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Limits and Advantages of X-ray Absorption Near Edge Structure for Nanometer Scale Metallic Clusters

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We consider the analysis of the K edge of 3d or 4d transition metals when nanometer-scale metallic clusters are considered. From a practical point of view, numerical simulation of the XANES part of the K absorption spectrum of most elements of the periodic table can be performed through full multiple scattering calculations. Then, on the basis of a linear combination of the XANES spectra of reference compounds, the presence of the different phases present inside the materials can be quantified. Here, we show that for nanometer scale metallic clusters, it is not sufficient to consider only the electronic state of the metal of interest to perform a linear combination analysis. In the case of these peculiar materials, special attention has to be paid to different structural parameters, for example, the size and morphology of the cluster, the interatomic distance (taking into account contraction/dilatation processes), and the presence of heterometallic bonds (in the case of bimetallic clusters). Moreover, this approach is not specific to the metallic state. As a conclusion, the quantitative measurement of the structural parameters coming from EXAFS analysis constitutes an invaluable starting point for the FEFF-PCA simulation. The fact that major results coming from the emergence of dynamical studies, namely, Quick-EXAFS or energy dispersive EXAFS, are now obtained will lead to significant breakthroughs in the understanding of the genesis/reactivity of nanometer-scale entities.

Introduction

Nanometer-scale metallic clusters, containing between 10 and 1000 atoms, are of great importance for exploring, as well as understanding, fundamental questions such how atomic-scale properties develop into bulk properties.^{1,2} Such a family of nanomaterials is widely used in heterogeneous catalysis.^{3–6} From a theoretical point of view, we have now the possibility to describe/predict in a realistic way the electronic structure of such entities and then to understand both their atomic and chemical rearrangements.^{7,8} Regarding the experimental aspects, synchrotron radiation related techniques have the required abilities to characterize such nanomaterials.^{9–11} Thus a combined theoretical and experimental approach is needed.¹² Due to the high reactivity of these nanoentities, the fact that the description of the electronic and structural properties is made in situ is crucial.^{13,14} The possibilities offered by various techniques, namely, anomalous wide-angle X-ray scattering,¹⁵ soft X-ray absorption spectroscopy,^{16–18} and X-ray absorption spectroscopy^{19,20} as well as the complementary aspect of different techniques related to synchrotron radiation have already been discussed.^{21–23} We focus here on the near-edge part of the X-ray absorption spectrum.

Regarding the L edges, we have shown recently in the case of nanometer-scale platinum clusters that a strong correlation exists between the intensity of the white lines (i.e., the large threshold spikes) which appear at the L_{II,III} edges of transition metals and the size of the cluster through ab initio calculations.^{24–26} Thus, this paper focuses on the analysis of the K edge of 3d or 4d transition metals when nanometer-scale metallic

clusters are considered. From a fundamental point of view, the numerical simulation of the XANES (X-ray absorption near edge structure) part of the K absorption spectrum of most elements of the periodic table can be performed through full multiple scattering calculations.^{27–30} In a second step, on the basis of a least-squares fitting of the XANES spectra as a linear combination of reference compounds, namely, the “Principal Component factor Analysis” (PCA), the presence of the different phases present inside materials can be quantified.^{31,32} More precisely, the PCA analysis assumes that the absorbance in a set of spectra can be mathematically modeled as a linear sum of individual components, called factors, which correspond to each one of the copper species present in a sample, plus noise. In this paper, we would like to show that significant breakthroughs can be obtained in the understanding of the physicochemical processes specific to nanometer scale entities if the analysis of the XANES part of an absorption spectrum is conducted using a combined full MS and PCA approach.

After a brief summary on the physics on which the full multiple-scattering FEFF code is based, we consider several physical parameters, namely, the size and the morphology of the nanometer-scale metallic cluster, the interatomic metal–metal distance, and the presence of heterometallic bonds (in the case of bimetallic systems). We will see that these structural parameters can affect the detailed features present at the edge, each numerical simulations being performed with copper atoms in their metallic state, Cu⁰. Based on these considerations, we thus discuss the choice of the reference compounds. To illustrate this approach, we choose the case of copper, this metal playing a key role in several physicochemical processes in heterogeneous catalysis. For example, Cu-ZSM-5 has been the subject of many recent theoretical and experimental studies since it was discov-

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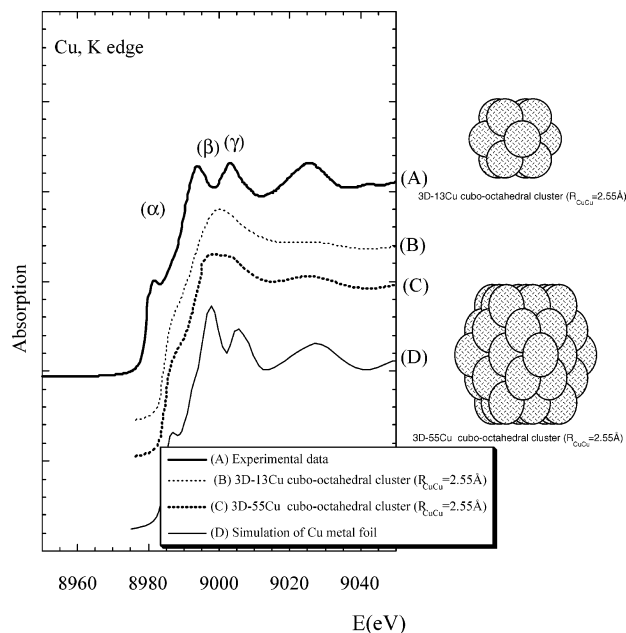


Figure 1. Near K edge part of the absorption spectrum as measured for the copper foil (A) and as calculated with the FEFF program for cubo-octahedral clusters of 13 atoms (B) and 55 atoms (C) of copper and a cluster of 200 atoms of copper for the theoretical simulation of the Cu metal foil (D).

ered to thermally and photoactively catalyze the reduction of NO_x species.^{33,34}

I. Basic Principles Regarding the K Edge of 3d–4d Transition Metals

Full multiple scattering calculations (see ref 35 for a recent review) in real space can be performed by using the ab initio FEFF8 code.^{29,36} Since the information of interest is contained in the oscillations superimposed onto the otherwise smooth atomic absorption coefficient μ_0 , one defined $\chi(k)$ as

$$\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k), \quad k = [(2m/h^2)E_c]^{1/2} \quad (1)$$

where the atomic absorption coefficient is expressed as function of k , the modulus of the wavevector, and E_c , the difference between the energy of the photons and the electron binding energy. In the FEFF code, the oscillations are expressed as a sum of different multiple scattering contributions. Each contribution can be expressed in the following form

$$\chi^n(k) = \chi_0^n(k) \exp(-L_n/\lambda_n - 2k^2\sigma_n^2),$$

$$\chi_0^n(k) = F_n(k) \sin(kL_n + \theta_n(k)) \quad (2)$$

Here, n represents different single or multiple scattering paths and L_n is the total path length. F and θ_n are the amplitude and phase which depend on k , on the specifics of the scattering path involved, and on the atomic potential parameters. Here what we want is to discuss the nature of information relative to this part of the spectrum.

We have already pointed out that the near edge part of the absorption spectrum of the Cu foil exhibits three main features, α , transition $1s$ to $4p$ in the $3d^{10}$ configuration which belongs thus to the NEXAFS part, β , and γ (Figure 1). Note that the program FEFF8 used no adjustable parameters, thus E_0 (the edge energy) in the simulations differs from the experimental value. This face centered cubic (fcc) lattice is generally reproduced in

the multiple scattering framework in the muffin-tin approximation by using large clusters in which absorbing atom is always at the center of the cluster, the surface atom contribution to the total cross section being negligible.

In the following sections, we will consider different structural parameters. The first one is the size of the cluster and two cubo-octahedral clusters are generated by fixing M–M distances to bulk values (i.e., $R = 2.55$ Å). The 13 and 55 atom clusters correspond respectively to one- and four-shell fcc clusters.

II. Cluster Size

In the case of a 13-atom cluster, it is essential to consider each kind of atom inside the cluster, as the signal coming from the surface and the central atoms are definitely not the same. Clearly, a 13-atom environment is not enough to produce the resonance γ (Figure 1). The same approach was made for a 55-copper-atom cluster. The major point that has to be underscored is that the features β and γ of the copper foil K edge are already present. Since the surface atoms have a nonisotropic environment, features are present but with lower intensities than for the copper foil spectrum. Thus, this feature is size dependent. Note that these simple calculations on nanometer-scale Cu clusters have been confirmed by different experimental results.^{37,38}

At this step of the numerical simulation, we have to emphasize that the same tendency is expected at the K edge of 4d transition metals.

III. Cluster Morphology

From an experimental point of view, several authors have pointed out that nanometer-scale metallic clusters exhibit some “anomalous” crystallographic structures.^{39–41} In fact, nanometer-scale metallic clusters display quite a large range of morphologies.^{42–46,26} The interaction of the support may play a key role too. For example, in the case of copper, Musolino et al.⁴⁷ have studied the energetic and structural properties of copper clusters adsorbed on MgO(100) by means of first principles density functional calculations. These authors find that Cu–Cu interactions dominate over Cu–surface interactions, so that three-dimensional (3D) structures are largely preferred with respect to two-dimensional (2D).

Similar results have been recently obtained by Lykhach et al.⁴⁸ The strong metal–support interaction that provoked the 2D-growth mode of Rh was found for the Rh/Al₂O₃ sample. On Rh/Al₂O₃ samples, the 3D-growth mode was registered and the particles deposited onto (0001) orientation were more spread. It was concluded that the metal substrate–interaction is stronger on this alumina orientation than on the other ones.

Using a quenched molecular dynamics procedure one finds, in agreement with experimental data, that the icosahedron is more stable than structures based on the fcc lattice (cuboctahedron and Wulff polyhedron) over a large size range, which depends on the chemical species. For example, Baleto et al.⁴⁹ have studied the growth of free silver nanoclusters by molecular dynamics simulations, from a small seed up to sizes $N = 150$. Not only the final outcome of the growth process depends crucially on the growth conditions (deposition flux and temperature, T). A reentrant morphology transition is obtained: at intermediate values of T a “decahedral window” is found; the window is surrounded by regimes where icosahedra are preferentially grown.

A set of numerical calculations are plotted on Figure 2 corresponding to two clusters of 13 atoms with a fcc network but with either a plane (2D) or a sphere-like (3D) morphology.

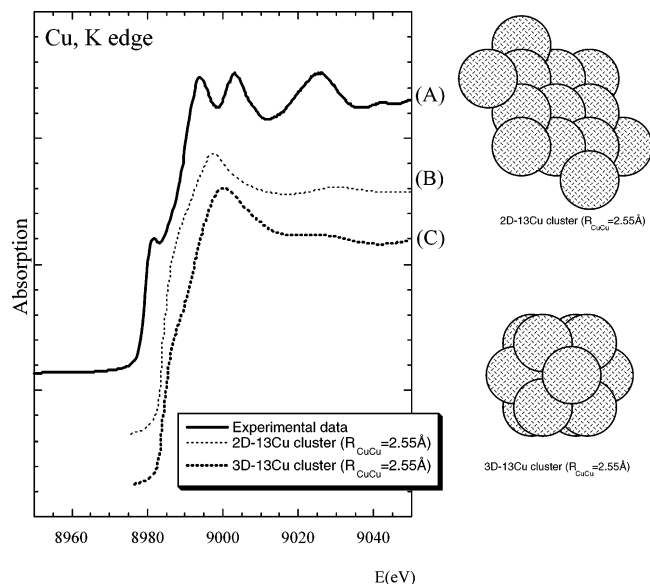


Figure 2. Near K edge part of the absorption spectrum as measured for the copper foil (A) and as calculated with the FEFF program for two clusters of 13 atoms of copper having a 2D (B) or 3D dimension, i.e., cubooctahedral morphology (C).

It is quite clear that the morphology of the cluster constitutes a significant parameter, leading to modification of the shape and the position of the edge.

IV. Interatomic Metal–Metal Distance

The metal–metal interatomic distance may vary significantly at the early stage of the genesis of the metallic particles. For example, Reifsnnyder et al.⁵⁰ have produced Pt clusters by heating in a vacuum at 300 °C and measured a contracted Pt–Pt distance (2.66 Å instead of 2.76 Å). More recently, Schneider et al.⁵¹ have studied the influence of the interaction of 1% NO (balance N₂) with the reduced platinum catalyst. They have checked for any effect of N₂ alone in the temperature range between 100 and 300 °C. A significant contraction of the Pt–Pt interatomic distance has been pointed out. In fact, this effect can be due to temperature and/or the effect of disorder.⁵² Note that a theoretical approach in quenched molecular dynamics (tight binding using model) has revealed that this radial relaxation is also assigned to the small size of the particles, i.e., a lack of neighboring atom for surface atoms of the nanometer-scale metallic clusters.⁵³

Also observed by electron microdiffraction⁵⁴ as well as X-ray absorption spectroscopy,⁵⁵ an epitaxy phenomenon leads to an enlargement of the metal–metal distance (the value of the metal–metal interatomic distance approaches the (111) interplanar distance of alumina (2.85 Å)). Note that different papers discuss the nature of the metal–support interaction in supported catalysts (see, for example, refs 56–58).

To evaluate the modifications coming from a slight variation of the interatomic distance, we have performed a set of numerical calculations for 13-atom clusters of copper with different Cu–Cu interatomic distances. As shown in Figure 3, it is clear that relaxation processes which occur at the very beginning of the genesis of these nanometallic entities modify the position and the shape of the near edge structure of the absorption spectra.

Note that associated experimental data may be rather complex to obtain metal–metal distance in the absence of influence from the gas-phase impurities, for example.

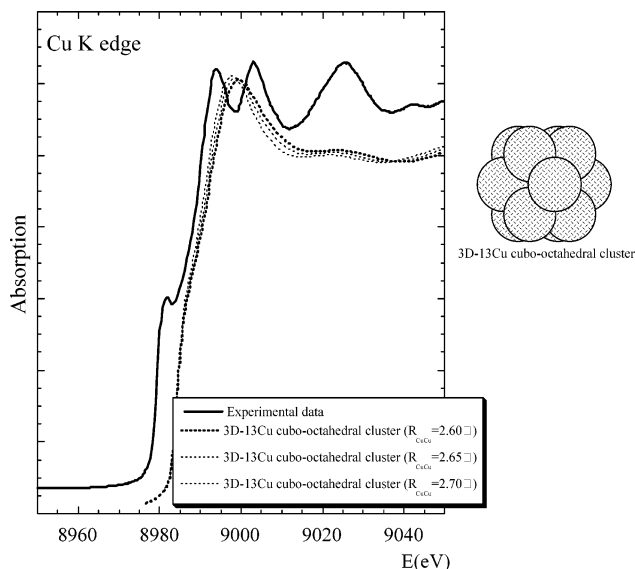


Figure 3. Near K edge part of the absorption spectrum as calculated with the FEFF program for a 13-atom cubooctahedral cluster of copper with different interatomic distances ($R_{\text{CuCu}} = 2.60$ Å, $R_{\text{CuCu}} = 2.65$ Å, $R_{\text{CuCu}} = 2.70$ Å).

V. Case of Bimetallic Systems

To optimize the activity/selectivity of heterogeneous catalysts, bimetallic systems have been developed (see ref 59 as an example of the design of new bimetallic systems). In fact, the term “bimetallic cluster” was first introduced into the literature by Sinfelt,³ a totally new concept which can be considered as the starting point of a new catalysis. The fact that the first work performed in catalysis using X-ray absorption spectroscopy was done by the research team of Sinfelt is thus not surprising.^{60,61} Regarding bimetallic systems, this technique is able to underline the presence inside the metallic part of the catalyst of heterometallic bonds (see ref 62 for the PdCu bimetallic system). Note that the presence of heterometallic bonds and thus the existence of nanometer-scale bimetallic clusters can be affected by the parameters of the preparation procedure such the calcination temperature.^{63,64}

Even in the case of bimetallic systems, the relaxation of the intermetallic distances as well as the chemical local ordering can be predicted from the electronic structure.⁶⁵ In a recent paper,⁶⁶ a comparison between these predictions at thermodynamical equilibrium and recent results obtained by using XAS for bimetallic systems Pt–M where M is a 4d transition metal has been made. It appears that these theoretical calculations are a valuable starting point for the study of such entities.

To take into account the possible presence of bimetallic clusters inside the material, we have considered a 13-atom cluster of copper and replaced some of the copper surface atoms by palladium atoms. Figure 4 shows clearly that this substitution process, which mimics the genesis of bimetallic clusters, changes the position and the shape of the near edge part of the absorption spectrum.

VI. Discussion

The emergence of dynamical studies⁶⁷ based on Quick-EXAFS^{68,69} as well as energy-dispersive EXAFS^{70,71,72} gives opportunities to give electronic and/or structural evidence of intermediate species, their knowledge leading to significant breakthroughs in the understanding of the peculiar properties of such nanoentities (for a recent review, see ref 73).

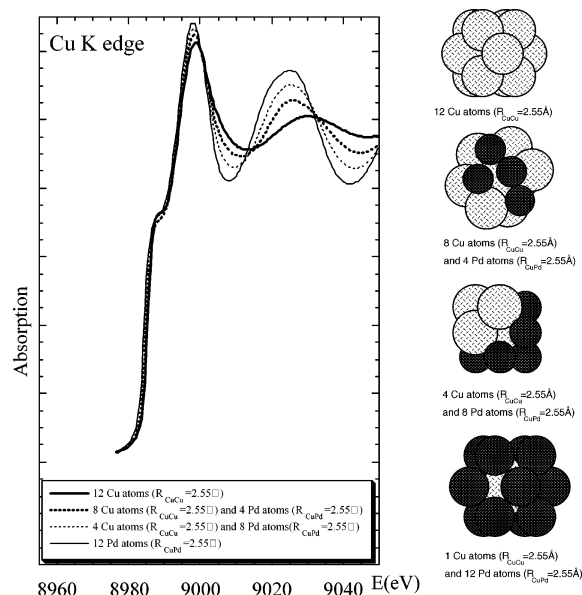


Figure 4. Near K edge part of the absorption spectrum as calculated with the FEFF program for a 13-atom cubooctahedral cluster. Then, three different simulations corresponding to a copper–palladium substitution are performed. More precisely, we considered the following cluster containing eight Cu atoms ($R_{CuCu} = 2.55\text{\AA}$) and four Pd atoms ($R_{CuPd} = 2.55\text{\AA}$); four Cu atoms ($R_{CuCu} = 2.55\text{\AA}$) and eight Pd atoms ($R_{CuPd} = 2.55\text{\AA}$), and finally one Cu atom ($R_{CuCu} = 2.55\text{\AA}$) and 12 Pd atoms ($R_{CuPd} = 2.55\text{\AA}$).

We have already pointed out the limitation of a phase analysis through the EXAFS, this technique being insensitive to polydispersity.^{21,74} Through simple calculations, it is easy to show that the results given by mixing clusters which have 13 atoms and 1415 atoms are similar to the coordination number associated to a cluster of 147 atoms. Thus, the PCA approach based on the near edge structure constitutes a real opportunity to get the distribution of the electronic state of the metal of interest.

At this step, one key point of the PCA analysis is to choose a significant set of reference compounds. As we have seen, the case of Cu^0 is not simple. The XANES part of the absorption spectrum collected at the K edge is a function of several parameters. The size and the morphology of the cluster, the interatomic metal–metal distances, and the presence of heterometallic bonds change significantly the details of the XANES. Through *ab initio* FEFF calculations, we have thus demonstrated clearly that for nanometer-scale metallic clusters, the XANES of the Cu metallic foil is definitely not a significant reference for a PCA analysis. As a consequence, if the set of reference compounds is not significantly selected in regards to the peculiar properties of nanometer scale metallic clusters, such an approach can lead thus to a misunderstanding of the physical process. On the other hand, in the case of a “large” cluster, a PCA analysis using Cu metallic foil as a reference for the Cu^0 state can give information on the different populations regarding the electronic species.

One limitation can come from the fact that, as underlined by Blint,⁷⁵ the copper can have three oxidation states (Cu^{2+} , Cu^+ , or Cu^0), which may have different binding sites depending on the oxidation state of the copper. Regarding the Cu^+ species, as underlined by R. Kumashiro et al.,⁷⁶ Cu_2O is not an adequate reference sample for estimating the amount of Cu^+ species. If we consider the case where the copper ions are engaged in a high-silica type of zeolite like ZSM-5 and are regarded as being dispersed, $[\text{Cu}(\text{NH}_3)_2]^+$ may be useful as a reference sample.

Also, from an experimental point of view, differences between isolated, size limited, and aggregated species XANES spectra have been measured.⁷⁷

Thus, the set of calculations we have performed for the Cu^0 species has to be done for Cu^+ and Cu^{2+} , structural parameters playing a key role in the position and the shape of the XANES. For example, Wu et al.⁷⁸ have simulated the Ti and O K edges for titanium oxides by multiple scattering calculations. These authors have noticed that the long-range order plays an important role in determining the near edge structure. To obtain a significant comparison between the experimental data and the numerical simulations, they increase the size of the clusters and used a $X-\alpha$ exchange correlation potential. Similar data have been obtained at the Ti K edge by Yeung et al.⁷⁹ More recently, Farges et al.⁸⁰ have proposed that the intensity of the main edge features can be used as a probe of disorder in the short- and medium-range environment of Ti. Note that a same approach has been done also for vanadium.⁸¹

The case of copper can be generalized. For the K absorption edge, previous works report the importance of structural parameters in the numerical simulations on oxide of different 3d or 4d transition metals. Let us quote the case of V_2O_5 ,⁸² VO_2 ,⁸³ MnO ,⁸⁴ copper oxide related systems,⁸⁵ and Mo oxide.⁸⁶ Finally, we can consider also sulfur compounds as well as nanocrystalline cerium oxides.⁸⁷ As we have already seen,⁸⁸ this part of the X-ray absorption spectrum is sensitive to the size of the MoS_2 crystallite.

Thus, we have to underline that the number of significant reference compounds in order to perform a PCA-FEFF analysis can be quite large. The simulation through a large number of absorption spectra of this part of the absorption spectrum which may contain only a small number of structures can be a real limitation. The correlation between the fitting procedure of the edge and the structural parameters obtained through the EXAFS analysis can probably be an elegant way to build a structural/electronic dynamic model.

VII. Conclusion

For nanometer-scale metallic clusters, it is definitely not sufficient to consider only the electronic state of metal of interest. In the case of these peculiar materials, special attention has to be paid to different structural parameters such as, for example, the size and morphology of the cluster, the interatomic distance, or the possible presence of heterometallic bonds. Moreover, this specific approach is not limited to the metallic state of the metal of interest, such numerical simulations have to be done whatever the electronic state of the metal and the structure in which the metal is embedded (oxide as well as sulfur compounds).

As a conclusion, regarding nanometer-scale entities, which are widely used in chemistry and more precisely in heterogeneous catalysis, significant breakthroughs can be obtained based on a PCA-FEFF analysis. Moreover, the quantitative measurement of the structural parameters coming from the EXAFS analysis constitutes an invaluable starting point for the PCA-FEFF simulation. The fact that major results coming from the emergence of dynamical studies, namely, Quick-EXAFS or energy dispersive EXAFS, are now obtained will lead to significant breakthroughs in the understanding of the genesis/reactivity of nanometer-scale entities.

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