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Mapping XANES spectra on structural descriptors of copper oxide clusters using supervised machine learning

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ABSTRACT

Understanding the origins of enhanced reactivity of supported, sub-nanometer in size, metal oxide clusters is challenging due to the scarcity of methods capable to extract atomic-level information from the experimental data. Due to both the sensitivity of X-ray absorption near edge structure (XANES) spectroscopy to the local geometry around metal ions and reliability of theoretical spectroscopy codes for modeling XANES spectra, supervised machine learning approach has become a powerful tool for extracting structural information from the experimental spectra. Here we present the application of this method to grazing incidence XANES spectra of size-selective Cu oxide clusters on flat support, measured in operando conditions of methanation reaction. We demonstrate that the convolution neural network can be trained on theoretical spectra and utilized to "invert" experimental XANES data to obtain structural descriptors – the

Cu-Cu coordination numbers. As a result, we were able to distinguish between different structural motifs (Cu_2O - like and CuO - like) of Cu oxide clusters, transforming in reaction conditions, and reliably evaluate average cluster sizes, with important implications for the understanding of structure, composition and function relationships in catalysis.

INTRODUCTION

Metal oxides as heterogeneous catalysts have received considerable attention in both fundamental research and industrial applications [1-4]. For instance, metal oxide catalysts (MOCs) possess high catalytic performance and robustness in water oxidation reaction [1,5,6]. In industry, MOCs are crucial for the asphaltene adsorption to enhance the oil discovery [2]. The metal oxide nanocatalysts, in particular, display unique electronic properties due to their non-bulk-like coordination geometry and redox properties [7-9]. To understand the activities of metal oxide nanocatalysts, identification of the active sites of the catalysts [10-13] and, importantly, the size and shape of the particles [14-16] are required. The geometric properties of nanoparticles play greater role in their activity mechanisms because of the larger surface-to-volume ratio [17] compared to bulk-like particles. Due to the large range of possible structures, the catalytic activities of nanocatalysts exhibit large variation with different geometry [14-16,18]. Besides, the nanocatalysts can undergo agglomeration under reaction condition [19,20], affecting their catalytic activity.

In a toolbox of characterization methods tailored for understanding catalytic mechanisms a prominent place is taken by the operando method, in which the structure of the catalysts is analyzed in real time, during the reaction, and the reaction products are detected simultaneously with the structural measurement to build the structure-reactivity relation [21-23]. Due to the formidable challenge that low metal loadings and high reaction temperature and/or pressure present to many techniques, extended X-ray absorption fine structure (EXAFS) spectroscopy [24-26], the workhorse method for catalytic studies, is limited in its applicability to MOCs. X-ray absorption near-edge structure (XANES) is measured in the same X-ray absorption spectroscopy experiment and has better signal-to-noise ratio than EXAFS, hence, it

can be advantageous for use in the in-situ/operando catalytic experiments [27]. XANES is also sensitive to the arrangements of atoms, electronic characteristics [28-31] and is less affected by structural disorder compared to EXAFS [24,26]. For some model catalysts, such as size-selective clusters supported on single crystal surfaces, for which EXAFS data cannot be obtained due to their ultra-low weight loadings, grazing incidence (GI) XANES becomes a unique tool to monitor the transformations in the oxidation state, structure and/or size of the cluster [32-34]. However, GI XANES has been rarely employed for structural characterization due to the limitations in its quantitative analysis. Recently, we demonstrated that a supervised machine learning –based method enabled the establishment of relation between XANES spectral features and structural descriptors of monometallic nanoparticles [35,36]. By employing an artificial neural network (NN) trained on the large set of theoretical XANES, we were able to obtain metal-metal coordination numbers (CNs) and investigate the structure of monometallic nanoparticles and size-selective clusters [35-39]. In all prior cases we deliberately selected well reduced systems, to eliminate metal-nonmetal bonding that would have complicated neural network training and applications. That limitation precludes the broad applicability of our NN-based XANES analysis for operando studies, in which the changes in chemical states of the catalysts may occur in real reaction conditions.

In this work, we report the application of the convolution neural network – based method to analysis of the structure and chemical state of size selective copper oxide clusters measured by XANES during their catalytic reaction process. Copper oxide catalysts are known for their good reactivity and selectivity in numerous oxidation and reduction reactions [40-47]. One of the important reactions is CO_2 methanation which can assist the conversion of CO_2 to chemical feedstock and benefit the inhibition of CO_2 emission [48,49]. We used GI XANES spectra collected for Cu size-selective clusters in the operando experiment during the process of catalytic CO_2 methanation to extract information about the oxidation state and size of the clusters. In what follows, we present our method for training and validating NN, describe the experimental data chosen to illustrate its application to MOCs, and demonstrate the applicability of this approach to extract their structural descriptors in operando conditions.

NEURAL NETWORK TRAINING AND VALIDATION

The common route for NN construction is preparing training sets, training the NN and validating the NN. From our previous works it is known that for the construction of training set, we need hundreds of thousands XANES data with unique and *a priori* known labels (that is, structural descriptors). It is not feasible to obtain such a large number of labeled data from experimental measurements for this purpose. *Ab initio* XANES simulations could be a good alternative to the experimental spectra, as demonstrated in our prior work [35,36,39]. Before planning the training with theory-generated spectra, it is important to verify that a given method or code used for simulations reliably reproduces standard compounds. For example, FEFF9 [50] is adequate for reproducing experimental XANES of bulk Cu oxides, as illustrated in Figure 1. The details of the XANES simulation are given in Note I of supplementary material.

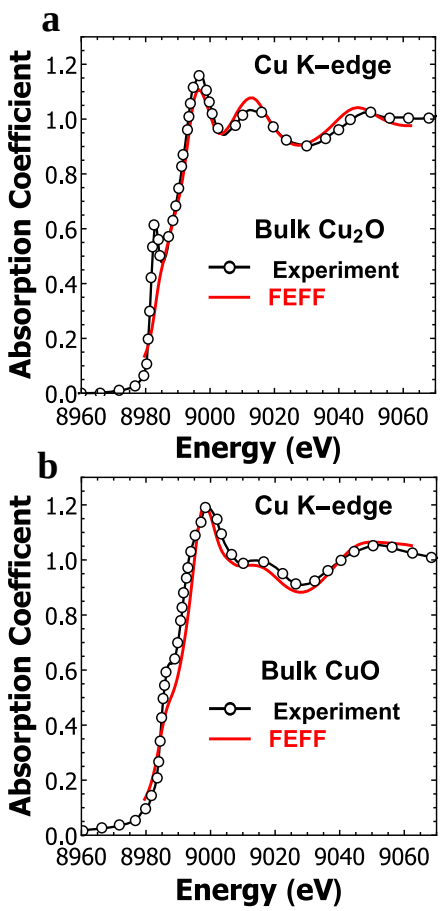

Figure 1. Experimental and theoretical (calculated with FEFF9) XANES spectra for the bulk CuO (a) and Cu_2O (b) standard compounds.

Verifying the sensitivity of XANES to the size and structure of the nanoscale oxide is the necessary first step for any regression-based method in general, and NN-based method in particular, to work. Following the strategy, first implemented in Ref. [36], we first examine the absorption site effect on XANES spectra, as illustrated in Figures 2a and 2b. Each spectrum in Figures 2 a, b is labeled with two Cu-Cu CNs (for the first coordination shell and second coordination shell) to represent the structure of copper oxide nanoparticles. By comparing the theoretical XANES (calculated by FEFF9) on different sites of CuO and Cu_2O models (indicated by their respective CNs of the 1st and 2nd nearest neighbors), more pronounced features are captured by XANES for the copper atom with the larger Cu-Cu CNs (Figs. 2 a,b). XANES spectrum for the copper atom in the inner shell of copper oxide model has greater resemblance of the XANES spectrum for the bulk of copper oxide. In contrast, XANES calculated for the copper atom on the surface has relatively more smooth features. After establishing the absorption site dependence, we examined the cluster size effect on XANES by averaging the site-specific spectra over all atoms in the simulated CuO – like and Cu_2O – like clusters of different sizes and stoichiometries (Figs. 2 c, d). That procedure is described in greater detail below. The simulated XANES spectra reveal that particles with larger sizes have more pronounced features compared to the smaller particles, as expected from their difference in the surface to volume ratios. As shown in Figure 2 e, experimental XANES spectra measured in the Cu oxide clusters show similar trend to have sharper features for larger sizes as obtained for simulated clusters of the same motif (CuO).

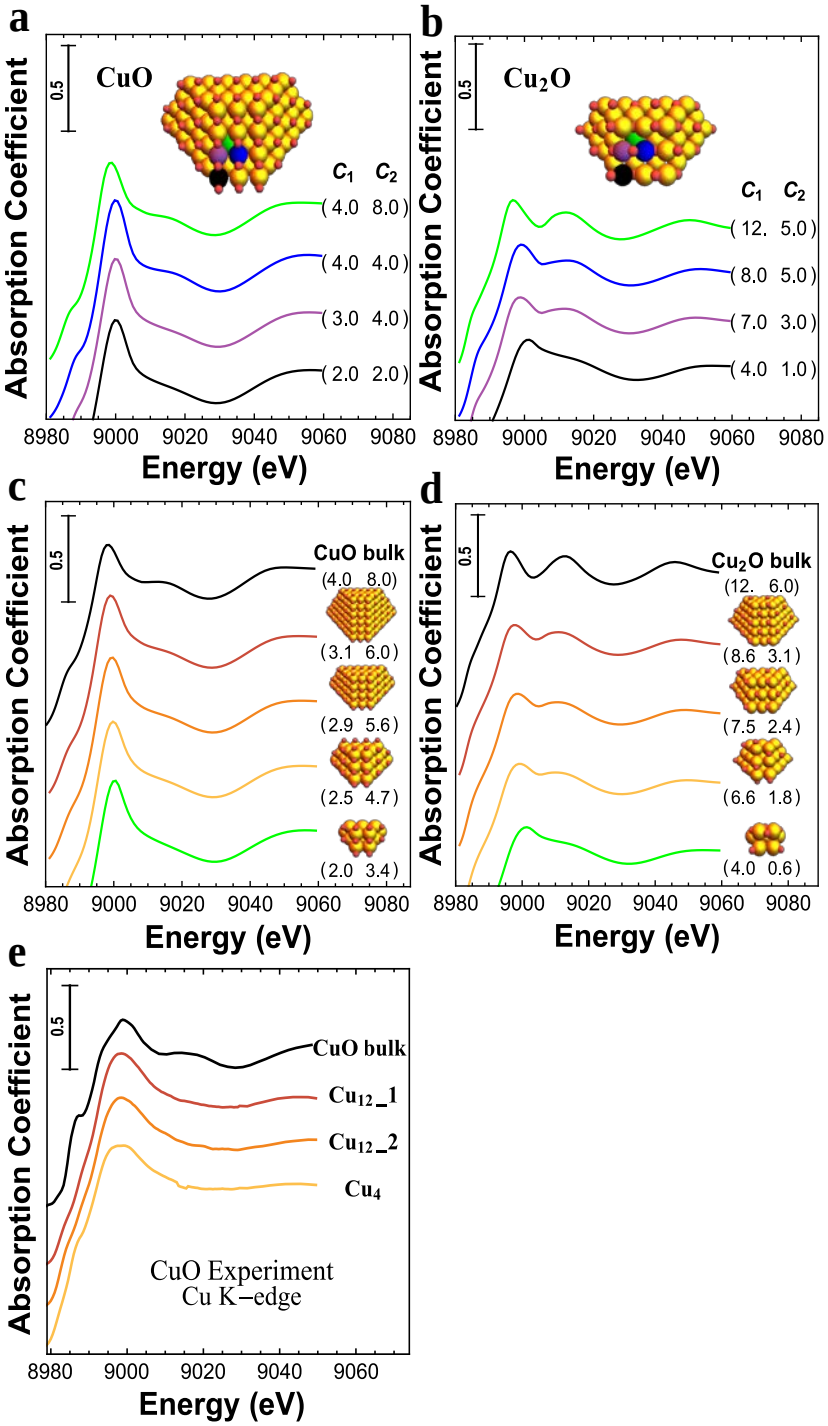

Figure 2. Absorption site, cluster size and motif effects on Cu K-edge XANES spectra. Each spectrum in the Figures 2a, 2b, 2c and 2d is correlated with Cu-Cu CNs on the first and second coordination shells. (a, b) Site-specific XANES (XANES for the specific atom) spectra for CuO and Cu_2O, calculated with FEFF9. (c, d) Particle-averaged XANES (averaged over all atoms in the particle) spectra for CuO and Cu_2O, calculated with FEFF9. (e) Experimental XANES of CuO bulk and CuO clusters containing 4 and 12 Cu atoms.

Similar to our previous work [36], to build the training set for NN, we first constructed several sets of Cartesian coordinates for atoms residing in the sites that correspond to the crystal structure of bulk CuO and Cu_2O, and truncated the lists of coordinates to simulate clusters with various shapes (tetrahedral, octahedral and cubic) and sizes. This was accomplished by creating the cluster surfaces using (100) and (111) planes of bulk CuO or Cu_2O. The details of lattice structure information for CuO and Cu_2O are listed in Table S1 of supplementary material. To generate more models, additional CuO and Cu_2O models were constructed by truncating the previous regular models with (100) and (111) planes. Furthermore, we also constructed the planar structures with one or two layers of (111) plane of CuO and Cu_2O to describe the active structural motif, thin film, which has been reported as active phase for catalysis [51-53]. As a result, we created 25 CuO models and 30 Cu_2O models to capture the diversity of Cu_xO nanostructures, which are relevant to catalysis.

In the nm-scale nanoparticles and sub-nm clusters, the interatomic distances can vary from those in their respective bulk compounds [42,54] due to the effects of size, adsorbates and support. For example, the nearest Cu-Cu distance for the bulk of CuO is 2.93 Å. However, the Cu-Cu distance of the CuO cluster were reported to be longer [54] or shorter [42] compared to the bulk. The shortening of the Cu-Cu distance in size-selected reduced Cu clusters was reported by us earlier [39]. To allow for this effect to be recognized in the process of NN-based analysis, we isotropically stretched or compressed the structures in our theoretical models to generate more training sets. The distance between nearest copper atoms varied from 2.784 Å to 3.077 Å for CuO models and from 2.879 Å and 3.182 Å in Cu_2O models. These ranges bracket the reported Cu-Cu distances for copper oxides available from EXAFS analyses or crystallography data [42,54,55]. To represent the size and shape of the clusters, we choose first few Cu-Cu coordination numbers as structural descriptors for each unique model. We preferred to rely on the Cu-Cu CNs rather than on Cu-O CNs for this purpose because the latter parameter is not a good descriptor of the cluster size, geometry and oxidation state in those cases when all Cu atoms are terminated by oxygens. The copper atoms on the surface have smaller Cu-Cu CNs compared to the inner copper atoms, thus providing the desired sensitivity

to the size and shape of the copper oxide clusters. We illustrate the sensitivity of Cu-Cu CNs to the different size and shape of the copper oxide models in Figures S1 and S2. For different copper oxide models (e.g., Cu_2O vs CuO), the Cu-Cu CNs exhibit unique values. With the increase of the size of the models, the Cu-Cu CNs also get larger. For the models with same Cu-Cu CNs of the first shell, the values of the Cu-Cu CNs of the second shell provides additional sensitivity to the task of classification of different models.

In order to construct a required (large) number of spectra in the training set using FEFF9, we adopted a combinatorial approach, first developed in Ref. [36] and relying on randomly mixing several site-specific XANES calculations for CuO and Cu_2O models prepared above. Each spectrum was labeled with first and second Cu-Cu CNs as structural descriptors. The total size of the training set was 100,000 spectra for each of the CuO and Cu_2O – type models. In order to compensate for the unknown X-ray energy shift between theoretical and experimental XANES spectra for each type of oxide clusters (CuO or Cu_2O-like) we shifted all the theoretical XANES spectra by ΔE (obtained from the difference in energy between experimental and theoretical XANES spectra for the respective bulk oxides). Such approach is reasonable because no visible shift was observed in the XANES spectra between different experimental copper oxide clusters. Furthermore, the convolution neural network we used for machine learning has the advantage of shift invariance [56] which means the results will not depend strongly on the possible, small (shown to be within a ±1 eV range, as tested in this work) mismatch in the X-ray energy origins used in theory and experiment. An alternative approach, relying on random energy shift between different spectra from the training set, was also recently proposed [57]. After the shift was applied, the spectra were interpolated to the same energy scale, from E_{min}=8981.5eV to E_{max}=9059.3eV. The step size for the energy scale is 0.15 eV near E_{min} and increases to 1.5 eV near E_{max}. Following this step, all spectra were represented as multi-dimensional vectors, containing 94 data points. Each data point corresponded to the value of absorption coefficient at specific energy.

The NN used in this work was a nonlinear function $f(\mu, \theta) = \{C_1, C_2\}$ where μ represents the preprocessed XANES spectrum (a vector with 94 points) as input and $\{C_1, C_2\}$ represents the first two CNs

as output. The parameter space θ consists of the weights and biases in the NN models [58]. The purpose of the training process is to optimize the parameter space θ to accurately correlate input with output. Once the optimal parameters are found, the training process is finished. More details of NN construction and training are described in supplementary material.

The accuracy of our NN was demonstrated by the theoretical XANES calculated by FFFF9 for particles with different sizes and shapes. Unlike the data set we used for the training, the spectra for validation are particle-averaged spectra (averaged XANES for the particle) corresponding to the real copper oxide models and not used in the NN training process. In Figure 3, we compare the true Cu-Cu CNs on the first coordination shell with the predicted Cu-Cu CNs for CuO and Cu_2O models. The validation for the Cu-Cu CNs on the second coordination shell is given in Figure S3 of supplementary material. According to the comparison result, NN can predict accurate CNs from the theoretical XANES for a large range of particle sizes.

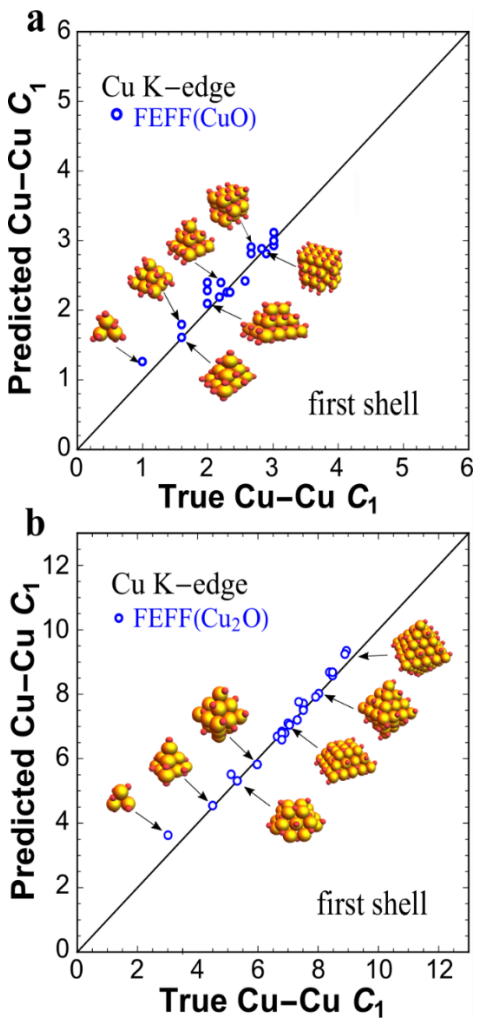

Figure 3. Validation of CuO (a) and Cu_2O (b) neural networks using theoretical XANES. True Cu-Cu CNs are compared with predicted Cu-Cu CNs on the first coordination shell.

APPLICATION TO EXPERIMENTAL DATA

After the validation of our NN, we applied our NN to the unknown structures of supported ultra-small size-selected clusters used in a recent work [59]. These copper-based clusters can be used for example as catalysts for conversion of CO_2 with hydrogen. The data discussed in this paper were extracted from in situ grazing incidence XANES (GI XANES) spectra collected on samples of 4-, 12- or 20- atom Cu clusters, deposited on zirconia support prepared by atomic layer deposition and by supersonic cluster beam deposition, as exposed to a CO_2 and H_2 under elevated temperatures reaching 375 °C. More experimental details are given in Note III of supplementary material.

The data extracted from the in situ XANES data were collected and analyzed by multivariate curve resolution with alternating least squares (MCR-ALS) method to obtain the mixing fraction of clusters of different oxidation states (CuO, Cu_2O and Cu) [59]. Because, our NN method is designed for an idealized, pure metal oxide phase (either CuO or Cu_2O-like), its test required access to the corresponding phase-pure clusters, which were not found in the series of spectra obtained in our operando experiments. We thus selected those spectra collected and analyzed in Ref. [59] which had the highest fractions of CuO or Cu_2O phases, based on the results of the MCR-ALS analysis. The fractions of individual copper components (CuO, Cu_2O and Cu) for the spectra are listed in Tables S2 and S3. The sampling chosen for testing our NN prediction correspond to those temperatures, for which the XANES data, as analyzed by MCR-ALS, indicated the presence of at least 70% of either CuO or Cu_2O phase. As a justification of validity of this approach, we note that their XANES spectra have similar features with either CuO or Cu_2O bulk XANES spectra, thus validating their designation as tests for NN validation purpose.

In Table S2, combining the spectra found (by MCR-ALS) to correspond to the CuO – like clusters, we show the application results of the CuO - trained NN model for extracting first and second Cu-Cu CNs from those XANES spectra. To interpret the results, the correlation between the number of Cu atoms and the first Cu-Cu CNs for the CuO models is shown in Figure 4a. All models shown there were selected from the NN training and validation steps. Such correlation demonstrates that our method can be used for measuring the cluster size, as evident here from the correct detection of the number of atoms which was known *a priori* from the cluster deposition experiment [60,61]). To check the capability of our NN to distinguish between CuO and Cu_2O motifs, we applied our trained Cu_2O NN model to the XANES spectra and showed the predicted CNs in Table S2. Not surprisingly, the predicted CNs from Cu_2O NN have larger error bars for the first nearest neighbors. It means that the result is unstable. By comparing the predicted CNs from two NN, we obtained that the oxidation state of the sample is consistent with that obtained by an independent chemometric approach, as reported in Table S2.

For the samples with large fraction of Cu_2O, we performed similar NN-XANES analysis, this time – by using our Cu_2O NN model. Table S3 lists samples which are mainly composed of Cu_2O. The first and second Cu-Cu CNs are extracted by our Cu_2O NN model. To validate the results, we present the correlation between the number of Cu atoms and the first Cu-Cu CNs for Cu_2O models in Figure 4b. The results demonstrate a correlation between predicted CNs from Cu_2O NN with the sizes of the cluster. Similar to the prior example, we used the CuO - trained NN to check the capability of our method to distinguish between the CuO and Cu_2O motifs. The predicted CNs from CuO NN give much larger error bars for the first nearest neighbors than those obtained from the Cu_2O NN for the same experimental spectra (Figure 4a). Thus, by combining the predicted CNs from two NN, and comparing them with the known CN values that correspond to the known cluster sizes, we demonstrated the oxidation state and structural information can be extracted from the spectra for Cu_2O like clusters (Table S3).

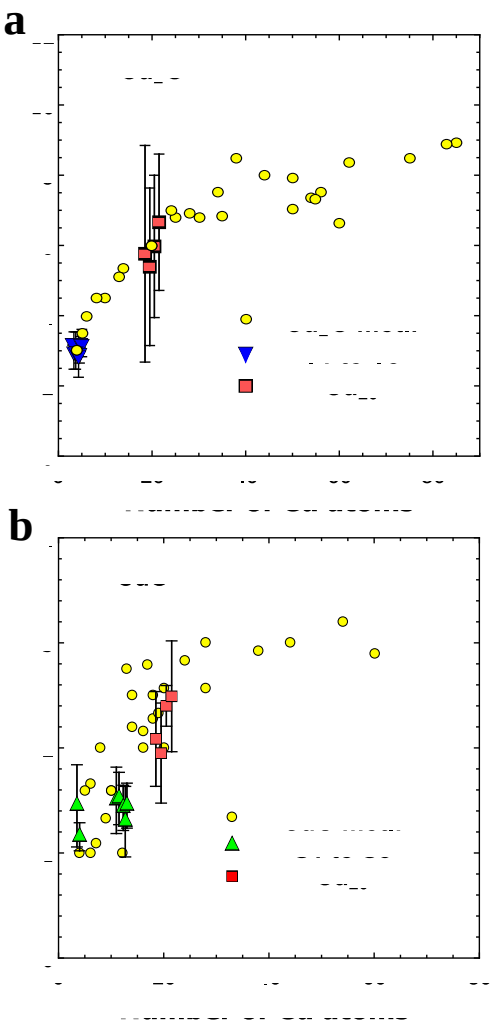

Figure 4. The correlations between the number of Cu atoms and true Cu-Cu CNs for theoretical Cu_2O (a) and CuO (b) models built during the NN training. The blue, green and red points are shifted horizontally around their actual values (4, 12 and 20) to show the error bars. S1 to S7, T1 to T7 and Cu_{20} represent the experimental samples with CNs extracted by the NNs. The detailed description of samples S1 to S7, T1 to T7 and Cu_{20} is given in Tables S2 - S4.

After validating the NNs using experimental spectra for clusters with the known sizes and structures (dominated by either Cu_2O or CuO clusters, as described above), we applied the NNs to analyze the spectra for samples of a nominal size of Cu_{20} and unknown structure and oxidation state. Our trained NNs were applied to answer the question whether the sample was mainly composed of a CuO-like or a Cu_2O – like phase. In Table S4, we present the first and second Cu-Cu CNs extracted by our CuO NN and Cu_2O NN. To analyze the results and determine the oxidation states, we correlate the predicted CNs with the sizes of the cluster and examine the relation between Cu-Cu CNs and the number of copper atoms in Figure 4. The

predicted CNs from CuO NN follow the size-dependent trend in Figure 4a. However, the predicted CNs from Cu_2O NN show large error bars when compared with the CuO NN prediction (Figure 4b). Based on the results for Cu_4 and Cu_{12} clusters, described above and summarized in Tables S2 and S3, larger error bars were always obtained when the incorrect NN models were applied. Therefore, by comparing the predicted CNs and taking into consideration the difference in the error bars (that were demonstrated to be an important factor in discriminating between two possible phases of the copper oxides) from CuO NN and Cu_2O NN, we conclude that the Cu clusters containing 20 atoms were dominated by the CuO phase.

CONCLUSIONS

In summary, a neural network method was utilized to build the relationship between the XANES spectra and structural parameters for copper oxide cluster systems. This method enabled the determination of the average particle size and the oxidation state of metal clusters during the catalytic reaction by "inverting" their XANES spectra. Since the metal clusters acted as important catalysts in many reactions, this method is poised to have many applications. For instance, for the carbon dioxide and nitrogen oxide related reduction reaction where the metal cluster acts as catalyst and gets oxidized [62], NN method can be soon utilized to analyze the structure of these metal oxide clusters and thus help decipher the reaction mechanism. At this stage, while our method is an improvement compared to the previously developed NN-based XANES analysis approach, because it is applied, for the first time, not to pure metallic clusters but to the metal oxides, the present NN method still has several important limitations. For example, it relies on the CNs as descriptors and thus cannot distinguish isomers with the same CNs. It is also favoring those speciations where one (CuO, Cu_2O or Cu) phase dominates and would not be helpful when these phases coexist with similar fractions during a particular reaction step. We envision that such recently developed techniques for XANES analysis as MCR-ALS, linear combination and principle component analysis will be used in combination with our approach for accurately obtain both the mixing fractions of different types of clusters and structural characteristics of each type. Our method, after the required training and validation,

is also applicable to a wide range of metal oxide cluster catalysts and for the understanding of structure, composition and function relationships in catalysis.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional details on the XANES calculation, neural network implementation and training, experiment, and results of speciation analysis of clusters used in this work.

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