a linear relationship between \( D \) and \( n \), the number of cluster shells, as shown in Table 3:

\[
D(n) = a \cdot r_B \cdot n + b. 
\]  

(13)
This relationship is derived from MATLAB code for calculating the cluster diameter.

**Table 3.** Linear constants for \( D(n) \).

|   |   | Nanocluster       |
|---|---|------------------|
| 1.722 | 0.2944 | Pt Truncated Cube |
| 1.414 | 0.0239 | Pt Cuboctahedron  |
| 1.0  | 0.0282 | Pt Octahedron     |
| 2.0  | 0.0273 | Pt Icosahedron    |

The energies of adsorbates have been shown to scale linearly with generalized coordination [23,24]. We use a DFT model for energies of adsorbates [23]:

\[
\bar{C}N_i = \sum \frac{c_{n_j} \cdot n_j}{cn_{\text{max}}} 
\]  

(14)
where the sum is over all nearest neighbors of \( i \), \( cn_{\text{max}} = 12 \) for top sites, 18 for bridge sites, and has other values for other types of sites [23]. In this equation, \( n_j \) is the number of nearest neighbors, thus each neighbor \( j \) of atom \( i \) has a weight of \( n_j/cn_{\text{max}} \) associated with the site. Adsorbate energy, \( E_{\text{ad}} \), is linear with generalized coordination [23]

\[
E_{\text{ad}} = \bar{C}N_0 + m \cdot \bar{C}N_i. 
\]  

(15)
Table 4 shows the values of the linear fits as determined by Equation (15).

**Table 4.** Linear fit of \( E_{\text{ad}} \) for adsorption.

| Species | \( \bar{C}N_0 \) (eV) | Slope \( m \) of \( E_{\text{ad}} \) vs. \( \bar{C}N_i \) |
|---------|---------------------|---------------------|
| Pt-O\(_2\) [23] | −2.418 | 0.227 |
| Pt-H\(^*\) [25] | −0.3405 | 0.0562 |
We construct our cluster-adatom Hamiltonian as follows,

$$H(i,j) \approx \begin{cases} E_{ij} & \text{i,j in the nanocluster} \\ E_{ad} & \text{for an adatom bond} \\ 0 & \text{otherwise} \end{cases}$$

(16)

with only nearest neighbor non-zero entries, i.e., a sparse matrix. In the Hamiltonian approach, the partition function is [10,26,27]

$$Z = \text{Tr} e^{-\beta H}$$

(17)

and $\beta = 1/k_B T$ is the inverse temperature, where $k_B$ is Boltzmann’s constant, $T$ is the temperature in Kelvin (we use $T = 300$ K), Tr is the trace of the following matrix, and $H$ is the Hamiltonian matrix, as given by Equation (16) [10]. The probability of each state is then $p_j = e^{\beta \lambda_j}/Z$, where $Z$ is the partition function, Equation (17), and $\lambda_j$ is an eigenvalue of the Hamiltonian matrix [27].

The Gibbs energy of adsorption in the nanoscale systems we examine is in joules (J), if we neglect the small $PV$ (pressure–volume) term, [10,26]

$$\Delta G = -RTN_n \ln Z,$$

(18)

where $Z$ is the partition function, Equation (17), and where $N_n = N_c + N_\theta$, with $N_c$ the number of atoms in the cluster and $N_\theta$ the number of adatoms at coverage theta. The Gibbs adsorption energy here is converted from more standard units by dividing by $N_\theta$ and using a conversion factor ($R/k_B$) to get units of (J/mol). We average several times over the nanocluster system, as especially for the kink sites, the statistics are low.

3. Results and Discussion

3.1. Langmuir-Hinshelwood Mechanism

In general, the TOF for reactions may display structure sensitivity which rises or decreases with size, or is not sensitive, or passes through a maximum [28]. The literature discusses several types of reactions, including a two-step sequence and its corollary, the Eley–Rideal reaction, and the Langmuir–Hinshelwood (L–H) mechanism [29]. The L–H mechanism is relevant for surface reactions [30]:

1. $A + Z \leftrightarrow ZA$ (quasi-equilibrium)
2. $B + Z \leftrightarrow ZB$ (quasi-equilibrium)
3. $ZA + ZB \rightarrow C + 2Z$

$$A + B \rightarrow C$$

(19)

where $A$ and $B$ are reactants, $C$ is the product, and $Z$ is a surface site. The reaction rate is [29]

$$v(D) = \frac{k_3 K_1 P_A K_2 P_B}{(1 + K_1 P_A + K_2 P_B)^2},$$

(20)

where we have

$$K_1(D) = K_A \exp \left\{ -\left(f_e \cdot \chi_A^e(D) + f_k \cdot \chi_A^k(D)\right) \right\},$$

(21)

$$K_2(D) = K_B \exp \left\{ -\left(f_e \cdot \chi_B^e(D) + f_k \cdot \chi_B^k(D)\right) \right\},$$

(22)

where $k_3$ is the reaction rate constant for sequence 3 (see (19)), $P_A$ and $P_B$ are partial pressures or concentrations (for liquids) of $A$ and $B$, and for reaction 3 we have

$$k_3(D) = K_C \exp \left\{ (1 - \alpha) \left(f_e \cdot \chi_e^e(D) + \chi_e^k(D)\right) + f_k \cdot \left(\chi_k^e(D) + \chi_k^B(D)\right) \right\}. $$

(23)
After some simplification we get

\[
v(D) = \frac{p_1 \exp \left\{ (-\alpha) \left[ f_n^A \chi_n^A(D) + f_n^B \chi_n^B(D) \right] \right\}}{1 + p_2 \exp \left\{ -f_n^E \chi_n^E(D) + f_n^k \chi_n^k(D) \right\} + p_3 \exp \left\{ -f_n^E \chi_n^E(D) + f_n^k \chi_n^k(D) \right\}}
\]

(24)

where \(p_1\) is a frequency and \(p_2, p_3\) are related to the rate constants and partial pressures of A and B [18,29]. Here, \(n\) refers to the dependence on complete shells of nanoclusters. As we are not aware of other analysis of the data, we use \(\alpha\) and the \(p_i\) as adjustable parameters. In principle, there are more experimental parameters (Polanyi parameter, kinetic constants, and partial pressures or concentrations) depending in a complicated way on the analysis than we use to model the data. We find that \(\alpha\) affects the full width half maximum, FWHM, \(p_1\) affects the peak intensity, and \(p_2, p_3\) affect the center of the peak position.

3.2. Pt ORR

For modeling the platinum mass activity, we assume the \(O_2\) and \(H^*\) react in a Langmuir–Hinshelwood mechanism (see (19)), and separate the kink, edge, and facet bonding as shown in Figure 1, below. We use platinum polyhedra of icosahedra, truncated cubes, octahedra, and cuboctahedra in our modeling, see Figure 1.

The ORR follows a L–H mechanism as shown in (25):

1. \(O_2 \rightarrow 2O_{ads}\)
2. \(H_2 \rightarrow 2H_{ads}\)
3. \(2H_{ads} + O_{ads} \rightarrow H_2O\)

\[2H_2 + O_2 \rightarrow 2H_2O\]

(25)

so that in the general scheme of Equation (19) above A is \(O_2\) and B is \(H_2\). We also assume the Polanyi constants are equal. We calculate the corresponding \(\chi_e\) and \(\chi_k\) as used in the TOF from Equation (24), for the various polyhedra as shown in Figure 2 below.

![Figure 1. Kink (row 1), edge (row 2), and facet (row 3) bonding of \(O_2\) to platinum clusters.](image-url)
Figure 2. Plots of $\chi_e$ and $\chi_k$ versus $D$ for the four polyhedra. In all four plots, the data for H-Edge and H-Kink overlap on the scale presented. (A) octahedra; (B) cubo-octahedra; (C) truncated cubes; (D) icosahedra.

The mass activity is basically the product of the dispersion and the TOF [31]

$$MA_{Pt} = \frac{F N_S \nu(D)}{AW_{Pt}} N_T \times 10^3 \text{ (A/mg$_{Pt}$)}$$

(26)

where $F$ is the Faraday constant, 96,485 C/mol, and $AW_{Pt}$ is the atomic weight of platinum, 195.08 g/mol. In principle, this gives an exact form of the mass activity, but the kinetic constants and corresponding concentrations are not completely known. We use $\alpha$ and the $p_i$ as modeling parameters and optimize the mass activity for the various clusters. We are not aware of previous modeling of the mass activity using the TOF, or Equation (26).
In the original paper on the experimental data of the mass activity for platinum clusters, it was assumed that the nanoclusters had cuboctahedral shape [4]. In Figure 3A, we plot the mass activity versus $D$ for cuboctahedra. The modeled tail of the distribution decays more rapidly than the experimental data. This tells us that the cuboctahedral modeling has a narrower distribution than that observed experimentally. However, if we presume that the experimental mass activity is composed of multiple components from several polyhedra and that the sum from the convolution of the component polyhedra results in an approximation of the experimental curve, we get Figure 3B. Here, we model the data with a lognormal distribution with parameters as tabulated in Table 5, while the polyhedra are approximated by cubic splines.

![Figure 3. (A) Mass activity for cuboctahedra. (B) Mass activity versus $D$ for adsorption on platinum polyhedra.](image)

**Table 5.** Mean, $\mu$, and standard deviation, $\sigma$, for the platinum oxygen reduction reaction (ORR) mass activity for Figure 3, using a lognormal distribution.

| Structure                      | $\mu$ | $\sigma$ |
|--------------------------------|-------|----------|
| Exp Fit                        | 2.46  | 0.77     |
| Cuboctahedron Figure 3A        | 2.31  | 0.38     |
| Sum Figure 3B                  | 2.77  | 0.88     |

To account for several shapes with independent distributions, we sum over the morphology

$$v(D) = \sum_i \rho_i \cdot v_i(D),$$  \hspace{1cm} (27)

where $i$ is one of the four shapes; octahedra, cuboctahedra, truncated cube, or icosahedra. The shape parameters for the platinum TOF are shown in Table 6.
Table 6. Shape parameters for the platinum turnover frequency (TOF) via the Langmuir–Hinshelwood (L–H) mechanism.

| Structure      | $\alpha$ | $p_1$       | $p_2$       | $p_3$       |
|----------------|----------|-------------|-------------|-------------|
| Octahedron     | 0.05     | $1.0 \times 10^{-10}$ | $1.0 \times 10^{-13}$ | $1.0 \times 10^{-13}$ |
| Truncated Cube | 0.05     | $5.0 \times 10^{-2}$  | $5.0 \times 10^{-7}$  | $5.0 \times 10^{-7}$  |
| Icosahedron    | 0.05     | $1.0 \times 10^{-2}$  | $1.0 \times 10^{-18}$ | $1.0 \times 10^{-18}$ |
| Cuboctahedron  Figure 3A | 0.05     | $5.0 \times 10^{-2}$  | $1.0 \times 10^{-10}$ | $1.0 \times 10^{-10}$ |
| Cuboctahedron  Figure 3B | 0.05     | $2.5 \times 10^{-2}$  | $1.0 \times 10^{-10}$ | $1.0 \times 10^{-10}$ |

If the assumption that the experimental platinum mass activity comes from cuboctahedra is valid, then the calculated curve in Figure 3A is what we find using these procedures. However, if we assume all the polyhedra contribute to the convolution of the experimental curve, good agreement is found for the platinum mass activity for the four polyhedra considered, Figure 3B. The L–H mechanism represents the TOF for platinum nanoclusters fairly well.

Alternatively, the mass activity may be calculated using a kinetic model [7] as

$$MA_{Pt} = j_s \cdot A_{sp}, \quad j_s = \sum_j f_j \cdot \exp(-\Delta G_f^2/(k_B T)), \quad A_{sp} = A_s/m_p = \frac{A_s \cdot N_A}{AW_{Pt} \cdot N_T},$$

where $j_f$ is 96 and 83 mA/cm$^{-2}$ for (111) and (100) surfaces, respectively, $N_A$ is the Avogadro number, $A_s$ is shown in Table 7, and $\Delta G_f^2 = 0.10$ eV or 0.12 eV, for (111) or (100) surfaces, respectively, is the DFT calculated free energy barrier for ORR at 0.9 V.

Table 7. Surface area $A_s$ for the polyhedra, where $r_B$ is the bond length for platinum.

| Structure      | $A_s$                  |
|----------------|------------------------|
| Octahedron     | $2\sqrt{3} \cdot (n \cdot r_B)^2$ |
| Truncated Cube | $12(n \cdot r_B)^2$    |
| Icosahedron    | $5\sqrt{3}(n \cdot r_B)^2$ |
| Cuboctahedron  Figure 3A | $(6 + 2\sqrt{3}) \cdot (n \cdot r_B)^2$ |

The specific activity (SA) of single crystal surfaces is known [5], however modeling the SA based on specific surface orientations and the surface dispersion is problematic as assumptions need to be made with respect to the non-contribution of edge and kink sites. In general, the SA follows a trend of facet dispersion [4]. The specific activity is defined as follows,

$$SA = \sum_{o \in \{f,x,k\}} f_o \cdot SA_{Pt(hkl)} \text{ (mA/cm}^2_{Pt})$$

where $SA_{Pt(hkl)}$ comes from single crystal surfaces and $f_o$ from Table 1. If one assumes that the edge and kink sites make a negligible contribution, then the SA follows the facet trend.

In Figure 4 below, we plot the surface dispersion $D_s = (N_e + N_k) / N_S \cdot 100\%$ for the four shapes from the equations in Table 1. As can be seen from the data, the surface dispersion is similar for the octahedron and cuboctahedron, and somewhat less for the truncated cube. The icosahedron has a somewhat larger surface dispersion due to the $30n$ factor in the edge sites from Table 1. On the other hand, octahedra have kink sites with coordination $cn = 4$, which is smaller than the other polyhedra.
4. Conclusions

This work represents the computational modeling of the mass activity for the platinum ORR based on a summed contribution of polyhedral distributions. The summed lognormal modeling represents the data reasonably well. These results confirm that coordination, shape, and $\Delta G$ have dramatic influence on the catalysis of reactions. The data is made quantitative through modeling with a lognormal distribution. We provided guidance on accounting for different distributions of the TOF based on morphology. We hope these results encourage further experimental work and theoretical modeling. In particular, the Polanyi parameter, the kinetic constants, and the partial pressures or concentrations are not known, and these results could in principle lead to a catalytic derivation from fundamental data.

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