

Bridging the Gap between the X-ray Absorption Spectroscopy and the Computational Catalysis Communities in Heterogeneous Catalysis: A Perspective on the Current and Future Research Directions

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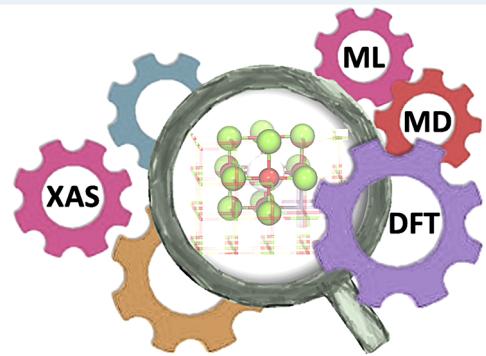
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ABSTRACT: X-ray absorption spectroscopy (XAS) [extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES)] is a key technique within the heterogeneous catalysis community to probe the structure and properties of the active site(s) for a diverse range of catalytic materials. However, the interpretation of the raw experimental data to derive an atomistic picture of the catalyst requires modeling and analysis; the EXAFS data are compared to a model, and a goodness of fit parameter is used to judge the best fit. This EXAFS modeling can often be nontrivial and time-consuming; overcoming or improving these limitations remains a central challenge for the community. Considering these limitations, this Perspective highlights how recent developments in analysis software, increased availability of reliable computational models, and application of data science tools can be used to improve the speed, accuracy, and reliability of EXAFS interpretation. In particular, we emphasize the advantages of combining theory and EXAFS as a unified technique that should be treated as a standard (when applicable) to identify catalytic sites and not two separate complementary methods. Building on the recent trends in the computational catalysis community, we also present a community-driven approach to adopt FAIR Guiding Principles for the collection, analysis, dissemination, and storage of XAS data. Written with both the experimental and theory audience in mind, we provide a unified roadmap to foster collaborations between the two communities.

KEYWORDS: X-ray absorption spectroscopy, heterogeneous catalysis, density functional theory, machine learning, FAIR Guiding Principles



1. INTRODUCTION

Structure–function relationships remain a central approach used by the catalysis science community to understand, rationalize, and predict the chemical reactivity of heterogeneous catalysts. Unlike well-defined molecular systems, the often complex structure of solid catalysts (e.g., mixed phases, distribution of nanoparticle sizes, range of composition, etc.) and their structural evolution from as-prepared material to the active catalyst makes it challenging to unambiguously identify the active site(s) responsible for experimentally observed catalytic properties.^{1–5} Complementary to the many characterization techniques used by experimentalists, theory has also played an important role in this regard. For instance, mechanisms derived from density functional theory (DFT) are now routinely used to explain the catalytic performance of the proposed active site(s) determined from X-ray absorption spectroscopy (XAS) (and other complementary techniques), while also being used to exclude the contributions of spectroscopically observed but inactive spectator species. Taken together, such integrated experiment–theory ap-

proaches continue to provide detailed structural insights that go well beyond what was possible only a couple of decades ago.

More recently, the successful adoption of open-source modeling software together with the development of standardized computational interfaces has contributed to a growing list of massive DFT property data sets used by the global theory community. Indeed, the ongoing machine learning (ML) revolution in computational catalysis leverages the strong foundation established by these three pillars (Figure 1).^{6–9} Recognizing this ongoing adoption of data-centric approaches by the theory community, the key question is whether similar disruptive changes (aimed at improving the accuracy, reliability, and data management of catalyst

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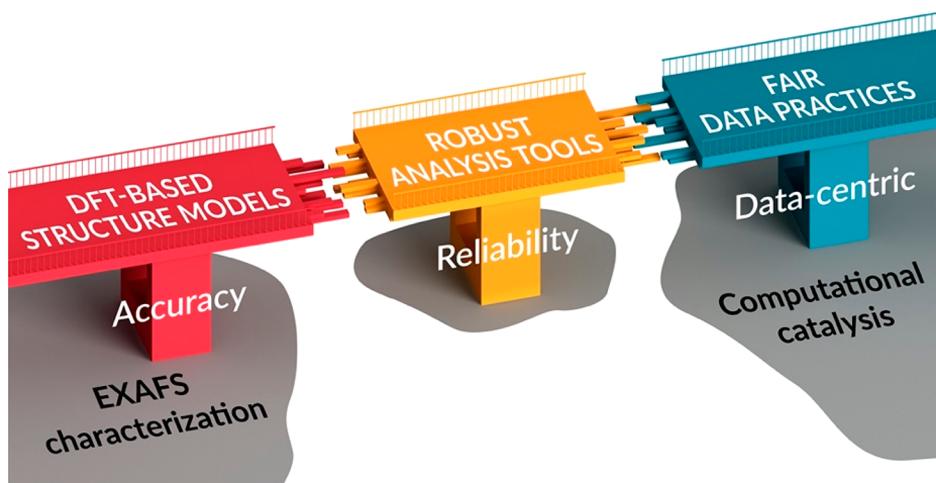


Figure 1. Bridging the gap between the computational catalysis and the EXAFS characterization communities to address the complexities associated with identifying active sites for various heterogeneous catalysts.

characterization experiments) can be encouraged and if so, how should they be implemented?

Thus, the overarching goal of this Perspective is to highlight how recent developments in analysis software and increased availability of reliable computational models can be used to improve the speed, accuracy, and reliability of the interpretation of XAS data.

Beginning with an introductory overview (Section 2) that highlights the challenges with EXAFS analysis (Section 3), we classify the published literature into three distinct categories (Section 4). Specifically, we demonstrate that using DFT-computed structures as a starting point for EXAFS interpretation can be superior to the conventional analyses, especially in identifying the catalytic sites for certain classes of materials. As with many other fields of science, various machine learning tools have been applied to address open questions related to XAS. Section 5 summarizes such advances, especially for improving the reliability of EXAFS analysis.

As the current user-driven nature of EXAFS modeling is not scalable to the interpretation of large quantities of EXAFS data sets (enabled by the current and planned availability of both continuous scanning and quick XAS beamlines throughout the world), Section 6 summarizes the possible strategies to enable high-throughput and more automated analyses.¹⁰ The data-centric approach proposed here requires fundamental changes in the way EXAFS data and analyses are reported. Specifically, inspired by the data science revolution in computational catalysis, we suggest specific strategies to improve the collection and dissemination of EXAFS results in the peer-reviewed literature. Finally, we present an outlook for the field and identify one specific open question that can be addressed by using a data-centric EXAFS approach.

Written with both the experimental and theory audience in mind, we also provide a roadmap to foster collaborations between the two communities. For example, Figure 2 illustrates that there is a significant opportunity for the theory and modeling community to contribute toward interpretation of experimental XAS data. This Perspective aims to bridge this gap between the X-ray absorption spectroscopy catalyst characterization and the computational catalysis communities. While we limit our focus to EXAFS, a similar discussion could readily be applied to other characterization methodologies.

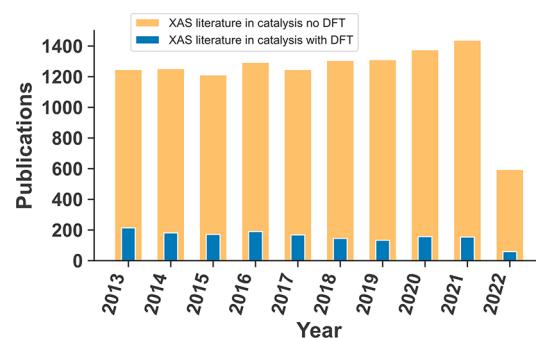


Figure 2. A significant opportunity exists for the theory and modeling community to contribute toward the analysis and interpretation of experimental XAS data. Compared to the thousands of XAS studies reported every year (orange), only a small fraction use density function theory (blue) to aid in determining the coordination numbers and bond distances (leading to a structure), to further support XAS results. The statistics are obtained using keyword search in Web of Science; orange, XAS or EXAFS or X-ray absorption spectroscopy and catalysis; blue, XAS or EXAFS or X-ray absorption spectroscopy and catalysis and DFT (accessed: July 28, 2022); the data tables are available at the GitHub repository (see the Data Availability Statement).

2. COMPLEXITIES ASSOCIATED WITH CATALYST CHARACTERIZATION AND THE UNIQUE ROLE OF XAS

Owing to the inherent complexity of heterogeneous catalysts, several complementary characterization approaches are routinely employed to probe the structure and properties of active sites. Each piece of information is like a piece of a jigsaw puzzle, and it is only when we have most of the pieces assembled that we see the underlying picture clearly. There have been continued advances in these characterization techniques (especially transmission electron microscopy, nuclear magnetic resonance, and X-ray-based methods); their impacts on catalysis science have been reviewed recently.^{11–14} One such technique, X-ray absorption spectroscopy, has long held a strong foothold in the field.^{15–24} This is due to the versatility of XAS to study a broad range of catalyst materials and reactions together with the wide geographic availability of XAS beamlines at synchrotrons (~90 synchrotrons globally). These enablers, when combined with the ability of XAS to

probe the local bonding environment of a specific element under reaction conditions, have resulted in XAS being applied to study a diverse range of heterogeneous catalysts. These include supported metal nanoparticles (including bimetallic), subnanometric clusters, atomically dispersed metals, and metal oxides with supports that range from amorphous or semicrystalline (e.g., carbon, silica, alumina, ceria, and zirconia) to crystalline materials (e.g., zeolites, metal organic frameworks).^{5,23–26}

In conjunction with other characterization techniques and kinetic measurements, XAS has played a prominent role in developing structure–property relationships and elucidating mechanistic pathways for various catalytic reactions.^{27–31} Indeed, while X-ray absorption near-edge structure (XANES) spectroscopy provides information about the electronic structure (e.g., the average oxidation state of a specific element in the experimental sample), extended X-ray absorption fine structure (EXAFS) spectroscopy probes the local bonding environment around the absorbing atom. Coupled with the easy ability to tune X-ray energies from ~2 to ~30 keV (covering the absorption edges of virtually all catalytically active elements) at the synchrotron, XAS is a versatile technique that is used to study a vast range of catalytic materials, including industrially relevant catalysts. The challenges and opportunities associated with using advanced XAS techniques for catalysis research have been recently reviewed.^{13,32–35}

2.1. Introductory Overview of XAS and the Theory of EXAFS Analysis. To appreciate the challenges associated with EXAFS analysis and interpretation particularly as applied to heterogeneous catalysts (in Section 3), we begin by providing a brief introduction to the technique. XAS is an absorption-based spectroscopy that uses tunable synchrotron radiation (with photon energies near or above the binding energies of core–electrons of a specific element) to probe the averaged electronic and geometric structure of all the atoms of the chosen element present in the experimental sample.^{36–38} While XANES provides information about the electronic structure of the absorbing atoms (e.g., oxidation state),^{34,39,40} the oscillations in the absorption coefficient in the EXAFS regime are used to determine the coordination environment around the absorbing atoms.⁴¹ As these oscillations arise due to the scattering of photoelectron waves between the absorbing atom and its neighbors, EXAFS interpretation relies on modeling the experimental data to a set of scattering paths generated using suitable atomistic models based on commonly used codes like FEFF⁴² and GNXAS⁴³ (where the EXAFS signal is expanded the contributions of many body functions).⁴⁴ Following the modern interpretation of EXAFS by Sayers, Stern, and Lytle,⁴⁵ Ravel and Newville in their respective works describe the process of, and have developed GUI-based codes for, EXAFS data reduction and data analysis; these remain highly valuable resources.^{37,38} Additionally, there are other groups that have significantly contributed toward GUI-based tools for XAS data analysis: WinXAS,⁴⁶ SixPACK,⁴⁷ XDAP,⁴⁸ RSXAP,⁴⁹ and EXAFSPACK⁵⁰ to list a few.

The underlying theory of EXAFS is well-established. As summarized in eq 1, the fine structure extracted from the experimentally measured spectrum is described as a sum of contributions of individual scattering paths to the overall signal. For a given set of scattering paths, “EXAFS modeling” involves identifying the values of the fitting parameters (e.g., N_i , coordination number; σ^2 , disorder term; R_i , average

effective scattering distances; etc.) that minimize the error between the experiment and the modeled spectra.

$$\chi_i(k) = \sum_i \frac{N_i S_0^2 F_i(k)}{2kR_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda_i(k)} \quad (1)$$

The quality of experimental data, the associated uncertainties, along with the amount of information encoded in the EXAFS spectrum and, correspondingly, the maximum amount of information that can be extracted from it set an upper limit to the precision of the structural interpretation. However, depending on how the analysis is performed and the experimental sample of interest (e.g., uniform atomically dispersed vs supported metal catalysts), one can access different degrees of information about the system. Thus, in addition to the technical aspects of data fitting (e.g., number of scattering paths, number of free variables, constraints used during fitting, etc.), the quality of an EXAFS interpretation depends significantly on the appropriateness of the models used for EXAFS analysis,⁵¹ as discussed below.

3. CHALLENGES WITH THE CURRENT APPROACHES FOR EXAFS INTERPRETATION

A distinguishing characteristic of XAS, and particularly of EXAFS, is the fact that the interpretation of the raw experimental data can often be nontrivial and time-consuming. Interpretation of EXAFS data requires several preprocessing and analysis steps including energy alignment, background subtraction, normalization, k -weighting (where k is the photoelectron wavenumber), and, most importantly, EXAFS modeling of the resulting $\chi(k)$ data, usually after taking the Fourier transform. Typically, the results from these analyses are presented as a tabulated list of coordination numbers, bond lengths, and the disorder terms (σ^2) related to a given photoelectron scattering path. As EXAFS is a bulk technique, these values will be the average of the environment of the element under study. The number of rows in the table corresponds to the number of unique scattering paths (often denoted as shells) used to fit the EXAFS data. The quality of the fit is measured by the R -factor (the R -factor is the sum of the squares of the differences between the data and the fit at each data point, divided by the sum of the squares of the data at each corresponding point) or reduced χ^2 (preferred); these metrics are used to assess if, and to what extent, a given model is representative of the averaged coordination environment of the absorbing atom.^{36,52} This modeling often includes adding or removing scattering paths or constraining the values of the fitting parameters in an attempt to improve the quality of the fit. More advanced methods such as simultaneously fitting multiple data sets are often used to improve (i.e., to minimize) these quality-of-fit metrics by reducing the error bars on the values by the constrained fit. More detailed studies evaluate several hypothesis-driven models (developed using chemical intuition) to fit the EXAFS spectra, with often only a few of the test cases published in the Supporting Information of the associated publications. For example, how many models were evaluated, which models were excluded, and how were the fitting parameters adjusted? Additionally, there are rules of thumb that are common in the community: physically relevant values for σ^2 factors (e.g., ranging from 0.001–0.002 Å² for very stiff bonds at room temperature to 0.008–0.012 Å² for weaker bonds or at higher temperatures), acceptable values of

R-factors for different systems (<5%), and initial guesses for scattering distances for different pairs of atoms (which depends on the typical bond distances).

Depending on the specifics of the sample being analyzed, the above EXAFS modeling procedure often results in noninteger coordination numbers. Although fractional coordination numbers are physically relevant for supported nanoparticle catalysts (as they represent the average coordination environment of all the metal atoms in the nanoparticle), such analyses have now become routine to determine the coordination environment of the metal in single atom catalysts (SACs).^{53–55} As practiced today, the EXAFS analysis procedures are material-agnostic; i.e., similar fitting approaches and quality-of-fit metrics are used to study supported metal, zeolite, metal–organic frameworks, and SACs. As the nature of the active sites (e.g., isolated cations in SACs vs step or terrace sites for metal nanoparticles) are inherently different among the various catalyst classes (revisited later in Section 3.2), it is useful to consider if developing material-specific EXAFS analysis approaches may be advantageous within the community.

Notwithstanding the shortcomings summarized above, there is no question that EXAFS analysis has been and will continue to be a cornerstone in our understanding of the structure of catalytically active sites. Specifically, even in its current form, EXAFS remains one of the most valuable techniques that provides quantitative information about the averaged local coordination environment for the chosen element, especially under operating conditions of temperature, pressure, and gas flow or applied potential.

3.1. Synergies and Inconsistencies between EXAFS Analyses and Computational Modeling. At this stage, it is useful to contrast the *de facto* standard EXAFS fitting procedures with the recent progress in the computational catalysis community.¹³ Most theory-led studies are focused on understanding the mechanism of, or identifying promising catalysts for, a variety of chemical reactions. The past decade has seen significant advances in the development of open-source software, computational databases (e.g., for adsorption energies), automated workflow managers, and postanalysis tools.⁵⁶ We emphasize that the creation of large, standardized data sets using automated high-throughput calculation protocols was the precursor for developing data science tools capable of addressing long-standing questions within computational catalysis.^{2,57–60}

Although various computational methods for modeling XAS are under active development,^{61–63} DFT studies within the catalysis community tend to be more focused on modeling reaction kinetics rather than on interpreting complex characterization experiments. For collaborative studies that combine experiment and theory, the initial structural models for mechanistic investigations (used by theorists to calculate free energy diagrams, for example) are often developed based on the structures derived from EXAFS modeling. A common strategy, often used as a validation of EXAFS-based interpretation, is to compare the DFT-calculated bond distances with those obtained from EXAFS fitting. Since the EXAFS analysis provides only averaged distances and coordination numbers for each shell (and the possible presence of multiple coordination environments), direct comparison with DFT (which imposes a specific orientation of the neighbors) is not intuitively obvious.

For the purposes of this Perspective, we denote the above approach that relies on using a list of scattering paths derived from the atomic coordinates of a known structure (e.g., a CIF file) (that may have limited direct relevance to the experimental sample or the reaction conditions at hand) and yields a tabulated list of parameters that relate to the modeled scattering paths as “conventional EXAFS” analysis. With a few exceptions, it is uncommon to find reports where the atomistic model (obtained based on conventional EXAFS analysis by the experimentalists) is fully consistent with the experimental kinetics. Conversely, if a system-specific database of hypothetical structures that are thermodynamically stable at given conditions is obtained, and a few structures are well-representative of experimental EXAFS data, these structures can be further correlated with other experimental results by performing required theoretical calculations. For example, a reaction mechanism obtained using the nudged elastic band approach can be compared to apparent activation energies. Similarly, other complementary characterizations such as CO vibrational frequencies are often compared to DRIFTS experiments presented in the study. We suggest that similar mindset is necessary for EXAFS interpretation when possible.

3.2. Fundamental Differences between EXAFS-Derived and DFT-Optimized Models. For studies that are focused on identifying the structure of the active site(s), the central challenge is the fact that EXAFS provides averaged information about the coordination environments of all the absorbing atoms present within the sample. As illustrated in Figure 3, various factors such as presence of multiple sites,

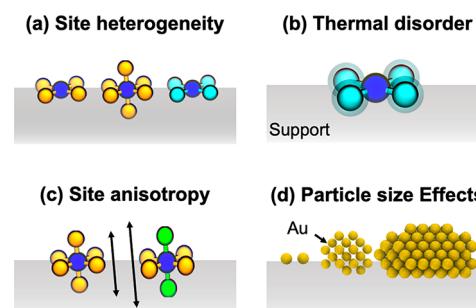


Figure 3. Experimental EXAFS measures the averaged coordination environment of an absorbing atom (blue). The averaged information may arise due to (a) heterogeneity of the sites due to differences in the number and/or type of neighboring atoms (denoted as yellow or cyan), (b) thermal vibrational effects, (c) anisotropy within similar sites (axial green atoms form a longer bond than the yellow neighbors), and (d) particle size effects (Au nanoparticle is shown as an example).

anisotropy within similar sites, thermal effects, and particle size effects can contribute to nonuniformity of the bonding environments. Since the complexities of the experimental sample are typically not known *a priori*, it may be difficult using conventional EXAFS analysis by itself to determine the uniformity (or lack thereof) of the coordination environment.

Note, however, that the underlying cause of the averaging depends on the specific characteristics of the type of a catalyst material. For example, while an average Ni–O coordination number of 5 may arise due to the presence of a 50:50 mix of two distinct 4 coordinate and 6 coordinate Ni sites on the support, a similar Pt–Pt coordination number for a Pt nanocluster catalyst arises due to the difference in the

coordination environment of Pt atoms within and at the surface of the nanocluster. More importantly, while materials containing largely tetrahedral (or octahedral) metal sites can, in theory, be created using precise synthetic techniques, the average coordination number for the Pt nanocluster is an inherent property of the supported nanocluster catalyst. Thus, as practiced today, the conventional EXAFS analysis approach does not consider such inherent differences among the various catalyst classes.

In contrast to the averaged picture obtained from EXAFS experiments, DFT-optimized structures can be more realistic (i.e., thermodynamically feasible) and can include the anisotropies (e.g., small but important variations in the bond lengths) in the local environment. While it is theoretically possible to enumerate all possible unique binding sites for simple materials (e.g., atomically dispersed metals supported on crystalline oxides such as MgO, metals, or alloys)^{64,65} using DFT, similar approaches are impractical for amorphous supports or supported metal catalysts. Indeed, unlike atomically dispersed catalysts, the latter class of materials are not uniquely described by a single set of DFT-optimized structures. Thus, analogous to the above discussion, the ability of DFT to provide realistic atomistic models depends on the type of catalyst material being investigated. For instance, in case of nanoparticles where a variety of shapes and sizes can exist or when considering catalyst fluxionality, having a unique structure to represent the nature of an active site is challenging. Zhai and Alexandrova have discussed the fluxionality of cluster catalyst matters and suggested some methods to address it.⁶⁶ In this work, the authors suggest to treating dynamic and complex cluster catalysts as a statistical ensemble to successfully capture experimental reproducibility, catalytic and deactivation trends, and structure–property relationships. A review on the effects of structural and dynamic complexities in catalytic structures is presented by Frenkel et al., where the authors discuss the challenges in characterization of such complex catalytic systems.⁶⁷ The mapping of the kinetic and mechanistic behaviors of the catalytic sites at challenging operating conditions using XAS and TEM techniques has been discussed, and the role of multiscale, *ab initio* DFT and MD modeling to guide the experimental studies is discussed.⁶⁷ There are several other studies to illustrate the structural heterogeneities and dynamics during reaction conditions in supported nanoscale catalysts using DFT, MD, and ML-assisted XAS.^{68–70}

While nominally exact models can be constructed to represent certain uniform and precisely synthesized catalysts, computational studies for supported nanoparticle catalysts or more complex and dynamical systems rely on approximate slab models to qualitatively rationalize experimentally observed trends.⁷¹ Along with size heterogeneity and structural disorder, thermal disorder contributes to the complexity in EXAFS interpretation. Vila et al., in their work, discuss the anomalous structural disorders in Pt nanoparticles. Here, the authors demonstrate that support-induced structural heterogeneity has large effects on the nature of structural disorder as a function of temperature. Unlike bulk Pt, where disorder can be decomposed into static (*T*-independent) and thermal (*T*-dependent) contributions, small nanoparticles exhibit *T*-dependent anomalous structural disorder (ASD). Contrary to other forms of disorder, ASD decreases with temperature. This effect arises from the preferential disappearance of longer Pt–Pt bonds with rising temperature that in turn results in the

contraction of the average bond length. There are several other studies that have captured the impact of thermal disorders in catalytic systems.⁷²

Indeed, a qualitative or a quantitative EXAFS interpretation may be more appropriate depending on the catalyst of interest (e.g., atomically dispersed vs supported nanoparticle) and the focus of the study (i.e., identifying a specific active site vs using computational methods to support an experimental observation). The inability of conventional EXAFS analysis to deconvolute the complexities of the averaged bonding environment coupled with the intense focus by the theorists on studying catalyst activity (with less focus on modeling characterization experiments), in our opinion, has caused both communities to overlook the potential wealth of information contained within an EXAFS data set. However, it begs the question if there could be a more general approach to modeling XAS data that explicitly considers the material-specific complexities outlined in Figure 3. As a step toward accomplishing this goal, we now discuss a categorization scheme and provide an overview of the published EXAFS literature.

4. HOW IS EXAFS BEING CURRENTLY USED BY THE CATALYSIS SCIENCE COMMUNITY?

To provide an overview of how EXAFS is currently being used by the catalysis community, we first classify the published literature into three distinct categories. As summarized in Figure 4, the categorization is based on two criteria: (1)

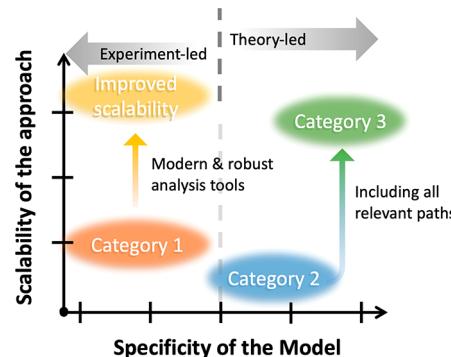


Figure 4. Two criteria (i.e., specificity of the model derived from EXAFS analysis and scalability of the fitting approach) are used to classify the published EXAFS literature into three distinct categories. While Category 1 studies provide structural information using conventional EXAFS fitting, both Category 2 and 3 studies use DFT-derived structures. The gray arrows emphasize that the role of theory depends significantly on the class of materials being investigated.

specificity of the model derived from EXAFS analysis and (2) scalability of the fitting approach. While Category 1 studies provide structural information using conventional EXAFS fitting, Category 2 uses DFT-derived structures to guide the interpretation of the experimental EXAFS. Finally, Category 3 studies consider all possible unique scattering paths, in addition to using libraries of structures obtained from DFT, and are scalable to a large number of experimental data sets. In the discussion that follows, we have considered what atomic structures (if any) are used to obtain the initial list of scattering paths, and if the fitting approach can be automated and scaled to multiple (i.e., thousands) of experimental data sets.

Table 1. Meta-Analysis of Category 1 Studies

study	catalyst used	ref	analysis software ^a	k-range
1	Pd/Al ₂ O ₃	1	Athena, EXCURVE98	3–10 Å ⁻¹
2	Pt, Pd, and Au-NPs; and Pt, Pd, and Au-SAs	3	not stated	not stated
3	Pt SAC on CeO _x -TiO ₂	17	not stated	not stated
4	Pt/CeO ₂	18	Artemis	not stated
5	SAC Pt/CeO ₂	20	Artemis	3–10.5 Å ⁻¹
6	SAC Rh/phosphotungstic acid	21	not stated	3.5–10.5 Å ⁻¹
7	SAC Ir/ZIF-8	53	Athena and Artemis	not stated
8	SAC Cu ₃ N ₄	54	not stated	not stated
9	M-SACs in nitrogen-, sulfur-, and fluorine-co-doped graphitized carbons (M = Fe, Co, Ru, Ir, and Pt)	55	Athena and Artemis	not stated
10	CuO-CeO ₂ /Al ₂ O ₃	77	XDAP	not stated
11	Cu-CHA deNO _x	81	not stated	2.5–12.4 Å ⁻¹
12	Cu dendrites on Ag and Pt foils	82	Artemis	not stated
13	[Ce ₆ O ₄ (OH) ₄]-based MOFs	83	not stated	4–16.8 Å ⁻¹
14	SAC Pt/CeO ₂	84	not stated	not stated
15	SA Au-oxo clusters	86	not stated	not stated
16	Co–N–C catalyst	85	not stated	3–11 Å ⁻¹
17	formation of Ni ⁴⁺ sites from Ni	87	CTM4XAS	not stated
18	SAC M/N–C (M = V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Mo, Ru, Rh, Pd, Sn, W, Ir, and Pt)	89	not stated	not stated
19	low loading Ru clusters on graphitic carbon nitride	90	Rigaku EXAFS analysis program	3.5–11 Å ⁻¹
20	SA Pt/CeO ₂	98	Athena and Artemis	3–13 Å ⁻¹
21	MgO supported SA Ir complexes	99	XDAP	not stated
22	Fe-doped Co-based perovskite oxide	101	Demeter	not stated
23	Ag nanocrystal	102	Athena and Artemis	not stated
24	Pt/TiO ₂	92	Athena and Artemis	3–12 Å ⁻¹

^aThe software listed in the table is based on the terminology used by authors in the associated publication.

The following discussion aims to demonstrate that using DFT-computed structures as a starting point for EXAFS interpretation can be superior to the conventional analyses for identifying the catalytic sites for certain classes of materials. Indeed, if DFT can be used to create a library of possible bonding environments and if the focus of the study is to identify a specific active site, then we recommend using a quantitative EXAFS analysis approach (i.e., using scattering paths derived from DFT structures). In situations where reasonable structures cannot be obtained easily from DFT (e.g., amorphous catalysts, polydisperse nanoparticles, nonuniform sites), traditional EXAFS modeling will continue to provide useful information.

4.1. Category 1. The central goal of conventional EXAFS analysis is to determine the coordination number(s) and effective scattering distances around the absorbing atom and thus from these values to propose a structure that is consistent with the experimental measurement. A list of scattering paths is required; this is generally obtained using reference structures from public databases (e.g., Materials Project,⁷³ Inorganic Crystal Structure Database,^{74,75} Cambridge Structural Database,⁷⁶ etc.). While there have been many programs developed over the years, the Demeter suite of programs is now the most widely used program worldwide, but it is no longer being supported or developed.^{77–79} Larch is a newer Python-based tool that includes both a GUI and a scripting-based interface; this is discussed later in Section 6.2.⁸⁰

From the plethora of EXAFS papers available in the literature, we now highlight a few prototypical studies that use the conventional EXAFS analysis approach to investigate the nature of the catalytic sites. Lomachenko et al. studied the temperature-dependent (150–400 °C) ammonia-assisted selective catalytic reduction (SCR) of nitrogen oxides by Cu

CHA catalyst using *operando* XAS and X-ray emission spectroscopy (XES). This work combined XANES, EXAFS, and XES to identify the two regimes of catalytic behavior of the Cu sites in the catalyst. The SCR activity at a low temperature (~200 °C) was attributed to Cu(I) and Cu(II) sites, while at a high temperature (above 250 °C), Cu(II) sites led to a steep increase in catalytic activity.⁸¹ This study identifies the average coordination environment of the dominant active sites for nitrogen oxide SCR in reaction conditions. The conventional EXAFS approach has been used to identify the nature of plasma-modified dendritic Cu sites used as a catalyst for CO₂ reduction by Scholten and co-workers. The authors use *operando* EXAFS and XPS to demonstrate that the presence of a Cu oxide phase prior to CO₂ electroreduction does not impact the catalyst performance for electrocatalytic conversion of CO₂.⁸² Other studies include elucidation of the nature and structural properties of PdO and Pd transformation of Pd/Al₂O₃ catalyst using XAS at temperatures ranging from room temperature to 900 °C,¹ using XAS to understand the redox catalytic behavior of Ce⁴⁺ cations in MOFs,⁸³ and the study of Pt–O–Pt ensembles formed from seeding of atomically dispersed Pt on CeO₂ using EXAFS and STEM.⁸⁴ It is clear that EXAFS has provided structural and mechanistic insights that are inaccessible using other characterization techniques for a diverse array of catalysts and catalytic processes.

Recent studies report the use of DFT to design active sites for target reactions like CO₂ reduction, CO oxidation, methanol self-coupling, and water oxidation.^{85–88} While these studies use XAS for structure determination, atomistic structures obtained from DFT are not used as initial parameters for EXAFS modeling. Including the latter step in the analysis could potentially improve the consistency between the computationally predicted and experimentally realized

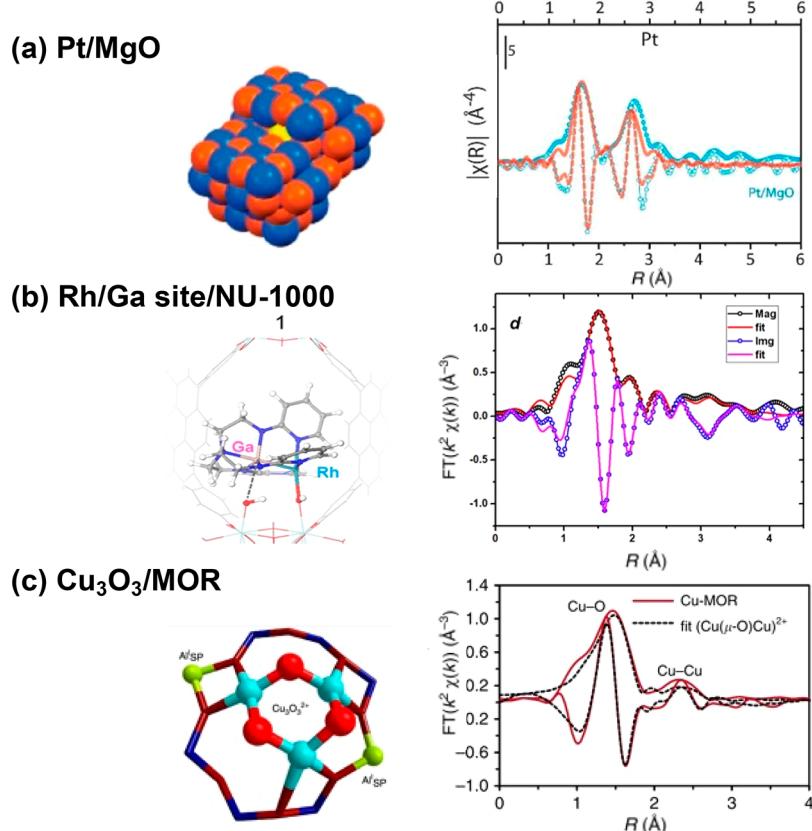


Figure 5. Examples from Category 2 wherein a DFT-optimized structure (left) was used to fit/directly compared to EXAFS data (right) for different catalytic materials: (a) Pt/MgO,²² (b) Rh/Ga site/NU-1000,¹⁰⁵ and (c) Cu₃O₃/MOR.¹⁰⁷ To emphasize the key role of DFT, the structure of the proposed site is presented alongside the corresponding EXAFS fit. Part a reprinted (adapted) with permission from ref 22. Copyright 2020 American Chemical Society. Part b reprinted (adapted) with permission from ref 105. Copyright 2018 American Chemical Society.

active site. Identification of the local coordination environment from EXAFS can assist in designing catalysts with high selectivity toward the target reaction. For example, He et al. used a combination of techniques, including XAS, to study atomically dispersed catalysts with high regioselectivity and chemoselectivity during hydrogen treatments. They prepared 24 different catalysts (both noble and non-noble metals) using a precursor dilution strategy. Specifically, the authors discuss a Pt₁/N-C catalyst for the selective conversion of terminal alkynes to alkene.⁸⁹ Wei et al. used EXAFS in combination with other spectroscopic and imaging techniques to observe the transition of noble metal nanoparticles (Pt, Pd, and Au-NPs) to thermally stable single atom catalyst when calcined above 900 °C under inert conditions.³ Similarly, review articles focused on atomically dispersed catalysts frequently highlight the significance of EXAFS in understanding the local structure of the active species, thus reemphasizing the relevance of using theory to model EXAFS data.^{91,93–97}

A common feature in the studies by Lomachenko et al. and Wei et al. is that important information was obtained based on the changes in the average coordination environment around the absorbing atom. Since the experimental samples (e.g., Cu oxides or various nanoparticle catalysts) are not described by a unique or uniformly distributed arrangement of atoms, conventional EXAFS analysis provides qualitative insights that link experimental observations to structural changes in the catalysts.

Using the above publications as a representative set, Table 1 presents a meta-analysis of the EXAFS fitting approaches that

are typical of Category 1 studies. It is clear that specific details of the fitting procedure are not always available. While most reports focus on qualitative interpretation and provide significant details of the fitting procedure, other studies compare the experimental EXAFS (e.g., TM₁/N-C catalyst) with metal and metal oxide references to prove the absence of metal–metal coordination. Indeed, using scattering paths derived from DFT structures improves the confidence in their EXAFS interpretation; such studies are classified as belonging to Category 2 and are discussed next.

4.2. Category 2. To mitigate the limitations of using nonrepresentative compounds (e.g., bulk metal oxides to represent atomically dispersed catalysts), a few studies have used DFT-derived structures to generate a list of scattering paths for EXAFS analysis.^{22,100,103,104} For example, Desai et al. have elucidated the mechanism of promotor-controlled stereoselectivity of alkyne semihydrogenation to E-alkynes using a rhodium–gallium/NU-1000 catalyst.¹⁰⁵ In this study, the authors collect both Rh K-edge and Ga K-edge EXAFS and interpret the data using models obtained from periodic DFT; a total of 8 structures are used. In contrast to Category 1 studies listed above, the initial list of scattering paths is obtained from DFT structures. In addition to considering the quality of fit, the authors also compare the energetics of the various plausible structures. Another example of using DFT and EXAFS to get structural insights is demonstrated by the work of Roscioni et al.¹⁰⁶ In this study, the authors evaluate a set of plausible docking sites for the chemisorption of monodispersed rhodium dicarbonyl species on γ-Al₂O₃ surfaces. In addition to

considering the energetics of different configurations, the authors leverage previously published EXAFS data and their own XANES simulations to highlight the inconsistencies in the reported Rh¹(CO₂)/γ-Al₂O₃ literature. Grundner and co-workers showed that highly selective trinuclear copper-oxide clusters stabilized in mordenite are promising catalysts for methane to methanol conversion. This is an example of a detailed EXAFS study that simultaneously compares coordination numbers and bond distances obtained from experimental EXAFS fitting with the DFT-simulated structures.¹⁰⁷

The above reports highlight the advantages of utilizing DFT-calculated structures for EXAFS analysis. As the DFT-derived structures are also used for further mechanistic investigations, Category 2 studies show superior consistency between the structure (i.e., the EXAFS-derived model) and function (i.e., the mechanism) of the proposed active site(s).^{108–112}

In addition to the procedural differences between Category 1 and 2, the latter studies also demonstrate a clear shift in the mindset of the authors. While Category 1 studies typically use EXAFS experiments as an exploratory tool, the Category 2 studies discussed above use EXAFS to evaluate if the hypothesized active site motifs are consistent with the measured experimental data (a few examples are presented in Figure 5). An example of this philosophy is demonstrated by Sarma et al.²² Here, the authors use DFT-optimized structures of atomically dispersed transition metals (Pt, Ir, Rh Ru, and Pd) supported on MgO to model the EXAFS data. This work, like the Grundner study, features an extensive Supporting Information section that provides sufficient detail that would allow an interested researcher to reproduce their EXAFS analysis.

It is important to appreciate the utility of well-defined systems like atomically dispersed catalysts as a class of materials where one can aim to determine a rather accurate and realistic bonding environment of the metal sites. While these materials are conducive to detailed, theory-guided EXAFS analyses as discussed above, the technical aspects of EXAFS modeling remain similar to Category 1 studies (as summarized in Table 2). Thus, the fitting process tends to be

Table 2. Meta-Analysis of Category 2 Studies^a

study/ count	catalyst	ref	analysis software ^b	k-range
1	Cu and Ce exchanged Y zeolites	5	Athena and Artemis	not stated
2	(Ru, Ir, Pd, Pt, Rh)-SACs/MgO	22	Demeter	0–12 Å ⁻¹
3	Rh–Ga sites in MOFs	105	Athena and Artemis	2–9 Å ⁻¹
4	Rh ¹ (CO) ₂ /γ-Al ₂ O ₃ catalysts	106	not stated	not stated
5	single-site trinuclear copper oxygen clusters in mordenite	107	Athena and Artemis	2.5–13 Å ⁻¹
6	Pt/Al ₂ O ₃ and Pt–Mn/Al ₂ O ₃	108	not stated	not stated
7	Pd–Fe bimetallic catalyst on carbon	109	Athena and Artemis	2.5–13 Å ⁻¹
8	CuO _x /SiO ₂	110	Athena and Artemis	not stated
9	bimetallic In–Pd catalysts	111	Athena and Artemis	not stated
10	Pt sub-nanocluster catalysts	112	Demeter	3–12.5 Å ⁻¹

^aThese studies are classified as being semiquantitative since they use DFT-derived structures to guide EXAFS interpretation but are limited to utilizing only a few (typically <5) averaged scattering paths. ^bThe software listed in the table is based on the terminology used by authors in the associated publication.

cumbersome, is limited to considering only a few scattering paths, and cannot be scaled to analyze large databases of DFT-derived structures. Indeed, the Sarma study was limited to considering the averaged coordination environment around the Pt cation (i.e., a scattering shell-based approach), as including all possible unique scattering paths was likely not feasible. Although the use of DFT-derived structures for EXAFS interpretation is a major accomplishment of Category 2 studies, large-scale adoption of such approaches requires the use of advanced analysis tools; examples of this approach are discussed below in Category 3.

4.3. Category 3. The studies that used more realistic atomic structures to model EXAFS data are discussed in Category 3. Yancey et al. reported a methodology to analyze 1–2 nm diameter nanoparticles of thiolated gold clusters using EXAFS and *ab initio* molecular dynamics. This work demonstrates the advantage of using an integrated experiment–theory approach to obtain structural insights for systems that are not amenable to conventional analysis.¹¹³ Using pristine and thiolated gold nanoparticles as model systems, subsequent studies^{114,115} from the same team have proposed metrics to quantify the limitations of conventional EXAFS analysis. These series of papers are particularly fascinating as they highlight how collaborations between theorists and experimentalists can result in the development of new analysis methods.

QuantEXAFS is a recently reported theory-guided Python-based EXAFS analysis approach that uses the open-source Larch software for EXAFS preprocessing, analysis, and fitting.⁸⁰ This method begins by creating an exhaustive database of DFT-optimized structures that can be used to model the experimental EXAFS.^{116,117} While uniform atomically dispersed catalysts are more amenable to analysis by QuantEXAFS, this approach has been extended to more complex systems such as Pt/ZSM-5.¹¹⁸ The latter study is particularly interesting due to the complexity of the zeolite support; the authors use a zeolite-specific simulation codebase¹¹⁹ to enumerate all possible bonding sites of Pt²⁺ and [Pt–OH]¹⁺ species in the MFI topology. Although questions about the uniformity of the proposed Pt²⁺ site remain open, a key advantage of QuantEXAFS is the ability to compare the modeled EXAFS spectra of different types of sites (e.g., all possible Pt²⁺ vs all possible [PtOH]¹⁺) rather than only considering a few plausible configurations. Figure 6 illustrates a subset of studies that use approaches discussed in Category 3.

5. EMERGING ROLE OF MACHINE LEARNING WITHIN THE XAS CHARACTERIZATION COMMUNITY

The computational catalysis community has enthusiastically embraced the development of machine learning tools to predict various relevant properties as an approach to reduce the high cost associated with performing DFT calculations. Similarly, theory-driven and data-centric approaches have also been used to create databases of structural models for EXAFS interpretation^{120,121} and facilitate XANES analysis.¹²² Significant efforts by several groups have focused on XANES data analysis for a range of different materials.^{7,8,70,123–131} In our opinion, these studies lay the foundation for the development of analogous methods for EXAFS analysis.

While Section 4 focused on the process of identifying one or more structures that are consistent with the experimental EXAFS data, we now highlight the implementation of supervised and unsupervised machine learning methods,

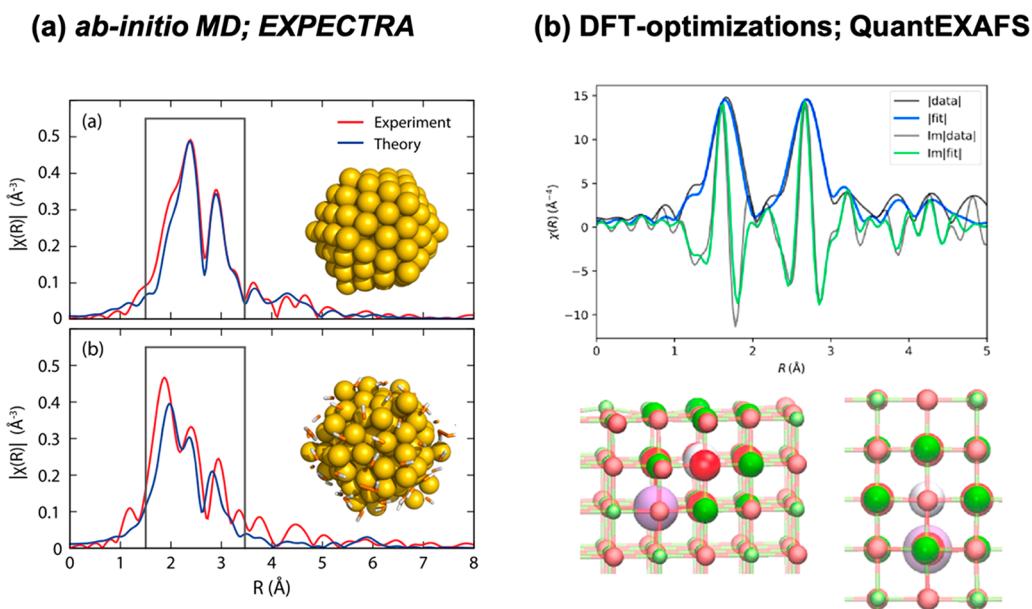


Figure 6. Examples for Category 3 studies wherein (a) *ab initio* MD (EXPECTRA)¹¹⁴ and (b) DFT-optimized structure (QuantEXAFS)¹¹⁷ were used to interpret the experimental EXAFS data. A key feature is the use of analysis approaches (i.e., EXPECTRA and QuantEXAFS) capable of incorporating the full structural details of a given DFT-derived structure. Part a reprinted (adapted) with permission from ref 114. Copyright 2015 American Chemical Society. Part b reprinted (adapted) with permission from ref 117. Copyright 2022 American Chemical Society.

Reverse Monte Carlo (RMC) and molecular dynamics (MD), to extract information from the experimental EXAFS and XANES spectra. There are studies that report the use of RMC for perovskites (CaFeO_3 and SrFeO_3) and for high-entropy alloys (HEA) to identify the local structure and transformation of the material under *in situ* EXAFS conditions.^{132,133}

Timoshenko et al. extracted the radial distribution function (RDF) of atoms in different phases of bulk iron during transient thermal conditions from 300 to 1273 K by using an artificial neural network (ANN) trained on MD–EXAFS data.¹³¹ Lüder presented a comprehensive review of the local structure of transition metal ions (Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+}) using ANNs.¹³⁴ The metal was placed in a crystal field that is representative of the chemical environment. The method was further extended to estimate core-hole lifetimes for temperature and experimental broadening. This work highlights the ability of ANNs to predict the experimental XAS spectra assuming the background signal contributions are appropriately handled. With further developments, such methods have the potential for predicting XAS spectra without requiring expensive electronic structure theory calculations. Within the context of catalysis science, we anticipate that similar ML methods will play an important role in elucidating the structural characteristics of systems that are not amenable to direct DFT calculations.^{70,120,122,130,135,136}

Timoshenko and Frenkel, provide a perspective on the catalytic activity descriptors with a focus on XAS, predominantly focusing on ML.¹³⁷ While the use of ANN is mostly restricted to XANES analysis, there are studies that use classical MD, force fields, and related quantum chemistry methods to generate models to fit experimental EXAFS spectra.^{128,138–146} The structural disorders can be modeled with the help of reverse Monte Carlo (RMC) and can also assist in simplifying these approaches for accountability of numerous scattering paths by common ML techniques like clustering.¹⁴⁷

6. OUTLOOK

The year 2020 marked the centenary of the first X-ray absorption spectrum published by Fricke in Manne Siegbahn's laboratory at University of Lund.¹⁴⁸ In light of the tremendous impact that XAS has had on the catalyst characterization community (as summarized in Sections 3 and 4) and growing adoption of data-centric tools by the field of catalysis science, it is now timely to examine the opportunities and challenges associated with using XAS to probe the structure and properties of the active site(s). Specifically, while it is clear that XAS should, and will, continue to play important role in *ex situ* and *operando* structural characterization within the catalysis science community, we present four specific strategies that could be used to maximize the impact of this versatile technique in the near future.

6.1. Toward a Materials-Centric EXAFS Analysis Approach That Considers the Structural Characteristics of the Experimental Sample. Prof. John Rehr, while discussing the frontiers in XAS theory during the recent XAFS2022 conference, concluded that “XAS theory is in better shape than ever.”¹⁴⁹ Although it is true that the EXAFS community has witnessed significant advances related to understanding the underlying physics of XAS,¹⁵⁰ there are multiple opportunities for applying theory and various computational chemistry tools to obtain detailed insights into several types of catalytic systems.

Specifically, the categorization scheme developed in Section 2 emphasizes the importance of choosing an EXAFS analysis approach that is (1) specific to the properties of the experimental sample (e.g., uniformity) and (2) consistent with the overall focus of the study. Although experimental EXAFS always provides averaged information about the coordination environment of the absorbing atom, the chosen analysis approach should depend on the type of catalyst being considered. For catalysts hypothesized to consist of largely one type of site (e.g., precisely synthesized atomically dispersed

Table 3. Overview of the Various Tools That Can Be Used to Facilitate the Processing of EXAFS Data

Methods	Fundamentals	Transformation of Structural Information to EXAFS Signal	Applications
FEFF ⁴²	Real-space Green's function calculations of XANES and EXAFS based on the muffin-tin potential approximation, and using a variety of core-hole and self-energy approximations	Path by path EXAFS engine for fitting programs like Artemis	
GNXAS ⁴³	Advanced program for EXAFS analysis based on multiple scattering calculations	Direct use of EXAFS raw data without preprocessing, accounts for complex background multielectron excitations and flexible to user intervention at every stage	
Corvus ⁴²	Property-driven workflow tool designed to combine multiple codes for enhanced XAS simulations	EXAFS-focused workflows include generation of EXAFS spectra including <i>ab initio</i> Debye–Waller factors and MD-averaged EXAFS	
FDMNES ⁶¹	Full potential <i>ab initio</i> code to simulate XANES spectra	Uses finite difference method near-edge structures (FDMNES) and density functional theory (DFT); specifically applicable to simulation of K edges	
	EXAFS data processing		
Athena ⁷⁹	One of the most widely used Windows-friendly interactive graphical interfaces for processing EXAFS data	Preprocessing Converts raw EXAFS signal to energy; data calibration, normalization, and merging allows for forward and backward Fourier transform of the data	
ProQEXAFS ¹³⁹	Extraction, normalization, and interpolation of time-resolved XAS data	Python-based infrastructure for QEXAFS data analysis; file compression (1000-fold), on-the-fly averaging of encoder data	
EXAFS-Neo ¹²⁰	Genetic algorithm-based EXAFS analysis tool	Theory-Driven Analysis Functional under a number of simple and complex cases	
EvAX ¹⁵⁶	Evolutionary algorithms and Reverse Monte Carlo (RMC) methods	Disorders in well-defined systems where the coordination number is predetermined	
Larch ⁸⁰	Coding interface that works on similar infrastructure like Athena and Artemis and Python-friendly; front-end of FEFF or IFEFFIT to generate scattering paths	Programmable and fast, able to deal with large data sets unlike Athena and Artemis	
QuantEXAFS ¹¹⁶	Quantitative analysis of EXAFS data using database of DFT-optimized structures	Python-based workflow for automated and unique structural identification for catalytic materials using EXAFS	
	GUI-Based Analysis		
Artemis ⁷⁹	One of the most widely used Windows-friendly interactive graphical interfaces for EXAFS data analysis; front-end of FEFF or IFEFFIT to generate scattering paths	GUI-based interface that uses FPEF simulations to model EXAFS spectra	
Larch ⁸⁰	GUI version of programmable Larch that works similar to Artemis and Athena combined	Friendly and robust version for the nontheory community to enable EXAFS and XANES data modeling	

materials), it is likely that the theory-guided approaches of Categories 2 and 3 will help in identifying the atomic structure of the active site. While the conventional EXAFS approach can be used to guide the construction of the initial DFT models in such cases, it is critical that the DFT models used for mechanistic studies are also directly used to fit the EXAFS data. As this workflow may overlook the underlying heterogeneity of the catalytic sites, theorists must be cautious about using the averaged coordination numbers and distances (obtained from conventional EXAFS analysis) to create DFT models for downstream mechanistic studies.

Although studies of both Categories 2 and 3 use DFT structures to generate a list of scattering paths, the key difference lies in how the data are analyzed. While the Category 3 approach (e.g., QuantEXAFS) considers all possible scattering paths individually (i.e., hundreds of paths are included for each DFT structure; $N_i = 1$ in eq 1), the work of Desai, Grundner, and Sarma only calculates the average coordination numbers, average σ^2 , and average scattering distances for each “shell”.^{22,105,107} One possible reason for this approximation (i.e., the anisotropy of the DFT structure is lost with the averaged analysis) is the use of conventional analysis approaches that require significant user-intervention during EXAFS fitting. Thus, for catalysts that can be represented as single or few DFT structures, we recommend using tools like QuantEXAFS (built using Larch, or other codes with a similar concept), which create one-to-one mapping between the DFT structures and the resultant spectra. Similar to how many computational catalysis tools are open sourced and are community-driven,^{57,73,151} our group is now focused on making QuantEXAFS available to the broader community.

Another important benefit of using structure databases explicit to the specific study is the ability to validate the structure that is well-representative of the experimental EXAFS data in combination with testing it with high-energy-resolution fluorescence detection X-ray absorption near-edge structures (HERFD–XANES) data. HERFD–XANES overcomes some of the main limitations of conventional XAS regarding energy resolution.^{152,153} Chen et. al, use a similar approach to model HERFD–XANES data using DFT structures shortlisted based on thermodynamics and EXAFS fits and compare it to experimental HERFD–XANES data.^{116,117}

6.2. Transitioning toward the Use of More Robust and Scalable Analysis Tools. The DFT-centric approaches of Categories 2 and 3 are only possible when theory can provide a reasonable atomistic structure that is representative of the experimental sample. For materials that inherently consist of distributions of coordination environments (e.g., supported nanoparticle catalysts), EXAFS interpretation is currently limited to the conventional Category 1 analysis. Although GUI-based tools remain popular, these interfaces require significant user-involvement during the fitting process. In their current form, such tools are not scalable to handle thousands of EXAFS data sets (e.g., describing catalyst evolution under reaction conditions).

With the advent of data-rich techniques such as continuous scanning and Quick-EXAFS, it is important for the community to begin the transition toward more efficient analysis workflows. As an example, Hidalga and co-workers have demonstrated the advantages of using Larch over other user-driven approaches.¹⁵⁴ In addition to a more user-friendly GUI, better data management, and fast processing, Larch also features a Python-based scripting interface and is currently

been supported with new features being added by the community. The implementation of Larch with Python rather than Perl (as with Demeter) is appealing to the computational catalysis community. As discussed earlier, this has already led to the development of QuantEXAFS, which integrates Larch with the Python-based Atomic Simulation Environment library and the development of CatXAS which allows both automated XAS data workup (e.g., alignment, normalization, background removal) integration with other process parameters of interest to the catalysis community (e.g., mass spec data, GC data, flow rates, temperature, etc.) to allow structural correlations to be made.¹⁵⁵

Although the above discussion has focused on EXAFS modeling, Table 3 summarizes several tools that help facilitate other aspects of EXAFS analysis. For instance, a Python-based deglitching program was recently developed to automatically detect and deglitch the spectra. The program uses both a Savitzky–Golay filter for data smoothening and a generalized extreme Studentized deviate (ESD) test to detect outliers. This program enables reproducible and selective deglitching of the EXAFS spectra.¹³⁸

6.3. Embracing Findability, Accessibility, Interoperability, And Reusability (FAIR) Data Practices within the XAS Community. The development and use of tools like Larch provide an opportunity to both further strengthen the application of machine learning to XAS data and to streamline data analysis, dissemination, and storage. Here, the XAS community can also learn from the continuing evolution of computational catalysis: from appending a long list of atomic coordinates (e.g., XYZ files) in the Supporting Information document to including a set of representative structures, the theory community now relies on using convenient database files (e.g., ase-db) or cloud-hosted storage solutions. While several computed property databases exist for catalyst materials¹⁵⁷ (an effort led by the battery research community),^{73,158} similar community-driven or centrally managed repositories remain rare for catalysis-specific XAS data.

Nevertheless, there are already larger efforts underway in, e.g., Japan and Germany for the creation and curation of XAS databases for typically inorganic materials. This has also been an ongoing activity within the International XAFS Society, particularly through the q2EXAFS subgroup within the XAS Commission of the IUCr. Within the US, and in particular the catalysis community, there is currently no centralized funded effort for a similar XAS database relevant to catalysis research.

To inspire direct support from the funding agencies to create such databases in the future, in our opinion, the responsibility currently falls to the community to embrace and interpret FAIR Guiding Principles for their own XAS data set.¹⁵⁹ As a reminder, the FAIR Guiding Principles emphasize that all research objects should be findable, accessible, interoperable, and reusable (FAIR), by both machines and humans. As peer-review publications remain the cornerstone for sharing XAS data and interpretation, in addition to embedded EXAFS analysis figures (typically k -space and r -space) in the manuscript document, we suggest that the raw XAS data set(s) (such as X-ray Data Interchange (XDI) files) are included in the Supporting Information. These can then be automatically mined by the interested users, especially if they are provided in a convenient format. To spearhead this process, we provide the data and analysis scripts for three of our recent publications as initial templates for use by the community.

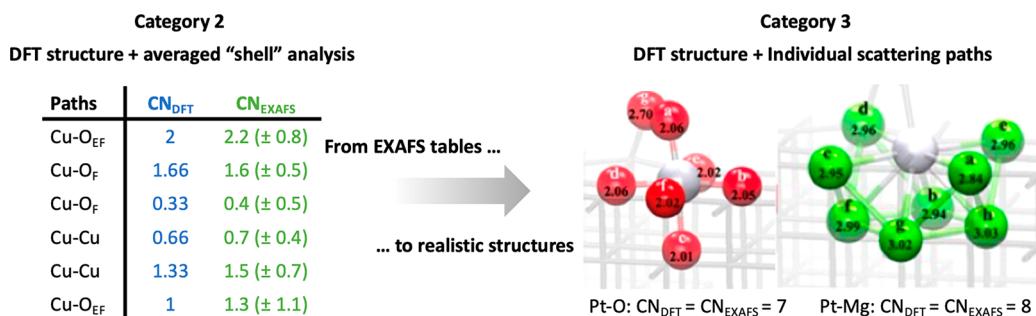


Figure 7. The development of improved analysis tools capable of including the anisotropies of the coordination environment requires a new approach for representing structures derived from EXAFS analysis. While both ref 107 and ref 117 use DFT to guide EXAFS interpretation, the latter study explicitly includes the contributions of individual Pt–O and Pt–Mg scattering paths. Reprinted (adapted) with permission from ref 117. Copyright 2022 American Chemical Society.

The theory community has a central role to play in this initiative. The key takeaway of **Section 4** is that the EXAFS analysis approach should be intricately coupled with the properties of the catalyst. For studies that aim to elucidate the structure of the active site(s) for well-defined uniform materials, we recommend that, where feasible, the community utilize the Category 3 approach based on directly using the DFT-derived structures for EXAFS interpretation. We do note a limitation in this approach in that not all XAS experimentalists have ready access or collaborations with theory groups. Since methods such as QuantEXAFS aim to correlate a DFT structure with the associated EXAFS spectra, the machinery used for sharing DFT data (e.g., relative stabilities) can also be used to share the EXAFS analysis. As an example, we have provided a simple Jupyter notebook and an ase-db file that facilitates access to our EXAFS analysis for the Pt/ZSM-5 study on the GitHub repository (details provided in the [Data Availability Statement](#)).

While the community can and should take a lead in laying the necessary groundwork, support from the funding agencies is necessary to create and maintain production-level databases and software. As graduate students and postdoctoral associates in the field are not formally trained in software development and spend a relatively short time within a research group, it will prove necessary to seek support from professional software engineers to establish centralized FAIR XAS repositories for catalysis science. Support from funding agencies to promote collaborations between experimental and computational catalysis communities, for instance, in the theoretical simulation of structure and associated XAS, will be greatly beneficial in strengthening the fundamental understanding of catalysts and the overall performance of the catalysis community. In particular, we envision specific funding for the concurrent experimental and theoretical characterization of catalysts, in order to maximize the information generated at the synchrotrons.

6.4. Enabling Effective Use of the Allocated Beamtimes by Coupling XAS Data Collection with Real-Time EXAFS Interpretation. Even with the relatively large number of XAS beamlines worldwide, these beamlines are still typically oversubscribed by 400% or more. Thus, it is crucial to ensure that the precious allocated beamtime is used as effectively as possible. Typical catalysis XAS beamtime is used to test a hypothesis about the specific structure that gives rise to the catalytic activity. Thus, the data are collected first; the postprocessing and data analysis may occur many weeks after the beamtime. Our previous discussion (**Section 3**) has

highlighted some of the factors that may be responsible for this disconnect. Also, note that this approach typically results in a table of averaged coordination numbers and scattering distances.

It is usually only at that point that thought is given to use modeling (i.e., DFT for heterogeneous catalysts) to aid in the analysis. With the advances in computational catalysis, the development of robust EXAFS analysis workflows, and advent of XAS data repositories, we posit that this approach should be reversed or at least modified significantly (as illustrated in **Figure 7**). For example, for materials that are amenable to Category 3 analysis, a library of DFT structures should be calculated ahead of the beamtime; these structures can then be used to fit the EXAFS data *as it is being collected*. Based on our experience with QuantEXAFS, this analysis procedure takes a few minutes and can be performed in parallel with the data collection at the beamline. Similarly, tools such as Larch can also be used for similar on-the-fly analysis of materials even when DFT structures are not available. Although GUI-based tools can be used, from the perspective of the senior theory author, it is always advantageous to learn a programming language (e.g., Python).

Transitioning toward real-time analysis is beneficial as it will allow the user to modify the experimental plan (e.g., increase data collection time, change gas composition, swap out a damaged sample, etc.) as necessary. With the continued improvements in estimating Debye–Waller factors^{160–163} and armed with DFT-derived models, it may be feasible to *a priori* estimate the *k*-range signal/noise ratios, etc., necessary to test a particular hypothesis or confirm the presence of certain types of active site motifs.

7. CONCLUSIONS

Extended X-ray absorption fine structure (EXAFS) spectroscopy remains a key technique within the heterogeneous catalysis community to probe the structure and properties of active site(s) for various catalytic materials. However, the interpretation of the raw experimental data to derive an atomistic picture of the catalyst requires modeling and analysis. Specifically, the current “EXAFS fitting” approaches are often nontrivial and time-consuming; overcoming these limitations remains a central challenge for the community.

In this Perspective, we have highlighted how recent developments in analysis software and increased availability of reliable computational models can be used to improve the speed, accuracy, and reliability of EXAFS interpretation. Specifically, by classifying the published literature into three

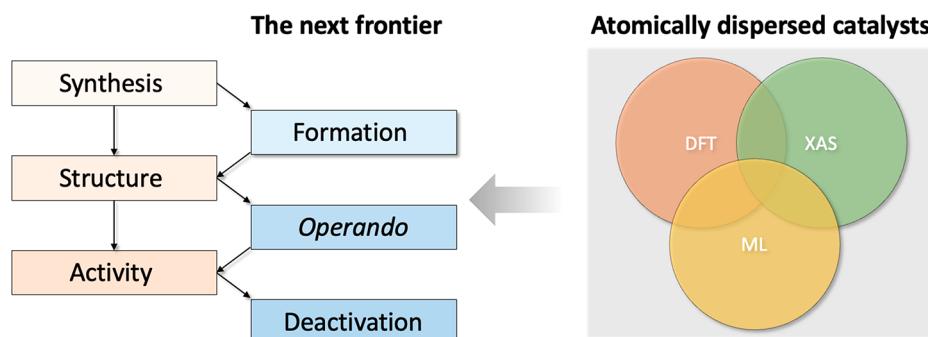


Figure 8. Advances in X-ray absorption spectroscopy, machine learning, and density functional theory can be combined to elucidate the synthesis–structure–activity relationships for atomically dispersed materials.

distinct categories, we first demonstrated that using DFT-computed structures as a starting point for EXAFS interpretation can be superior to the conventional analyses, especially in identifying the catalytic sites for certain classes of materials. In scenarios where DFT does not provide realistic structures, we have emphasized the advantages of using more robust and scalable analysis tools (e.g., Larch). For such complex catalytic materials, it is likely that adoption of machine learning and other data science tools will greatly enhance the interpretation of the XAS data. Furthermore, to facilitate the upcoming data-driven revolution in this field, it is necessary for the community to adopt FAIR Guiding Principles for the collection, analysis, dissemination, and storage of XAS data. In our opinion, the computational catalysis community will play a key role in enabling the transition.

The evolution of EXAFS from the current two-step model (i.e., data collection step followed by model fitting and interpretation) to a real-time characterization technique may have far reaching impacts on the field of heterogeneous catalysis. Indeed, while structure–function relationships are well-established, less attention has been focused on elucidating the mechanism of catalyst synthesis. Recognizing that the overlap between of EXAFS analysis and theory (both DFT and machine learning) is especially well-suited for studying precisely synthesized materials, Figure 8 motivates one such interdisciplinary challenge for the researchers studying atomically dispersed catalysts.

We encourage the heterogeneous catalysis community to identify similar challenging questions that can perhaps be addressed by combining the advances in XAS experiments and the continued collaborations with the theorists. Based on the recent developments in this arena, we are confident that the next decade will provide unprecedented insights into physiochemical phenomena that currently remain inaccessible.

■ ASSOCIATED CONTENT

Data Availability Statement

The data files from Web of Science for Figure 2, the Jupyter notebook, and an ase-db file that facilitates access to our EXAFS analysis for the Pt/ZSM-5 study are all provided on GitHub at https://github.com/kul-group/kul-repository/tree/main/repo_2022_ACS_Cat_Bridging.

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Notes

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