

Speciation of Nanocatalysts Using X-ray Absorption Spectroscopy Assisted by Machine Learning

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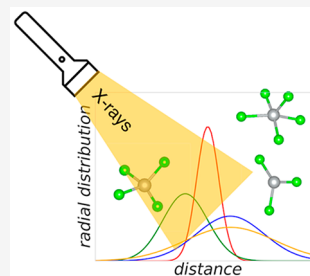
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ABSTRACT: The structure and morphology of supported nanoparticle catalysts play important roles in many industrial reactions. Recent progress has identified key aspects of structure–activity relationships at the nanoscale and novel methods to study the local environment of the active sites. X-ray absorption fine structure (XAFS) spectroscopy, despite being a leading technique for this purpose, is hampered significantly by its ensemble-averaging nature which often leads to a bias toward a single “representative” structure. Learning heterogeneous distributions of nanostructures at the inter- and intraparticle levels from the average XAFS spectrum is a formidable challenge that can be overcome in some cases described in this Perspective. We also discuss emerging machine learning techniques for extracting the information about the heterogeneity of metal species from XAFS data.



1. INTRODUCTION

In the last few decades we have witnessed tremendous progress in synthetic methods designed for the exquisite control over the size, shape, structure, and elemental composition of nanoscale catalysts.¹ The quest for developing effective size and shape control strategies resulted in a wide range of unique one-, two-, and three-dimensional architectures, and the list of well-defined structures in the size range exceeding 1 nm is rapidly growing.^{2–8} The situation is less optimistic toward the subnanometer structures, where inherently heterogeneous isomers of size-selective clusters coexist in samples prepared by even the most accurate deposition methods.⁹ Supported nanometer-scale catalysts have a relatively high degree of bonding disorder, hence embedding strong heterogeneities.¹⁰ In general, heterogeneity in the nanoscale catalysts can vary in the process of their use. From being relatively well-defined as a result of precise synthesis, the size and size distribution may change in the course of catalytic pretreatment.¹¹ In supported metal nanoparticles, the distribution of the states of crystalline order or disorder within the ensemble can be modified in reaction conditions by the interaction with support¹² and adsorbates.^{10,13} In addition to these forms of interparticle heterogeneity, there are also several types of intraparticle heterogeneity. Those range from the charge distribution within the catalytic particle to the variation of bonding strain between the support interface or surface toward the particle interior.^{14–16} Recent results obtained for mono- and bimetallic nanoparticles highlighted their fluxional character and redistribution of atoms and charges within each nanoparticle.^{15,17,18} Atomically dispersed catalysts on supports (also known as “single-atom” catalysts or SACs) adopt different binding sites that may range from substitutional to interstitial (within the support oxide) and different sites on the oxide particle surfaces.¹⁹ Active species on the surface of dilute

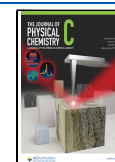
bimetallic alloy catalysts are described in terms of A_nB ensembles (for example, the dilute element A = Pt, Pd, or Rh is alloyed with the host B = Au, Ag, or Cu, and *n* varies from 1 (monomers) to 2 (dimers) to 3 (trimers)).²⁰ In the SACs and dilute bimetallic catalysts (including “single-atom” alloys, or SAAs), the distribution of coordination states can also vary in pretreatment and reaction conditions,²¹ and its understanding is the subject of intense research.^{22–28}

Schematically illustrated in Figure 1 are the fundamental challenges in studying heterogeneous systems by different experimental probes, which usually result in ensemble averaging over heterogeneous units, and a homogeneous model often assumes unimodal distribution of “representative” structural species. Determining accurate distributions of structurally and temporally heterogeneous systems offers new opportunities in catalyst design (e.g., targeting a certain static or dynamic structure of a catalyst may be possible by rationally tuning up the temperature, pressure or pretreatment conditions). On the other hand, such heterogeneities present a formidable challenge to the efforts aimed at capturing the details of local environment and electronic properties in each “unit” in space or time domains, be it a particular bimetallic ensemble or a SAC or a metal complex in a zeolite, limits our understanding of those units—their volume or mass fractions and identities. The chief reason for that is the inability of most imaging and scattering techniques to

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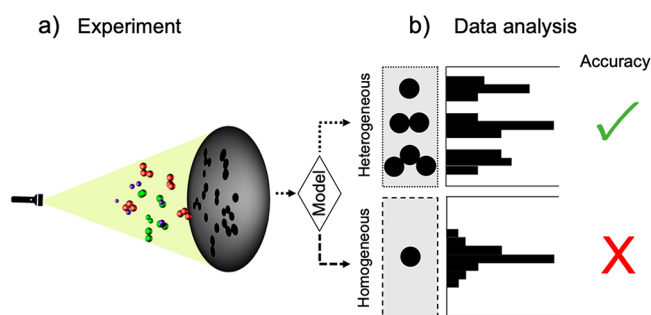


Figure 1. Schematic representation of the challenge presented by heterogeneous systems. In (a) the light cone represents an experimental stimulus interacting with a heterogeneous sample (colored spheres), and the shadow represents the observable space that contributes to the ensemble-average spectrum. In data analysis step (b), the spectrum can be either represented by a “homogeneous” model, which, erroneously, treats the sample as comprised of the same species, or an average of unique species shown schematically as monomers, dimers, and trimers—a more accurate, “heterogeneous” model. The proper choice of the model is the key to evaluate the heterogeneity of the ensemble.

resolve the coexisting species of nm-scale dimensions at the desired level of detail and to do so in real time, under *in situ* or *operando* conditions.

X-ray absorption fine structure (XAFS) spectroscopy has been a premier method for investigating nanoparticle catalysts in reaction conditions, and its advantages and limitations have been discussed multiple times, including recent reviews.^{29–31} In this Perspective, we will summarize existing and emerging strategies for solving the complexity of nanoparticles by relying, primarily, on the recently developed XAFS-based methods assisted by using machine learning approaches. A relatively recent contribution to the XAFS data analysis, machine learning has rapidly gained attention after the first reports that demonstrated its utility for “inverting” the X-ray absorption near edge structure (XANES)³² and extended X-ray absorption fine structure (EXAFS)³³ data and mapping the XANES and EXAFS spectra on various structural descriptors of nanoparticles,^{32,34–37} clusters,^{38–42} and SACs.⁴³ We will leave the use of multimodal characterization approaches^{44,45} and single-particle spectroscopy methods⁴⁵ that are rapidly developing fields, suitable to address many challenges highlighted in this article by either a clever combination of local and bulk probes or by using nanoprobe, and well covered in recent publications^{46–48} out of the scope of this Perspective, focusing predominantly on the new opportunities of machine-learning-

assisted data analysis of XAFS spectra for studying heterogeneous catalytic species.

The task of speciation and/or identification of heterogeneous catalytic structures (we call them sources, in terms of their role for the corresponding spectroscopic signals) from the signals can be formulated in terms of a general framework of “blind source separation (BSS)”⁴⁹ problems, where source signals are obtained from a mixed signal without using any *a priori* information about the mixing matrix. This lack of information on the mixing matrix is usually compensated by additional assumptions on source signals, such as, e.g., linear separability. Independent component analysis (ICA) was one of the first proposed solutions to BSS, which factors pure source signals by maximizing the independence of each source signal, and is still a widely used technique.⁵⁰ More recent source separation algorithms developed for the cocktail party problem, are of significant interest for solving speciation problems using XAFS. In the remainder of this Perspective, we will summarize the challenges in the speciation at the interparticle and intraparticle level (for nanoparticle catalysts), discuss strategies for solving the structures of atomically dispersed catalysts, and outline the existing and emerging opportunities, drawing examples from recent publications including our own work. Furthermore, we also provide a brief outlook on developing new approaches for speciation using neural networks (NNs) and self-supervised embeddings.

2. HETEROGENEITY OF NANOPARTICLE CATALYSTS

XAFS is an ensemble-averaging technique. Each atom of a given element has an equal chance to be excited by an incident X-ray photon regardless of the details of its chemical state and local environment (we assume that the sample has been well prepared for a quality XAFS measurement; i.e., the density variations are at the size scale much lower than one absorption length). Hence, by imposing prior information on noninteracting (linearly independent) heterogeneous species constraints, the task of chemical speciation, i.e., the task of finding the number N of different types of species in a sample (only those are counted that contain atoms of the selected X-ray absorbing element) and obtain structural information about each species, is reduced to the task of algebraically deconvolving multiple mixed spectra comprising the measured spectrum at each experimental condition as shown schematically in Figure 2.

2.1. Interparticle Heterogeneity. When the distribution of sizes (and compositions for the bimetallics) within nano-

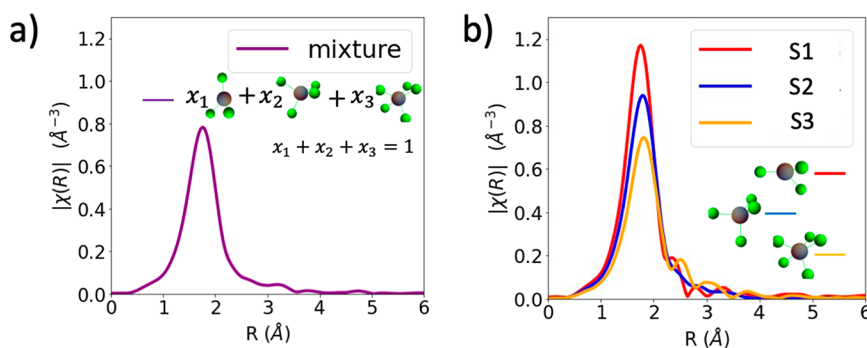


Figure 2. Chemical speciation of a mixture encoded in the EXAFS spectrum. For example, given a mixture of three species (S1, S2, and S3) with different coordination environments of metal ion complexes, the total EXAFS (shown in (a)) is a weighted average spectrum of these complexes (shown in (b)). More details are given in ref 51.

particles is relatively narrow and EXAFS data are of high quality, the size, shape, morphology, and structure of a “representative” particle with “effective” values of the first (and second, third, etc., as long as the particles are self-similar, the structure is relatively open, and the data quality is high) nearest-neighbor coordination numbers can be reconstructed from EXAFS.⁵² For bimetallic nanoparticles, compositional motifs such as segregation or uniformity or, in the case of the latter, the degree of the short-range order can be extracted by data analysis and modeling.⁵³ Due to the ensemble averaging described above, the original speciation of different sizes, shapes, and compositions of nanoparticles is impossible to extract from the data, at least at the present state of knowledge of EXAFS theory that currently relies on the notion of the “transferability of the photoelectron amplitude and phase”, that is, if the data fitting is routinely performed with FEFF-calculated photoelectron scattering functions based on the bulk metal counterpart of the unknown size/shape metal catalyst. While this transferability is a suspect at the size limit reaching 1 nm and below and is particularly dubious for dimers, trimers, and other metal clusters, the lack of well-defined experimental model systems (but not the lack of interest to challenge the notion of transferability) is the main reason one of the main pillars of EXAFS analysis remains intact for the time being. The practical result of this is that the inversion of the EXAFS spectra of heterogeneously (at the interparticle level) mixed nanoparticles is an *ill-posed* problem. The effect of this heterogeneity on the interpretation of the size and composition of such “representative” nanoparticles, at least in the limit of broad size and compositional^{54,55} distributions, has been possible to estimate and use in several recent practical cases. A correlative use of EXAFS—the average technique—with electron microscopy—a local, statistical method—was utilized to deconvolve between the coexisting structures comprising a metal catalyst and separately follow each species—the unreduced Pt atoms, the subnanometer clusters, and the nm-scale and larger nanoparticles—and their transformations in reaction conditions.⁴⁶

There is an interesting case of size-selective clusters that are inherently heterogeneous and have multiple isomers that have comparable total energies, even if the clusters have a well-defined chemical formula. In addition, we cannot exclude further heterogeneity induced by the catalytic conditions with fragmentation or fusion of clusters. As an initial test of the capability of XAFS to detect isomeric heterogeneity, we have considered the two lowest-energy structures of alumina-supported Pt₇ clusters calculated by the group of Alexandrova.⁵⁶ Their corresponding radial distribution functions (RDFs) $g(r) = \left\langle \frac{dN}{dr} \right\rangle$, where dN is the number of neighbors to a given atom in a concentric shell of radius r and thickness dr and angular brackets denote averaging over all atoms in the cluster, are shown in Figure 3, together with the ensemble average structure, calculated with the theoretically predicted weights of 0.66 and 0.34 that correspond to the temperature of 700 K. The dynamic component to the $g(r)$ is not included in Figure 3, but the changes in the region shown by arrows are significant enough to be detected even at 700 K, if the high energy isomer is present. Hence if isomers present a small energy difference ($\sim kT$), EXAFS at multiple temperatures could reasonably allow the detection of intercluster heterogeneity. Machine learning methods will be particularly valuable for this purpose because (1) the $g(r)$ can be strongly asymmetric and hence the “inversion” (neural network (NN)-assisted EXAFS analysis)

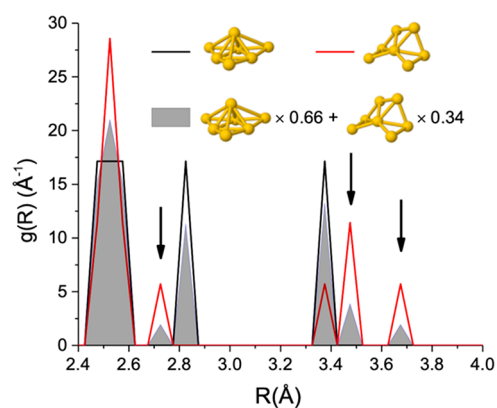


Figure 3. Radial distribution functions $g(R)$ calculated for the two lowest energy isomers of Pt₇ on alumina (lines) and for their ensemble average (shaded area) using theoretical weights (at 700 K). The regions shown by arrows are contributed by one isomer only and thus could be used for *operando* detecting and analyzing heterogeneous contributions.

method³³ is advantageous over the traditional fitting approach, and (2) the NN-EXAFS is demonstrated to work better in cases of low catalyst loading and high temperature compared to the fitting analysis.³⁴

2.2. Intraparticle Heterogeneity. Different atoms in the nanoparticles see different environments, due to their locations with respect to other metal atoms, atoms of the support, and/or adsorbates. Reliable methods for separating the contribution of atoms interacting with adsorbates (“active species”) from the total X-ray absorption signal that include contribution from “spectators” is one of the holy grails in catalysis. Identification of priors for a heterogeneous model is highly specific to the system and depends on the additional information. For example, in recent work, separation between Pd_nAu in 8% Pd in a Au catalyst was enabled by machine-learning-assisted XANES. This method takes advantage of the better sensitivity of XANES to the relatively small number of Pd–Pd bonds per Pd atom compared to traditional EXAFS analysis.²¹ By coupling the partial Pd–Pd and Pd–Au coordination numbers to information obtained via transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), electron energy loss spectroscopy (EELS), catalytic experiments, and extensive theoretical calculations, a heterogeneous model with surface and subsurface species of the Pd_n ($n = 1, 2, 3$) ensembles was obtained. As a result, the difference between $n = 1, 2$ (monomers and dimers) and $n = 3$ (trimers) was detected, explaining the changes in reaction outcome as a function of catalyst pretreatment (Figure 4).

In addition to the steady-state perturbation of the catalyst structure by the atmosphere, one can also study the dynamic response by using a pulsed method of data collection, using which both XANES and EXAFS spectra of active species can be identified with better signal quality. It is possible to resolve this heterogeneity by studying the dynamic response of the catalyst in a modulation excitation spectroscopy (MES) experiment, in which an external stimulus, such as composition of the reaction mixture, activates only species on the catalyst surface that respond at the same frequency as the driving force. This approach, which is an experimental equivalent of the digital lock-in amplifier, enables an enhancement⁵⁷ in signal-to-noise ratio by application of digital processing and machine learning tools and helps extract the dynamic response of heterogeneous species by using the time- and phase-dependent correlations. MES is usually coupled with IR and XPS measurements, but recently

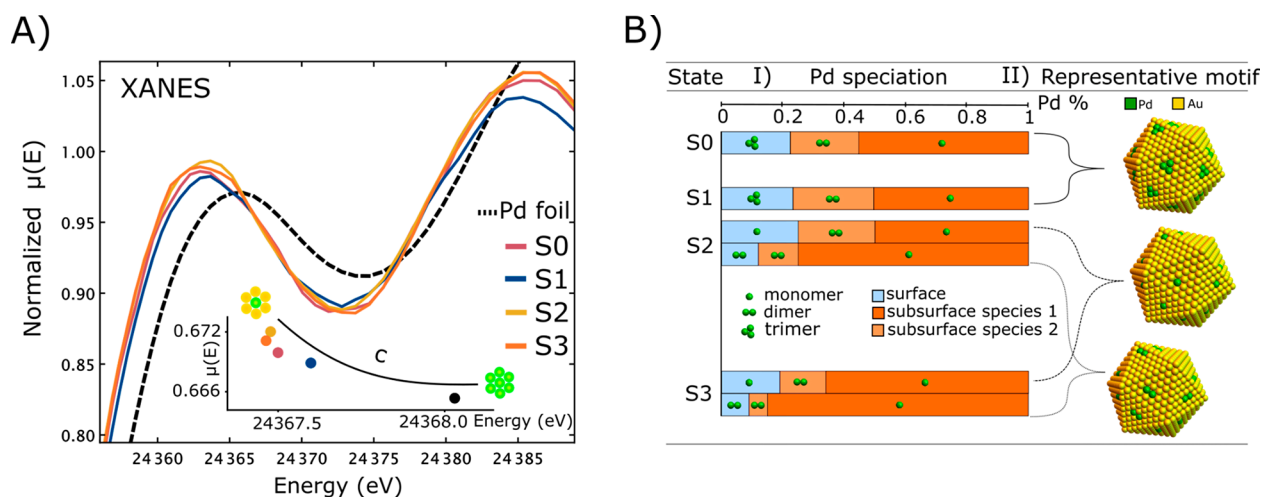


Figure 4. (A) XANES from 8% Pd in Au dilute nanoparticles supported by RCT-SiO₂ is measured for the sample as-received (S0), after oxygen treatment (S1) and after 2 sequential hydrogen treatments (S2 and then S3) and compared to the XANES of Pd foil measured during the same experiment. The XANES changes in response to the treatment and thus the signatures of 4 unique states are recorded. (B) The changes in XANES are quantified by NN-XANES analysis in terms of partial Pd–Pd and Pd–Au coordination numbers. The coordination numbers are parametrized in terms of Pd–Pd surface and subsurface ensembles. The average particle size and particle shape (via TEM) are used to constrain the problem. The Pd speciation is found by assuming one dominant species on the surface. The best fits are shown, where trimer surface species best fit S0 and S1 and dimer surface species best fit S2 and S3. Reprinted with permission from ref 21. Copyright 2022, The Author(s).

MES-XAFS has gained traction as a versatile method to study the dynamic behavior and fluxional nature of heterogeneous species.⁵⁸

3. HETEROGENEITY OF ATOMICALLY DISPERSED CATALYSTS (SACS)

Kottwitz et al.³⁵ emphasized in a recent review on characterization methods of SACs the complications for the interpretation of XANES and EXAFS spectra due to the coexisting of several binding sites. Due to the very nature of these atomically dispersed catalysts, the lack of metal–metal bonding and the heterogeneity of multiple binding geometries wash out the EXAFS signal beyond the first peak in *r*-space. Given that in most studied SACs and SAAs based on Pt,^{46,59–65} Rh,^{66–68} Pd,^{67,69,70} Ir,^{71–73} and Co^{43,74–79} the XANES features are often quite featureless, the methods of data modeling are severely limited in their ability to perform their speciation quantitatively and, in many cases, even qualitatively.

A counterpart to a SAC on an oxide support is an atomically dispersed catalyst coordinated to a framework such as a zeolite, providing a crossover between a homogeneous catalyst (e.g., Cu–enzymes) and a single-site heterogeneous catalyst. The problem with heterogeneity arises due to the inequivalent sites available for Cu occupancy in zeolites and the dependence of Cu speciation (the oxidation states and the local coordination environments) on the loading and NH₃-assisted selective catalytic reduction (SCR) reaction conditions.⁸⁰ K. Lomachenko et al. demonstrated that Cu in their work occurred as monomeric species only, and the temperature-dependent changes in the distribution of Cu sites are primarily due to the redistribution of Cu interactions with O-bonding extra-framework groups and reactants from the gas phase as well as Cu(II) coordinated to the framework. The latter species were shown to dominate in the SCR reaction conditions. In that work, appropriate experimental references for Cu(I) and Cu(II) states were used that adequately mimicked framework-interacting Cu species and those bound to extra-framework groups.⁸⁰ The linear combination fitting method of Cu XANES data was used

to analyze the mixed state of the catalyst and obtain the mixing fraction of each state at different temperatures and reaction conditions.

While LCF is an efficient method when the spectra of different coordination states of atomically dispersed catalysts are known, many SACs supported on oxide or inert supports (such as C₃N₄, graphene, aerogel, carbon nanowires, and nanotubes) do not have bulk counterparts, and thus reference spectra required for the use of the LCF method are unavailable. Principal component analysis (PCA)⁸¹ and multivariate curve resolution-alternating least squares (MCR-ALS)^{82,83} do not use prior knowledge or hypotheses about the *a priori* unknown reference spectra. Both of them are excellent tools for lowering the dimensionality of the data matrix and interpreting all the spectra in a series in terms of a, typically, small (2–4) number of pure species. The key difference between the PCA and MCR-ALS is that the PCA-yielded spectral components are abstract and cannot be readily identified, while several constraints applied in the MCR-ALS method enable the successful search for the spectra of pure compounds and the recovery of their mixing fractions (concentration profiles).⁸⁴ The challenge for atomically resolved catalysts is to interpret the XANES spectra of pure compounds in terms of the candidate structures of the nearest environments in the absence of suitable references and useful EXAFS data. In recent works, S. Xiang et al. and Y. Liu et al. combined PCA and MCR-ALS, respectively, with machine learning to not only isolate the pure spectra in Co SACs⁴³ and Cu–Pd clusters⁴² but also refine them using the machine-learning-based XANES “inversion” method.^{32,36} Routh et al.⁸⁵ also developed an autoencoder-based unsupervised machine learning method which allows for identification of spectral information content and descriptors in the XANES spectra.

4. MACHINE LEARNING APPROACHES

Among the solutions for heterogeneous source separation (*vide supra*), partitioning and matrix factorization are most commonly applied for XAFS analysis. Partitioning of time- or temperature-dependent XAFS data involves identification of a decision

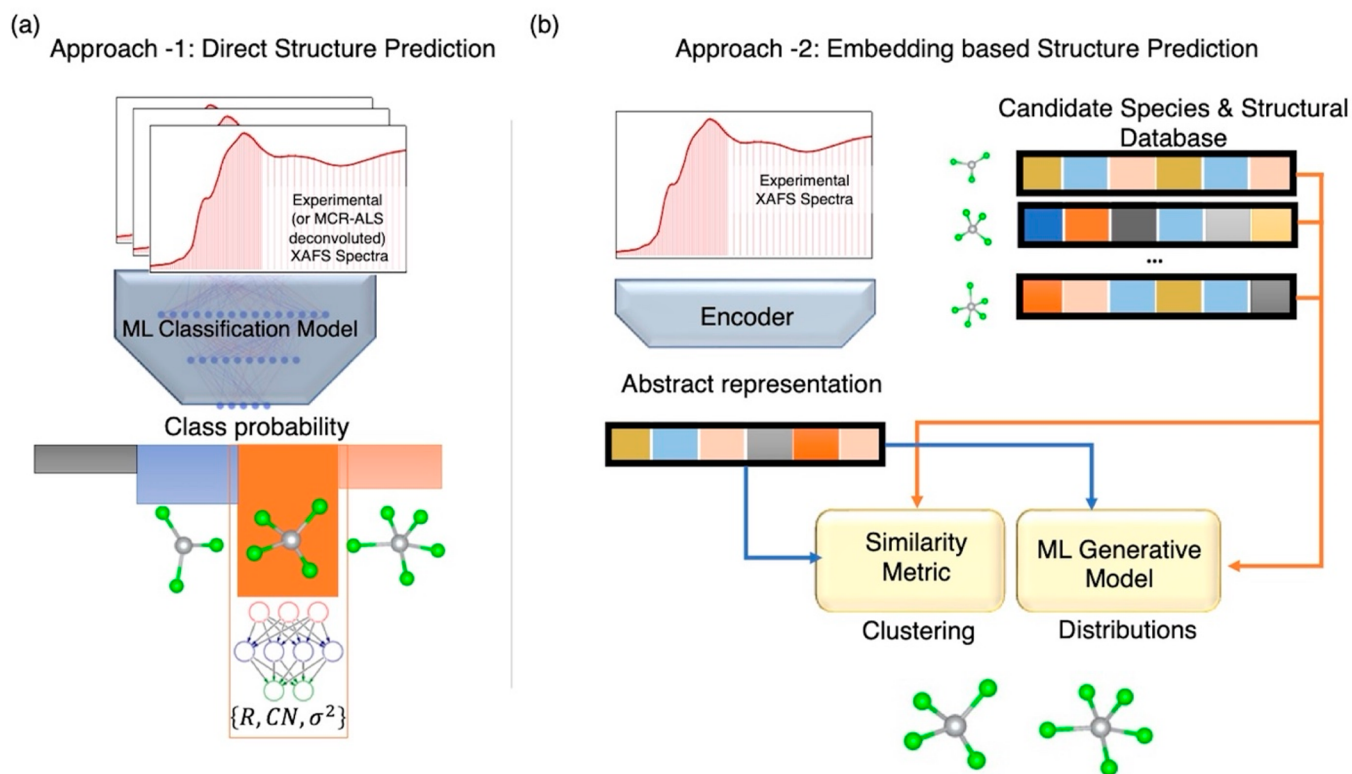


Figure 5. Schematics showing the two most common approaches in dealing with heterogeneous data. (a) Classification is used to identify the structural model which can be refined further using NN. (b) Embedding-based structural similarity in a low-dimensional in-silico database to find candidate structures and their distributions. Adapted with permission from ref 89 Copyright 2022, The Author(s).

boundary, which provides a clear separation between two clusters representing different phases/species and is often followed by a group-specific regression model for each partition to obtain the respective structural descriptors. However, partitioning also often assumes that each group is homogeneous within the decision boundaries, and hence a single representative (or mean) source signal is chosen as the model source species before doing further structural refinement. On the other hand, matrix factorization approaches such as MCR-ALS factorize the data into mixing matrix and pure source signals by adding additional constraints, which produce meaningful decomposition of heterogeneous sources. Despite the advantages of the partitioning and linear decomposition methods, the main limitation is the lack of knowledge of structural information stored in the decomposed spectra. For example, in the study of coexisting states of Cu–Pd species in bimetallic, size-selective cluster catalysts, the resultant decomposed spectra (by using MCR-ALS for decomposition) were attributed to different species by comparison with known experimental standards.⁴² Methods based on classification offer an attractive alternative to link structural candidates and spectra in a more unbiased way.

Clustering and supervised classification are a natural choice for the collection of spectral data which contain mixed sources but have known variations in experimental parameters, such as in composition, temperature, or time-dependent measurements. From the XAFS spectra classification point of view, there are two main approaches, as shown in Figure 5.

1. *Direct classification.* First, the supervised classification of the spectra is performed, based on direct application of such techniques as Logistic Regression, Support Vector

Machines, Random Forest, artificial neural network, etc. Identification of multiple sources giving rise to the averaged XANES spectra can be handled by the multilabel classification algorithms, where the goal is to learn a classifier that maps from a vector of features ($\mu(E)$, the values of the absorption coefficients at different X-ray energies) to a vector of output labels ($y = y_1, y_2, \dots, y_N$), indicating the presence or absence of the classes. The first challenge in solving the multispecies spectral classification is identification of reliable classes. We propose, based on the bulk of previous literature demonstrating the suitability of theoretical standards for regression-based inversion of XANES spectra, that theoretical standards can be used to define reliable classes for XANES spectra as well. After the classification step, the previously developed inversion methods (*vide supra*) follow, mapping the spectra in each class to the class-specific descriptors. This approach can be incorporated in the analysis workflow in which the step prior to the classification is the MCR-ALS analysis of the spectra (see Figure 5a), resulting in the extraction from the spectra of a discrete number of pure species.⁸⁶

2. *Embedding-based approach.* Spectral embeddings are the low-dimensional latent space representation (a.k.a. dense representation) of spectra which are learnt via a self-supervised learning. Embeddings are useful features of spectra which can be used for a variety of tasks, such as classification, regression, data visualization, etc. This vector space representation of embeddings also allows different similarity metrics⁸⁷ to cluster input data in different groups, pulling similar data points closer and

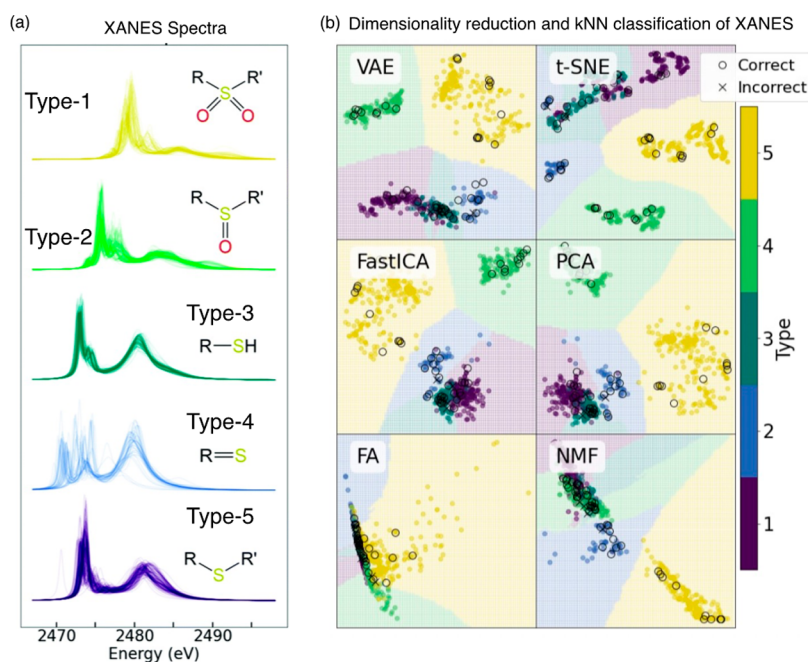


Figure 6. Comparison of different linear and nonlinear dimensionality reductions applied on XANES followed by classification of sulfur bond type. (a) XANES spectra of species with different S-bond types. (b) kNN classification comparisons of reduced XANES spectra using different dimensionality reduction algorithms. Reprinted with permission from ref 94. Copyright 2021 Royal Society of Chemistry.

pushing dissimilar data points further apart as shown in Figure 5b. Furthermore, the decoder or a generative model can be used to learn the probability distribution of potential candidate structures as a direct pathway to “invert” the spectra to the structure.⁸⁸

Neural network (NN)-based classification for X-ray diffraction (XRD) and other (than XAFS) spectroscopy techniques has been implemented to identify the crystal structure,⁹⁰ space groups,⁹¹ etc. An embedding-based approach has also been used to decompose the observed signals into underlying species and their distribution by applying additional constraints and reasoning on the embeddings, as recently shown by crystal structure phase mapping of mixed species using XRD patterns.⁹² While direct application of a machine-learning-based classification model of raw spectral spaces seems more intuitive than utilizing embeddings, feature engineering and signal processing methods are usually needed to separate the desired variability among spectra from the undesired ones (caused by, e.g., instrumental noise) before classification. Such feature engineering, while advantageous, can be extremely problem-specific, and direct classification is much more susceptible to false outcomes due to label noise in training data showing a larger generalization gap as compared to embedding-based classification.⁹³ Nevertheless, direct classification of XAFS spectra (or MCR-ALS deconvolved spectra) before structural descriptor extraction provides an objective framework to select candidate structural species and reduce any selection biases based on an *ad hoc* structural model.

Classification of XAFS spectra using an embedding approach, reported recently, utilizes dimensionality reduction methods such as uniform manifold approximation and project (UMAP), t-distributed stochastic neighbor embedding (t-SNE), and variational autoencoder (VAE), etc. Tetef et al. compared various linear and nonlinear dimensionality reduction methods by applying unsupervised classification of the XANES embeddings (Figure 6) and developed an approach to validate

classes as a step prior to any structural refinements of the candidate species.^{94,95} However, all embeddings are not the same. t-SNE and UMAP embeddings are easier to obtain, and these embeddings also preserve local information (spectral variation) as well as global information (structure class). VAEs, on the other hand, while somewhat harder to train, are shown to encode key structural characteristics in the disentangled latent space of XANES.⁸⁵ VAEs explicitly learn the underlying probability distribution of latent factors, making them more suitable for “inverse problems” and potential heterogeneity characterization.

5. COMMON LIMITATIONS AND CAVEATS OF ML APPLICATION IN XAFS

The machine learning field has the potential to solve various long-standing challenges in XAFS such as *ill-posed* problems. However, it is important to keep in mind that machine-learning-driven inversion and classification models are ultimately data-driven modeling approaches; i.e., any strong assumptions implemented during training data generation propagate to the final model predictions. Hence, outputs from ML models should always be considered as new hypotheses based on the prior information implemented in the training data. Furthermore, forward modeling limitations of theory to reproduce features in training data and limits on information content in the experimental data should be analyzed carefully before finalizing a machine learning model. ML predictions should also be validated, wherever possible, by other information available about the system. In machine learning terminology, out-of-distribution prediction⁹⁶ is an open problem. Nevertheless, it is imperative to reduce the gap between training data distribution and experimental data distribution.⁹⁷

6. CONCLUSION AND OUTLOOK

In this Perspective, we reviewed the recently developed methods for analysis of heterogeneous mixtures based on their X-ray

absorption spectra. We concluded that, in addition to the traditional methods of source separation that are already widely applied toward spectral analysis of mixtures, classification and deep generative model-based distribution learning are potentially very attractive and have a wide scope in XAFS applications. While classification performed after spectral decomposition done by MCR-ALS can help reduce selection bias, generative models provide a new pathway to learn the underlying distribution that gives rise to the observed signals. Tasks of mixture analysis by XAFS from heterogeneous sources are a good match to the “latent variable approach”, in which the latent variables can potentially capture the heterogeneity of the system itself. Whether the learnt distribution of latent variables can accurately describe the distribution of original heterogeneous sources from a mixed signal is an open question which is not answered yet but is of very high significance to heterogeneous catalysis research. We note that VAEs are only one example of the deep generative models that have an explicit model of probabilistic distribution learning built in.⁹⁸ While the use of invertible embeddings is still in infancy in XAFS, other fields of chemistry and catalysis in general have adapted these methods for a range of applications, from denoising, demixing,⁹⁹ and classification to generating potential solutions to ill-posed problems.¹⁰⁰ Recent revolution of generative models has been very successful in utilizing these invertible embeddings for “inverting” novel structures of small molecules with targeted properties, and efforts are underway to expand the application to crystalline materials.¹⁰¹ Further advances in the generative model with bidirectional mapping between structure and spectra by the use of a generalized and invertible embedding are needed to help learn heterogeneous distributions of nanocatalysts.

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Notes

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Prahlad K. Routh is a postdoctoral researcher at Department of Materials Science and Chemical Engineering at Stony Brook University. He received his Ph.D. from Stony Brook University, Stony Brook, NY, and carried out his research work at Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL). He was a Science Fellow and Lecturer in Discipline of Physics at Columbia University from 2016 to 2019. His research work is focused on investigating structure and its relationship with catalytic activity as well as optoelectronic properties of nanoparticles and functional hybrid

nanomaterials using synchrotron and advanced optical spectroscopy methods with the most recent focus on developing machine learning assisted data analysis methods for analyzing X-ray absorption spectroscopy.

Nicholas Marcella received his Ph.D. in materials science and engineering from Stony Brook University and is currently a visiting postdoctoral researcher with the Structure and Dynamics of Applied Nanomaterials (SDAN) group at Brookhaven National Laboratory. Nick is interested in developing new ways to unveil and analyze the complex dynamics of nanomaterials while they are active, as this information is required to fully understand, optimize, and eventually create novel materials.

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