A Theory-Guided X-ray Absorption Spectroscopy Approach for Identifying Active Sites in Atomically Dispersed Transition-Metal Catalysts

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ABSTRACT: Atomically dispersed supported metal catalysts offer new properties and the benefits of maximized metal accessibility and utilization. The characterization of these materials, however, remains challenging. Using atomically dispersed platinum supported on crystalline MgO (chosen for its well-defined bonding sites) as a prototypical example, we demonstrate how systematic density functional theory calculations for assessing all the potentially stable platinum sites, combined with automated analysis of extended X-ray absorption fine structure (EXAFS) spectra, leads to unbiased identification of isolated, surface-enveloped platinum cations as the catalytic species for CO oxidation. The catalyst has been characterized by atomic-resolution imaging and EXAFS and high-energy resolution fluorescence detection X-ray absorption near edge spectroscopy. The proposed platinum sites are in agreement with experiment. This theory-guided workflow leads to rigorously determined structural models and provides a more detailed picture of the structure of the catalytically active site than what is currently possible with conventional EXAFS analyses. As this approach is efficient and agnostic to the metal, support, and catalytic reaction, we posit that it will be of broad interest to the materials characterization and catalysis communities.

1. INTRODUCTION

Atomically dispersed metals on reducible (CeO₂, TiO₂, Fe₃O₄) and nonreducible (Al₂O₃, MgO, ZrO₂) metal oxide supports have drawn considerable attention recently as catalysts for a wide range of reactions including CO oxidation, water–gas shift, and other oxidations and reductions. These catalysts offer the advantages of maximum accessibility of the metals, which are often expensive (e.g., platinum, palladium, iridium, rhodium), and have catalytic properties distinct from those of the conventional supported metal clusters and nanoparticles. Like most single transition-metal (TM) atoms in organometallic complexes, those on metal oxide supports are positively charged, having properties that are strongly influenced by their surroundings. These surroundings (bonding environments) are challenging to identify because the support surfaces are inherently heterogeneous. Even when the most incisive experimental methods are used (e.g., aberration corrected scanning transmission electron microscopy (STEM), X-ray absorption spectroscopy (XAS), and probe molecule experiments with spectroscopies), the results often provide only average structural models of the dominant metal bonding environment; the possible contributions of minority catalytic species are often overlooked.

Common research approaches involve using experimentally determined structure parameters (e.g., bond lengths and coordination numbers from extended X-ray absorption fine structure (EXAFS) spectroscopy) with complementary information characterizing local geometry and electronic structure from X-ray absorption near-edge structure (XANES) spectra. These techniques are often combined to create plausible atomistic models that are subsequently investigated using density functional theory (DFT) calculations to derive quantitative structural and mechanistic insights. More recent approaches have benefited from...
We emphasize that, as conventionally practiced, the initial development of atomistic models relies predominantly on thorough EXAFS modeling, which is often quite demanding and time intensive for the user, especially when multiple scattering paths are considered. Today’s “hands-on” EXAFS modeling approaches fall short of determining the existence of multiple metal bonding environments—a central limitation in the field. Moreover, structures inferred for the sites may not be consistent with all the complementary experimental results. As atomically dispersed catalysts continue to be reported for new reactions, there is a clear potential scientific benefit to developing computationally guided approaches for characterization of these materials, specifically, for the quantitative identification of the metal site environment(s).

As a point of departure from reported investigations, we now describe a theory-led workflow for characterizing atomically dispersed supported metal catalysts. Our approach combines state-of-the-art characterization techniques (high-angle annular dark field (HAADF) STEM, EXAFS spectroscopy, and high-energy resolution fluorescence detection (HERFD) XANES spectroscopy) with DFT-level theory for critical identification of the local environments for a prototypical catalyst—atomically dispersed platinum cations on MgO (Pt/MgO). We chose MgO as a prototypical support because it (a) is nonreducible, (b) consists of low-atomic-number elements for excellent contrast with platinum atoms in STEM, and (c) is available as robust, high-area crystalline materials used in industrial catalysts.5,10 Crystalline MgO supports are expected to present limited numbers of sites for stable anchoring of isolated metal atoms, making Pt/MgO an excellent test case to exemplify our methodology.

Figure 1a is a summary of our strategy that combines microscopy and conventional EXAFS analysis (sections 2.1 and 2.2), large-scale DFT calculations (section 2.3), automated DFT-based EXAFS analysis (section 2.4), and FEFF-XANES spectroscopy (section 2.5) to characterize Pt/MgO and identify the structure most consistent with data obtained through all the complementary techniques. As shown throughout this report, the outcome of this approach, represented as a radar plot (Figure 1b, details in Table S1), identifies subsurface platinum sites within MgO (denoted Pt°/[100]Mg-vac) to be the most populated sites for platinum atoms for this material. Although the approach is applied for atomically dispersed Pt/MgO (section 2.6), we emphasize that
the strategy is agnostic to the metal, the oxide support, and the reaction. Moreover, this approach can be extended to simultaneously fit multiple DFT structures to the experimental EXAFS. To our best knowledge, this work flow is unique in the field and represents a significant step toward the goal of comprehensive, validated integration of theoretical and experimental methods to describe the structure and catalytic function of isolated noble metal cations stabilized by a metal oxide support.

2. RESULTS

2.1. Synthesis and Structural Characterization. Atomically dispersed platinum on MgO, prepared from ethanol–water solutions of K₂PtCl₄ and slurried MgO powder, was calcined at 700 °C. Low platinum loadings (∼0.05 wt %) were used to minimize the number of different support sites that the platinum atoms occupy. X-ray diffraction (XRD) patterns and TEM images show that MgO was present as the cubic phase consisting of approximately 200 nm diameter crystallites; there was no XRD evidence of metallic platinum (Figure S1). The calcined MgO was highly dehydroxylated, with only a weak OH band in the infrared (IR) spectrum, at 3741 cm⁻¹ (Figure S2). HAADF-STEM images show atomically dispersed platinum in the absence of clusters or nanoparticles (Figure 2, Figure S3). The bright spots in yellow circles (Figure 2a) show isolated platinum atoms on Mg columns in the (110) projection.¹⁸ Intensity profiles along the X–Y line in Figure 2b (Figure 2c) confirm the isolation of the platinum atoms.

2.2. Conventional EXAFS Analysis. Pt L₃-edge EXAFS spectra were modeled in Artemis¹⁹ using traditional methods. The best-fit model comprises three scattering paths: Pt−O (2.05 ± 0.01 Å), with a coordination number (CN) of 6.7 ± 0.8, and two Pt−Mg (3.01 ± 0.04 and 3.15 ± 0.04 Å), with a total CN of 11 (Figures S4–6, Tables S2–4). Addition of a Pt−Pt scattering path (expected at ∼2.7 Å for Pt₀ clusters) resulted in nonmeaningful results,²⁰ confirming the atomic dispersion of platinum demonstrated by HAADF-STEM. The continuous Cauchy wavelet transform (CCWT) heatmap of the sample (Figure S7a) shows two main scattering features arising from short and long distances.²¹ This analysis provides evidence that the longer features at 5 Å⁻¹ arise from a lower-Z scattering atom than platinum (i.e., magnesium) as it does not match the features of the CCWT for platinum metal (Figure S7b). The scattering feature with a short-distance, low-Z scattering component was best-modeled as a Pt−O path. The higher R (distance) component was modeled as two Pt−Mg paths at longer distances.

This conventional analysis of the modeled EXAFS data is insufficient to determine more than a single average, best-fit structure. Thus, it is difficult to define the actual bonding site. To address the possible presence of more than one significant supported platinum species and to exhaustively examine the possible platinum bonding environments, we developed an
automated, DFT-based workflow for EXAFS data fitting that reduces user intervention and thereby improves the objectivity of the data interpretation. We denote this methodology as the QuantEXAFS approach, a term that emphasizes the quantitative nature of our fitting (using hundreds of unique paths) based on structures derived from quantum chemistry calculations (i.e., DFT for the Pt/MgO system).

2.3. Comprehensive Library of DFT-Optimized Structures. We used a theory-guided characterization approach to elucidate the local platinum bonding environment—that is, using DFT calculations (PBEsol functional, implemented in VASP)\(^22\) to create a comprehensive library of all plausible Pt/MgO structures. As summarized in Figure 3a–c, we considered three representative MgO facets (terrace sites: [100], Mg vacancy terrace sites: [100]\(^{\text{Mg-vac}}\), step sites: [310]), various adsorbates (*O, *O\(_2\)\), vacancy types (\(\text{O}_\text{vac}^\text{Mg}\), \(\text{Mg}^\text{vac}\)), and subsurface platinum locations.\(^23\) The platinum sites are denoted according to the MgO facet, the platinum atom location, and any adsorbates or vacancies. For example, [100]\(^{\text{Mg-vac}}/\text{sub1}\) refers to a 100 facet with the platinum atom located in the first subsurface site next to a magnesium vacancy. These structures spanning a wide range of local platinum environments were used to construct the temperature-dependent phase diagram (using pMuTT, harmonic approximation for vibrational entropy) for each site.\(^23\) We chose to analyze each facet separately as the mechanism of platinum bonding for \([100]\) facets is different from that in the \([100]\) facet, platinum substitution in the first subsurface layer (0.8 eV less stable, [100]\(^{\text{Mg-vac}}/\text{sub0}\)) or the second subsurface layer (0.3 eV less stable, [100]\(^{\text{Mg-vac}}/\text{sub2}\)) (Figure 3d–f). These computational results are based on the PBEsol functional; similar calculations with other functionals (RPBE/D3(BJ) and PBE/D3(BJ)) did not qualitatively change the trends (Figure S8).

2.4. QuantEXAFS: Automated DFT-Based Workflows for Fitting EXAFS Data with Improved Thoroughness and Objectivity. Although conventional EXAFS modeling indicates high Pt–O and Pt–Mg CNs and the absence of a Pt–Pt contribution, this “hands-on” approach is limited to analyzing a few plausible, average scattering paths and does not identify a specific bonding configuration. This approach is therefore not sufficient to characterize the possible anisotropy of the individual Pt–O and Pt–Mg contributions. To overcome this limitation, we used the open-source X-ray analysis package Larch to perform EXAFS analysis of all 47 DFT-optimized structures mentioned above.\(^26\)

The DFT-optimized structures were used “as-is” in the fitting, with fixed CNs and spatial orientations of magnesium and oxygen atoms in the fitting. In contrast to the typical approach whereby the average nearest-neighbors fits (described by the average bond lengths and CNs) are used to create structural models, we considered all relevant scattering paths (>250 in some cases) for each DFT-optimized structure. Notwithstanding the increased sophistication of the QuantEXAFS approach, it provides a typical EXAFS fit for each candidate structure in a few minutes, without user intervention. As the contribution of each scattering path to the total EXAFS depends on various parameters, it is important to limit the total number of variables in the fitting. This efficiency is achieved by (1) hierarchically classifying the individual paths into distinct categories based on their effective scattering distances (\(R_{\text{eff}}\)) and the identity of the scattering atom (if \(R_{\text{eff}} < 3.2 \text{ Å}\)) and (2) limiting the number of EXAFS variables optimized across each category. Specifically, for each DFT-optimized structure, our algorithm uses the following EXAFS fitting parameters:

(a) one energy alignment parameter (denoted as \(\Delta E_0\)); a single value is used for all paths

(b) three distance scaling parameters, \(\alpha_1\), \(\alpha_2\), and \(\alpha_3\) one each for three different \(R_{\text{eff}}\) ranges, where \(R_{\text{eff,optimized}} = \alpha_i \times R_{\text{eff, DFT}}\)

(c) five mean square variations in path lengths that depend on the scatterer identity (e.g., \(\sigma_{\text{Pt-Mg}}\) and \(\sigma_{\text{Pt-O}}\) if \(R_{\text{eff}} < 3.2 \text{ Å}\)) and the effective scattering distance (e.g., \(\sigma_1^2, \sigma_2^2, \sigma_3^2\))

The hierarchical classification is summarized in Figure 4 and Table 1. The details of this approach and the strategy of this categorization are discussed in the Supporting Information.

The scattering path classification scheme described above ensures that (1) the constraints on the number of fitting parameters (calculated on the basis of the Nyquist criterion) are not violated and (2) physically relevant characteristics of scattering paths (e.g., different mean square variations in path length, that is, \(\sigma_{\text{Pt-Mg}}\) and \(\sigma_{\text{Pt-O}}\) for Pt–Mg and Pt–O scatters) are faithfully captured. The DFT structures serve as constraints making the EXAFS fitting more physically reasonable: They reduce the number of overall parameters that are needed for large numbers of paths to enable the modeling of the longer effective scattering distances (∼5 Å), including contributions from multiple scattering paths using distance-dependent fitting parameters (e.g., \(\sigma_i\) and \(\alpha_i\)) without overfitting the data. These points are illustrated by our analyses for the [100]\(^{\text{Mg-vac}}/\text{sub1}\) site (Figure 5d). As shown in Figure 4, only the parameters listed in Tables 1 and 2 are used to model all 158 unique scattering paths.
This interplay between thermodynamic stability of a structure and its consistency with the EXAFS data is quantitatively illustrated by comparing the quality of the EXAFS fits with the DFT-calculated Boltzmann fractions (at 300 °C) (Figure S5b). Unsurprisingly, only the most stable structures ([100]/sub0/*O/sub2 (orange circle), [100]/Mg/vac/sub1 (blue circle), and [310]/pos1/*O/sub2 (green circle)) were observed in any significant number (based on Boltzmann distributions). The EXAFS fits corresponding to the three stable platinum configurations (Figure S5c-e) are presented in Figure S5f-h, showing that the [100]/Mg/vac/sub1 (CN/subPt−O = 6, CN/subPt−Mg = 11) model agrees most closely with experiment. Specifically, although the [100]/sub0/*O/sub2 structure agrees satisfactorily with the Pt−O scattering path (CN/subPt−O = 7), the Pt−Mg path is underestimated, corresponding to the much lower Pt−Mg contribution (CN/subPt−Mg = 8). We emphasize that the [310]/pos3 site (as suggested by Sarma et al.27) has coordination numbers similar to those characterizing [100]/Mg/vac/sub1, but it does not agree well with the EXAFS data (Figure S10). These results demonstrate that both the effects of coordination number (i.e., [100]/sub0/*O/sub2 vs [100]/Mg/vac/sub1) and the local spatial orientation of the scattering atoms (i.e., [310]/pos3 vs [100]/Mg/vac/sub1) are captured in our EXAFS fitting approach.

At this stage, it is useful to highlight an additional advantage of our EXAFS fitting procedure, with [100]/Mg/vac/sub1 used as an illustrative example. Instead of using the average Pt−O (and/or Pt−Mg) distances and coordination numbers as the fitting parameters (as is done conventionally), in our approach each individual Pt−O (total 6 for [100]/Mg/vac/sub1 as an example) and Pt−Mg (total 11) scattering path is considered separately. This procedure allows us to capture the anisotropies of the local bonding environment, as indicated by the DFT-calculated bond lengths. Overall, we considered 158 total paths, which included single, double, and multiple scattering paths (involving up to five scattering atoms), using only nine fitting variables (Tables S1 and S2) to achieve unprecedented agreement with the experimental EXAFS across the entire R range (Figure S5g).

As the entire workflow relies on physically motivated models, it is possible to bolster the self-consistency between DFT structures and EXAFS fits. Beyond providing good models for the EXAFS fits, the DFT calculations also provide force constants that can be used to generate ab initio vibrational mean-square relative displacements for the EXAFS (i.e., ς²).28−30 Specifically, the values for ς² for Pt−Mg (0.005 Å²) and Pt−O (0.003 Å²) obtained from DFT-calculated harmonic frequencies are consistent with the results of the EXAFS fitting (Pt−Mg: 0.0067 ± 0.001 Å², Pt−O:

More broadly, the classification scheme in Figure 4 creates a 1:1 mapping between a DFT-optimized structure and the resultant EXAFS fit. Specifically, we focus on the physical structure of the platinum site and not on the optimization of the averaged scattering paths. This is the central difference between the QuantEXAFS methodology and conventional EXAFS fitting.

The above fitting workflow was repeated for each unique DFT structure. In addition to the reduced-χ² metric (commonly used by the XAS community), we quantified the agreement between the experimental and simulated EXAFS spectra for each DFT structure by using the Fréchet distance in R-space for the magnitude portions of the data and the model (denoted as δ₀, which measures the similarity between two curves). The histogram in Figure 5a shows the reduced-χ² of the EXAFS fit corresponding to each DFT structure, along with the Fréchet distance (a lower value is better), corresponding to each structure (Table S6). In general, we observed that the [100]/Mg/vac/sub1 structures (blue bars in Figure 5a) are in better agreement with experiment (reduced-χ² < 20, δ₀ < 2) than the others. Although some of the [100] and [310] platinum configurations (e.g., [100]/sub1 and [310]/pos3/ *O/sub2) show satisfactory agreement with experimental EXAFS (reduced-χ² < 35, δ₀ < 4.5), our DFT calculations show these configurations to be highly unstable (1.5 and 0.99 eV, respectively).

Table 1. Summary of Hierarchical Approach Used to Classify All Possible Scattering Paths into Five Different Categories

<table>
<thead>
<tr>
<th>Category</th>
<th>Classification criterion</th>
<th>Number of paths</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R/subg−O &lt; 3.2 Å and Pt−O scattering path</td>
<td>6</td>
<td>a₁, ς₁/subPt−O</td>
</tr>
<tr>
<td>2</td>
<td>R/subg−Mg &lt; 3.2 Å and Pt−Mg scattering path</td>
<td>11</td>
<td>a₂, ς₂/subPt−Mg</td>
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<tr>
<td>3</td>
<td>3.2 Å &lt; R/subg−O &lt; 4 Å</td>
<td>41</td>
<td>a₃, ς₃</td>
</tr>
<tr>
<td>4</td>
<td>4 Å &lt; R/subg−O &lt; 4.5 Å</td>
<td>58</td>
<td>a₄, ς₄</td>
</tr>
<tr>
<td>5</td>
<td>4.5 Å &lt; R/subg−O &lt; 5 Å</td>
<td>42</td>
<td>a₅, ς₅</td>
</tr>
</tbody>
</table>

*Only nine parameters (shown in red) were optimized in the automated EXAFS analyses.*

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Figure 4. Flowchart for hierarchically classifying all the possible paths into categories. The underlined numbers show the number of paths in the hierarchical classification approach, and the text in red identifies fitted parameters.
This point highlights the uniqueness of our approach: (1) the DFT-optimized structures are used to perform an objective, thorough EXAFS fitting and (2) the EXAFS fitting parameters (themselves determined using the automated Python workflows) are consistent with independently calculated thermal disorders (from DFT vibrations). This level of detail has not been reported for any atomically dispersed catalysts, and we posit that the method represents a significant step forward in automated analysis, self-consistent interpretation of EXAFS data.

2.5. XANES Evidence of Structure. In addition to the EXAFS, we also consider the XANES data (Figure S11; data characterizing reference compounds are shown for comparison). XANES spectra provide evidence of the platinum electronic structure, as the intensity of the white line at the platinum L3 edge is a measure of the unoccupied d-states and occupied p-states (2p3/2 → 5d3/2 or 5d5/2). The oxidation state of the supported platinum is close to that of Pt4+ in H2Pt(OH)6 and markedly different from that of the Pt2+ in (Pt(acac)2) (acac = acetylacetonato, [C5H7O2]−) and Pt0 in (Figure 5).

Table 2. Optimized Values of the Nine Fitting Parameters for the [100]Mg-vac/sub1 site

<table>
<thead>
<tr>
<th>Category</th>
<th>ΔE (eV)</th>
<th>c²</th>
<th>10² x c² (Å²)</th>
<th>Reff_optimized (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8 ± 1.9</td>
<td>0.994 ± 0.005</td>
<td>3.2 ± 1.0</td>
<td>2.01, 2.01, 2.02, 2.03, 2.04, 2.05</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>6.7 ± 1.6</td>
<td>2.96, 2.97, 2.98, 2.98, 2.99, 3.00, 3.00, 3.01, 3.01, 3.02</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.987 ± 0.011</td>
<td>6.3 ± 7.0&quot;</td>
<td>3.40 - 3.79&quot;</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>6.2 ± 5.4&quot;</td>
<td>4.02 - 4.40&quot;</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.996 ± 0.001</td>
<td>5.3 ± 4.3&quot;</td>
<td>4.59 - 4.98&quot;</td>
<td></td>
</tr>
</tbody>
</table>

*Details of each individual scattering path are presented in the Supporting Information. "Wide spans of σ̂², σ², σ̂² values arise as single and multiple scattering are considered together. 41 category 3 scattering paths. 58 category 4 scattering paths. 42 category 5 scattering paths.

0.0032 ± 0.001 Å² (Table S7). This point highlights the uniqueness of our approach: (1) the DFT-optimized structures are used to perform an objective, thorough EXAFS fitting and (2) the EXAFS fitting parameters (themselves determined using the automated Python workflows) are consistent with independently calculated thermal disorders (from DFT vibrations). This level of detail has not been reported for any atomically dispersed catalysts, and we posit that the method represents a significant step forward in automated analysis, self-consistent interpretation of EXAFS data.

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platinum foil (Figure S11). These data imply that isolated Pt4+ was present in six-coordinate octahedral geometry in cation vacancy sites, consistent with the STEM and EXAFS data. To account for charge balance, one Pt4+ in an MgO subsurface site requires one Mg 2+ vacancy, which implies a Pt

−

Mg coordination number of 11 and not 12, consistent with the EXAFS analyses. These results further agree with DFT-calculated Bader charges that show consistent oxidation states for the subsurface Pt4+ with one Mg vacancy and the Pt4+ in H2Pt(OH)6 (qBader = +1.35e and +1.41e, respectively) (Table S8). These values are much higher than qBader = +0.86e for the Pt2+ in Pt(acac)2 (Table S8).32

We also collected HERFD-XANES spectra; HERFD-XANES minimizes the limitations of energy resolution affected by core-hole lifetime broadening and beamline optics in conventional XANES.33 A comparison of the HERFD and conventional XANES data (Figure S11) shows the advantages of HERFD in resolving near-edge features including (a) the stable near-zero signal in the pre-edge; (b) strong intensities and sharpness without a long tail characterizing the white line;
Figure 8. Reaction free energy diagrams for CO oxidation on [100]Mg-vac/sub1 surface at 300 °C. (a) Eley–Rideal mechanism with the formation of a carbonate intermediate; (b) mechanism proceeds through the formation of an oxygen vacancy above the subsurface platinum. Calculated free energy (blue) and enthalpic (red) barriers are presented for each transition state. Insets show the optimized structures of the key intermediate species with the location of the magnesium vacancy marked with a black cross (colors: magnesium, green; oxygen, red; platinum, light gray; carbon, dark gray).

and (c) the clear resonance feature with little broadening beyond the white line.

The HERFD-XANES data provide insight into the catalyst structure beyond what is determined by the EXAFS data and DFT-guided analysis. The HERFD-XANES data were compared with FEFF-simulated XANES spectra based on the aforementioned DFT-determined structures (Figure 6). The agreement between experimental and simulated XANES spectra (quantified using the Fréchet distance (δF)) is compared with the thermodynamic stabilities (Figure 6a) of various platinum sites. Parts b and c of Figure 6 show a comparison of the experimental HERFD and the FEFF simulations for each of the most stable structures predicted from DFT-calculated Boltzmann fractions: [100]/sub0/O2 (99.2%), [100]/Mg-vac/sub1 (99.9%), and [310]/pos1/O2 (98.4%). The FEFF results were shifted 4.5 eV and scaled to match the normalized experimental results for values greater than 11650 eV. Of all the stable structures, both [100]/sub0/O2 and [100]/Mg-vac/sub1 show good agreement with the experimental XANES; however, by comparing the corresponding EXAFS spectra in Figure S6g, we see that the Mg-vacancy provides a notable improvement over [100]/sub0/O2. Although some [310] structures are more consistent with experiment than these (δF < 0.125), they are significantly less stable (Boltzmann fraction <10−9), and, we infer, unlikely to exist. The most stable [310] structures show poor agreement with experiment (Figure 6c (green)).

Taking together the unique combination of EXAFS and HERFD-XANES fits of [100]/Mg-vac/sub1 and the DFT-predicted stability, our results show that the Pt/MgO catalyst is well-characterized as an atomically dispersed Pt4+ ion embedded in the first subsurface layer (sub1) located adjacent to a magnesium vacancy site. As shown in Figure S12, our HERFD-XANES analyses and DFT calculations do not identify the exact location of the magnesium vacancy site; we used the most stable structure, with the magnesium vacancy in the surface layer (sub0) for further analysis.

To analyze the origin of the various features in the HERFD XANES, Figure S13 shows the locally projected, f-dependent density of states (f-DOS) of the [100]/Mg-vac/sub1 site. Overall, the platinum L3 HERFD spectra resemble the platinum d-DOS, as indicated by the vertical dashed lines. The white line is composed largely of platinum d-DOS with a small contribution from the oxygen p-DOS, with its position being largely insensitive to the local disorder. The second peak (~9 eV above the Fermi level) shows contributions from both the oxygen and magnesium atoms as well as the local platinum d-DOS, indicating that this feature corresponds to nonlocal states and arises at least in part from bonding of platinum to the neighboring atoms (Figure S13).

2.6. CO Oxidation Catalyzed by Pt/MgO. We characterized the Pt/MgO as a catalyst for CO oxidation as a probe reaction. The light-off curves (Figure 7a) show that the reaction became readily measurable at approximately 180 °C, with the CO conversion reaching nearly 100% at 280 °C under our conditions. Separate experiments were carried out to determine reaction rates (turnover frequencies, TOF, rates per platinum atom) from data obtained at low conversions (<5%), which were shown to be differential by the linear dependence of conversion on inverse space velocity at temperatures of 180–200 °C (Figure 7b,c). An Arrhenius plot (Figure 7d) indicates an apparent activation energy of 79 ± 2 kJ mol−1.

Data showing conversion as a function of time onstream in the flow reactor under steady-state conditions (Figure 7e) show that the catalyst was stable, retaining its activity for as long as it was onstream (48 h) at 210 °C. The catalyst remained white in color after use. The HAADF-STEM images of used Pt/MgO samples (after three light-off experiments) show that the platinum was still atomically dispersed (Figure S15), even at a high temperature (300 °C). As further checks of the catalyst stability, we recorded in-operando HERFD-XANES data during CO oxidation at 210 °C (Figure S16), demonstrating unchanged spectra.

This catalytic probe reaction provided yet another opportunity to verify the identity of the support sites for platinum. Figure 7e shows trends in CO adsorption for the stable [100]/Mg-vac/sub1 platinum terrace site at various temperatures. Unsurprisingly, stronger CO adsorption was found for the undercoordinated platinum site (i.e., [100]/sub0); we predicted CO adsorption at temperatures as high as...
about 83 °C (Figure S17). In contrast, the subsurface platinum site ([100]Mg-vac/sub1) is characterized by weaker CO binding (0.25 eV at 83 °C); negligible CO adsorption was predicted at room temperature. The trends for the [100]Mg-vac/sub1 site are consistent with (1) our IR experiments that do not show significant CO uptakes at room temperature (Figure S18) and (2) Sarma’s report of low-temperature (~163 °C) IR spectra of CO on a sample similar to ours; a 2166 cm⁻¹νCO band was observed, agreeing within error with our calculated frequency (2141 cm⁻¹).

It is significant, and a challenge to our interpretation, that our Pt/MgO catalyst, which consists of subsurface, highly coordinated platinum sites, does not bind CO substantially at room temperature but nonetheless is catalytically active for CO oxidation. Thus, we turned to DFT calculations (RPBE/D3-[BJ functional, nudged elastic band and dimer method for barriers) to investigate various possible mechanisms of CO oxidation on the [100]Mg-vac/sub1 site. The two most energetically favorable mechanisms are shown in Figure 8. Indeed, our calculations show that the insertion of CO into the surface-bound O₂ is the rate-limiting step—the calculated enthalpic barrier (107.4 kJ/mol) is in satisfactory agreement with experimentally determined apparent activation energies (Figure 8a); similar carbonate species were proposed by Sarma et al. for platinum at the step site on MgO. The subsurface platinum and magnesium vacancy site activates the bound O₂ and allows for CO insertion to form the intermediate carbonate. Charge density difference plots showing the change in the electronic structure of the O₂ compared with that on defect-free crystalline MgO are shown in Figure S19. Although the role of the platinum atom in this mechanism differs markedly from what has been reported by Sarma et al., the calculated free energy barrier at 300 °C in our work is slightly lower (169 kJ/mol vs 173 kJ/mol). Moreover, a similar Eley–Rideal mechanism has been inferred for an Ag/MgO catalyst. A second mechanism (similar to that presented by Sarma et al.) consisting of the abstraction of a surface oxygen by CO to form an oxygen vacancy as the rate-limiting step is shown in Figure 8b. The similarity of the free energy barriers of these two mechanisms (170.2 vs 168.8 kJ/mol) makes it challenging to discern which should be favored, and both are plausible according to our calculations.

A pertinent question is whether the catalyst underwent structural changes under the conditions of CO oxidation catalysis. The EXAFS data recorded after catalysis were not substantially different from those observed before, with [100]Mg-vac/sub1 again emerging as the best-fit model of the EXAFS spectra (Figure S20). This comparison in in line with the catalyst performance data, indicating that the MgO-supported platinum sites are stable under CO oxidation conditions.

3. DISCUSSION

The intense recent attention paid to atomically dispersed supported metal catalysts reflects the promise of catalysts with valuable new properties and the prospect that some of them will be so simple in structure as to propel significant atomic-level advances in the understanding of surface catalysis broadly. Some literature reflects the notion that these catalysts are straightforward to understand because the metals are atomically dispersed, but this view overlooks the intrinsic complexity of the supports and the need to incorporate the metal–support combinations in realistic models of the catalysts. Thus, there is a motivation to work with metal–support-site combinations that are nearly unique and can be understood in depth. Consequently, researchers have been motivated to use crystalline metal oxides as supports and to use low metal loadings to create catalysts that can be approximated as isolated metals in unique, stable surroundings.

The characterization data presented here validate that approach. They have a high degree of internal consistency and show that the structure of the catalyst consisting of platinum in a loading of only 0.05 wt % on crystalline MgO powder is well represented with a single, stably encapsulated—yet still catalytically active—structure that meets the criterion of near structural uniqueness. A full set of complementary experimental characterization combined with theoretical verification was needed to test the hypothesis that such a catalyst could be characterized structurally with some confidence.

The DFT-guided EXAFS fitting approach described here represents, we posit, a substantial advance in the characterization of such catalysts. Although previous approaches represent attempts to develop DFT models that are motivated by results of conventional EXAFS analyses, we instead used a library of DFT-optimized platinum-containing structures to identify the single best representation of all of our experimental results (EXAFS, HERFD-XANES, IR spectra of adsorbed CO, and catalytic kinetics). Although we focus on the Pt/MgO catalyst in this work, we emphasize that QuantEXAFS is broadly applicable to other related systems; our analysis for a recently reported Pt/TiO₂ catalyst is presented in Figure S21 and Table S9).

Going forward, we anticipate that further development of this combination of characterization techniques will help guide the choice of metal–support combinations to advance the field of atomically dispersed supported metal catalysts; help advance the understanding of the broad class of supported catalysts; and facilitate the development of new and improved methods for understanding of even more complex surface structures.

4. CONCLUSIONS

The QuantEXAFS methodology used in the fitting of EXAFS data is performed with a library of DFT models that are grounded in the known structure of crystalline MgO. The physically motivated, DFT-optimized structures are a significant improvement over today’s conventional EXAFS fitting procedures, which usually rely on bond distances for nominally comparable reference compounds for initial estimates of scattering distances. The conventional EXAFS analysis relies on the fitting of a few, average scattering paths, which may not be representative of physically motivated structures. A central point about the method reported here is the 1:1 mapping between a DFT-optimized structure and the resultant EXAFS fit. The focus of the method is on the physical structure of the material and not the individual scattering paths. We emphasize that there is more to using DFT structures than just positions of atoms in space; we have placed the stability of the structure (i.e., the Boltzmann distribution) at the center of the analysis. Our automated analysis and the path classification scheme allow efficient implementation of hundreds of unique paths, implying perhaps an order of magnitude improvement in the accuracy and reliability of the analysis compared with conventional analyses. The workflow presented in this work removes potential user bias from the EXAFS modeling.

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As QuantEXAFS is based on DFT-informed structures to generate the list of unique scattering paths, the validity of this approach depends on the crystallinity of the support and thus the uniformity of the binding sites. For example, when a single dominant metal environment does not exist (as, for example, in amorphous supports, in catalysts with nonuniform atomically dispersed metals, or metal nanoparticles with broad size distributions), QuantEXAFS will be limited by the lack of unique DFT structures. Many of these limitations, especially the heterogeneity associated with atomically dispersed supported catalysts, pertain to classes of catalysts that are investigated intensively today. They are clearly beyond the scope of this work.

5. EXPERIMENTAL AND COMPUTATIONAL METHODS

Synthesis of Pt/MgO Samples. MgO powder (1000 mg, US Research Nanomaterials) with a manufacturer-specified specific surface area of 25 m²/g was dispersed in 250 mL of ethanol in a 500 mL beaker with magnetic stirring. Aqueous K₂PtCl₄ 20 mL of 0.25 mM solution, and 40 mL of ethanol were transferred into the stirred beaker through a syringe pump at a rate of 5 mL/h. The resultant solid was collected by centrifugation, washed with distilled water, and then dried overnight in air in an oven at 80 °C. The resultant powder was calcined in flowing O₂ (10 mL(NTP)/min) and N₂ (40 mL(NTP)/min) as the temperature was ramped from room temperature to 120 °C and held for 2 h to remove any residual water and organics. The sample was then further calcined in a mixture of flowing O₂ (10 mL(NTP)/min) and N₂ (40 mL(NTP)/min) as the temperature was ramped at a rate of 5 °C/min until a final temperature of 700 °C was reached, which was held for 4 h.

X-ray Absorption Spectroscopy. XAS was carried out on beamlines 4-1 and 6-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). At beamline 4-1, which is a side station on a 20-pole wiggler beamline, the ring SPEAR3 was operated in top-off mode with a storage ring energy of 3 GeV and 500 mA stored current. A Si double-crystal (200) monochromator was detuned by 20–25% of maximum intensity to minimize harmonics at the platinum L₁ edge. XAS data were collected in fluorescence yield mode with a 30-element germanium solid-state detector array with each sample pressed into a pellet at 25 °C. For energy calibration, a platinum foil was placed between the transmission and reference channel ion chambers so that its spectrum was measured simultaneously with that of the sample.

At beamline 6-2, which is fed by a 56-pole, 0.9 T wiggler, high-energy resolution fluorescence detection HERFD-XANES experiments were conducted with a liquid-nitrogen-cooled double-crystal Si (311) monochromator to select the energy of the incident beam. A Rowland circle spectrometer (radius 1 m) equipped with three spherically bent Si (800) analyzers and a silicon drift detector were used to select the platinum L₁ emission line. A platinum foil was scanned in the transmission mode for initial energy calibration. For ex situ HERFD-XANES experiments, the sample was pressed into a pellet at 25 °C. In each in operando HERFD-XANES experiment, approximately 50 mg of catalyst sample was loaded into a flow-through cell that was a Kapton tube (i.d. = 2.8 mm) connected to a treatment gas line. The Pt/MgO foil was first heated in helium flowing at 20 mL (NTP)/min as the temperature was ramped from room temperature to 210 °C at a rate of 5 °C/min. Then the feed gas was switched to a mixture of CO flowing at 0.2 mL (NTP)/min + O₂ flowing at 0.8 mL (NTP)/min + helium flowing at 19 mL (NTP)/min with the sample in the cell held at 210 °C for 1 h as CO oxidation catalysis took place. Thereafter, the reactor was cooled to room temperature and the gas feed switched to helium flowing at 20 mL (NTP)/min. HERFD-XANES spectra were collected periodically during all these steps.

IR Spectroscopy. Transmission IR spectra of powder samples in the ν(OH) region were determined with a Bruker IFS 66/S spectrometer with a resolution of 4 cm⁻¹. Approximately 10 mg of sample was loaded between two KBr windows, and spectra were recorded at room temperature with the sample under vacuum, with an average of 256 scans per spectrum. IR spectra of samples with adsorbed CO were determined with approximately 40 mg of sample pressed into a wafer loaded into a cell (In-situ Research Instruments, South Bend, IN) that served as a flow reactor fed with various gases, and transmission spectra of catalysts in the presence of these gases were recorded with a liquid-nitrogen-cooled MCT detector.

CO Oxidation Catalysis in a Conventional Laboratory Plug-Flow Reactor. The catalyst samples were evaluated for CO oxidation in a once-through plug-flow reactor, with products analyzed with an online mass spectrometer (Hiden Analytical HPR20) equipped with a secondary electron multiplier detector used in multiple ion detection mode. Samples of catalyst powder (100 mg) that had passed through a 40 to 60 mesh sieve were loaded into a quartz tube reactor (i.d. = 4 mm), with the upstream and downstream sections packed with quartz wool. In experiments to determine light-off curves for CO oxidation, the feed was a mixture of 5.0% CO in helium flowing at 4.0 mL(NTP)/min + 5.0% O₂ in helium flowing at 16.0 mL(NTP)/min, the pressure was atmospheric. The reactor was heated from room temperature at a rate of 2 °C/min with the gases flowing and then held at 300 °C for 20 min before the reactor was cooled down.

In a separate flow reactor system, near-steady-state conversion data were obtained under the conditions stated in the preceding paragraph, except that the feed gas was a mixture of 5.0% CO in helium flowing at 5.0, 6.0, or 8.0 mL (NTP)/min + 5.0% O₂ in helium flowing at 20.0, 24.0, or 32.0 mL (NTP)/min. Catalytic reaction rates were calculated from low (differential) conversions (<5%) determined at temperatures in the range of 180–200 °C. In experiments determining the dependence of conversion on time on stream, the samples were kept on stream for up to 48 h to demonstrate stability at 210 °C; the feed was 5.0% CO in helium flowing at 4.0 mL (NTP)/min and 5.0% O₂ in helium flowing at 16.0 mL (NTP)/min.

Scanning Transmission Electron Microscopy. STEM imaging experiments were performed on a JEOL 200CF (NEOARM) transmission electron microscope with an acceleration voltage of 200 kV. The specimens were prepared by a direct dispersion of powder samples on lacy carbon grids. The HAADF images were acquired with a convergence angle of 28.5 mrad and an inner collection angle of 55 mrad.

Transmission Electron Microscopy. TEM images of as-prepared sample powders loaded onto copper grids were recorded with a Hitachi H-7700 microscope at an acceleration voltage of 100 kV.

X-ray Diffraction Crystallography. XRD patterns of the samples were collected on a Philips X’Pert Pro Super diffractometer with a monochromatized Cu Kα radiation source and a wavelength of 0.1542 nm.

Inductively Coupled Plasma Mass Spectrometry. The platinum loadings in the catalysts were determined by inductively coupled plasma mass spectrometry with a Thermo Scientific XSERIES 2 instrument.

DFT Calculations. Periodic DFT calculations were performed using the projector augmented wave method as implemented in the Vienna ab initio simulation package (VASP). Energies were calculated using a 500 eV plane-wave cutoff with a 2 × 1 × 1 Monkhorst–Pack k-point grid. A range of generalized gradient approximation functionals (PBE, RPBE, and PBEsol) were used. Electronic energies were converged to 10⁻⁶ eV, and all structures were relaxed until the forces were less than 0.05 eV/Å. The finite displacement method (0.02 Å) was used to calculate the entropic and zero-point energy corrections. For CO oxidation mechanism calculations, a 400 eV plane-wave cutoff was used with the RPBE functional, and dispersion corrections were considered with the DFT-D3 method with Becke-Johnson damping. Barriers were calculated using the climbing image nudged elastic band and dimer methods.

Conventional XAS Data Analysis. The EXAFS and XANES data were analyzed with the Demeter package. Preprocessing of data included alignment, edge calibration, deconvolution, normalization,
Automated DFT-Based Fitting of EXAFS Data. The EXAFS data were analyzed with the open-source X-ray Larch package.\textsuperscript{27} Data processing, such as alignment, edge calibration, deglitching, normalization, and background subtraction, was performed using the Python interface to Larch. The DFT-optimized structures were used to generate a feff.inp file using an in-house code. These feff.inp files were run in Larch, with FEFF used for generating scattering paths. The code uses Matplotlib for plotting the fitting results.

**FEFF and DOS Modeling.** All HERFD simulations used DFT-optimized (PBE-D3) structures and were performed with FEFF 9 using SCF and FMS cutoff radii of 6 and 9 Å, respectively, which ensured convergence of the spectra.\textsuperscript{16,15} The representative atomic potentials were chosen to reproduce chemical distinguishability for each atom type. On the basis of our experience with Pt-containing samples, we chose not to use a core-hole in the calculations.\textsuperscript{39,40} To properly simulate HERFD rather than the default XANES in FEFF, we also removed 1.8 eV from the default core-hole lifetime broadening of 5.2 eV. The self-energy was modeled using the density-dependent MPSE (many-pole self-energy) dielectric function approach based on a weighted average of the atomic loss functions.\textsuperscript{41} Moreover, to provide converged results up to about 200 eV above the edge, the maximum angular momenta for the site basis set were raised from the DFT structural simulations.\textsuperscript{28,29}

**Notes**

The authors declare no competing financial interest. The ASE database file and the EXAFS fitting routines are available on GitHub at https://github.com/kul-group/kul-repository/tree/main/repo_2021_JACS_Theory-Guided and https://github.com/kul-group/QuantEXAFS, respectively.
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