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ANALYSIS OF EXAFS DATA ON BIMETALLIC CLUSTERS

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Bimetallic clusters: (i) structure of, (ii) segregation of components, (iii) EXAFS studies of, (iv) coordination numbers, (v) interatomic distances, EXAFS, analysis of EXAFS data, X-ray absorption coefficient

In previous studies of the structures of bimetallic clusters using extended X-ray absorption fine structure (EXAFS), structural parameters were determined by fitting the single scattering expression for EXAFS to experimental data associated with an absorption edge of each component. The data for the two edges were fitted separately. Recently, with an extensive modification of the computer program for the analysis of EXAFS data, it has been possible to fit the EXAFS data for the two edges simultaneously. This improved method of analysis has the feature that *all* of the EXAFS data are used in the determination of *all* of the structural parameters, and permits one to impose in a direct manner certain necessary physical conditions regarding the system. Consequently, one has greater confidence in the values obtained for the parameters. The present paper first summarizes published results obtained by the previous method of analysis on a number of systems. For comparison, a summary is then given of results obtained from the same data on these systems with the new method of analysis.

Data on extended X-ray absorption fine structure (EXAFS), i.e., the oscillations in absorption coefficient which are commonly observed on the high energy side of an X-ray absorption edge, have been very useful for obtaining structural information on bimetallic clusters [1,2]. In this communication we present first an outline of the main features involved in the analysis of EXAFS data, including a brief discussion of particular features embodied in a method used previously by us in the analysis of data on a number of bimetallic cluster systems [3–9]. We then introduce a modification which has made a significant improvement in the method.

The oscillations in absorption coefficient constituting EXAFS are attributed to interference between waves associated with electrons ejected from atoms as a

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consequence of X-ray absorption and waves associated with the electrons after they are backscattered by atoms surrounding the absorber atom [10]. An electron ejected from a core level of an atom is characterized by a wave vector K, which is given by

$$K=(2mE)^{1/2}/\hbar \tag{1}$$

where m is the mass of the electron, $\hbar$ is Planck's constant divided by 2π, and E is the kinetic energy of the electron. The energy E is the difference between the X-ray energy and a threshold energy associated with the ejection of the electron. At such a threshold energy, an X-ray absorption spectrum exhibits an abrupt change in absorption, i.e., an absorption edge.

In the analysis of EXAFS data, one considers a function $\chi(K)$ defined by the expression

$$\chi(K)=(\mu-\mu_0)/\mu_0 \tag{2}$$

where μ and μ_0 are atomic absorption coefficients characteristic of an atom in the material of interest and in the free state, respectively [11,12]. The determination of $\chi(K)$ from experimental EXAFS data has been described in detail elsewhere [13,14].

A Fourier transform of the function $K^n \cdot \chi(K)$, where n is commonly an integer from 1 to 3, yields a radial structure function $\phi(R)$, where R is the distance from the absorber atoms [11]. Inversion of the Fourier transform over a limited range of R yields a filtered EXAFS function characteristic of electron backscattering contributions from neighboring atoms within that range of R. If the range of R is chosen appropriately, it is possible to isolate that part of the EXAFS, namely $K^n \cdot \chi_1(K)$, which is due to backscattering by nearest neighbor atoms only. The subscript 1 on χ signifies nearest neighbors.

For bimetallic clusters with components a and b, one can utilize this inversion procedure to obtain an EXAFS function which can be expressed as a sum of two terms, one due to nearest neighbor atoms of a and the other to nearest neighbor atoms of b about the absorber atom. The contribution $\chi_1'(K)$ of neighboring atoms of a given component is given by the equation

$$\chi_1'(K)=(N/KR^2)F(K)\exp(-2K^2\sigma^2)\sin[2KR+2\delta(K)] \tag{3}$$

where N is the number of neighboring atoms of that component at distance R from the absorber atom, and σ, commonly called the disorder parameter, is the root mean square deviation of the interatomic distance about R. The quantity $F(K)$ is a factor accounting for electron backscattering and inelastic scattering [3], and $2\delta(K)$ is the phase shift [11].

A plot of $K \cdot \chi_1(K)$ vs. K for the copper EXAFS (K absorption edge) of silica supported Ru-Cu clusters at a temperature of 100 K is shown in the lower half of fig. 1. For comparison, data on pure Cu clusters on silica are shown in the upper half of the figure [3,15]. The EXAFS functions in fig. 1 differ markedly, which is

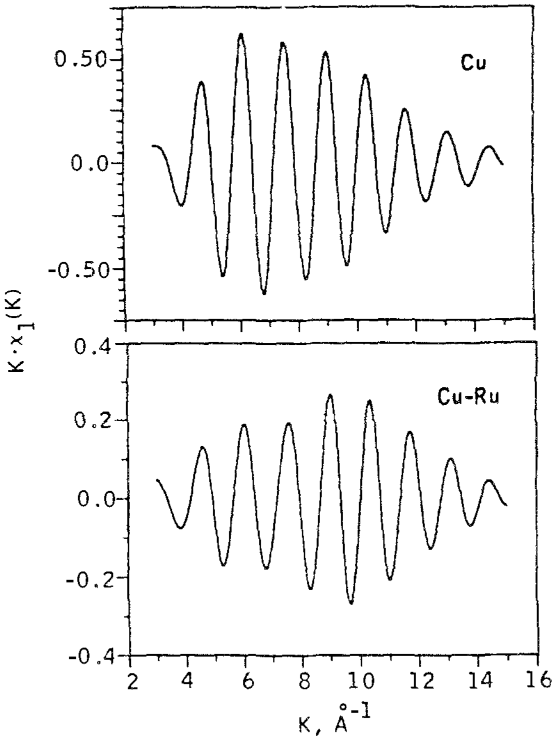

Fig. 1. Comparison of the copper EXAFS (K absorption edge) of copper and ruthenium-copper clusters at 100 K. The EXAFS shown is the part due to nearest neighbor metal atoms [3,15].

indicative of the different environment of the copper in the two types of clusters. The copper atoms in the Ru-Cu clusters are coordinated to ruthenium atoms in addition to other copper atoms, as one concludes immediately simply by inspection of fig. 1. Thus, from a purely qualitative analysis of the data, one finds evidence for the presence of bimetallic clusters of ruthenium and copper on the silica support.

An EXAFS investigation on bimetallic clusters typically involves data for two different absorption edges, one for each component of the clusters. A quantitative analysis can be made of the data to obtain information on the parameters N and R in eq. (3). A value of σ^2 relative to a value for a reference material, i.e., $\Delta\sigma^2$, can also be obtained. Details of the analysis used previously by us, which included the use of data on appropriate reference materials and an iterative least squares procedure for determining best fit values of the various structural parameters, have been described in various papers from our group [1,3,4]. The data for the two edges were fitted separately in the determination of structural parameters.

For the components a and b of a bimetallic cluster there are four possible combinations of absorber and backscattering atoms, namely aa, bb, ab, and ba.

For the combinations of like atoms *aa* and *bb*, the phase shifts were determined directly from EXAFS data on the reference materials, for which the values of R and N are known. From these phase shifts, the sum of the phase shifts for the combinations of unlike atoms *ab* and *ba* was determined from the relation

$$2\delta^{ab} + 2\delta^{ba} = 2\delta^{aa} + 2\delta^{bb} \tag{4}$$

which is based on the assumption that the phase shift function for a combination of atoms is expressible as a simple sum of phase shift functions characterizing the absorber and backscattering atoms separately [16]. A trial phase shift function for one of the combinations of unlike atoms, say *ab*, was obtained from a tabulation by Teo and Lee [16] of theoretically calculated phase shifts for various atoms, either as absorbers or backscatterers. The function for the combination *ba* was then obtained from eq. (4). With these phase shift functions for *ab* and *ba*, two independent determinations of the interatomic distance for the pair of atoms *a* and *b* were made. One value was obtained from the EXAFS data for component *a*, the other from the EXAFS data for component *b*. To decide whether or not the trial phase shift functions were satisfactory, we adopted the criterion that the distance values must be equal. Since this criterion was generally not precisely satisfied for the initial pair of phase shift functions assumed, it was then necessary to modify the trial functions in a systematic manner until a pair was found which gave the same distance for the two sets of EXAFS data. This was accomplished by altering the original phase shift function from Teo and Lee in a manner consistent with a small change ΔE_0 in threshold absorption energy [16].

The disorder parameter σ for the unlike pair of metal atoms *ab* should also have the same value in the analysis of EXAFS data for either component. Sakellson et al. [17] have made use of this criterion in another approach for obtaining structural information on bimetallic catalysts via the separate analysis of EXAFS data for the two components.

A summary of the structural parameters which have been obtained by our previous method of analysis for a number of bimetallic cluster systems is given in table 1. Results for Ru-Cu clusters, the first bimetallic clusters to be investigated by EXAFS [3], are not included in table 1 because the data were not analyzed in precisely the manner just described. The structural parameters in table 1 include interatomic distances for the various possible atomic pairs in the clusters, the average composition of the first coordination shell of metal atoms about a reference atom of either component, and the average number of nearest neighbor metal atoms in the first coordination shell (i.e., the total coordination number). As defined here, the first coordination shell includes nearest neighbor atoms of both *a* and *b*, although the distances of the two types of atoms from the reference atom are not generally equal. The differences in distance arise from the fact that the bimetallic clusters are seldom homogeneous solid solutions. Also shown in table 1 are values for the number N^{ab} of atoms of *b* coordinated to an atom of *a* (from EXAFS data for component *a*) and for the number N^{ba} of

Table 1
Summary of structural parameters previously reported for various bimetallic cluster catalysts

Bimetallic cluster system	Re-Cu	Os-Cu	Ir-Cu	Pt-Cu	Au-Cu	Rh-Cu	Rh-Cu	Ag-Cu	Ir-Rh	Ir-Rh	Pt-Re	Pd-Re
Component *a*	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Rh	Rh	Pt	Pd
Component *b*	Re	Os	Ir	Pt	Au	Rh	Rh	Ag	Ir	Ir	Re	Re
Support	SiO_2									Al_2O_3		
b : *a* atomic ratio	1	1	1	1	1	1	2	1	1	1	1	1
Reference number	7	4	7	7	8	5	5	8	6	6	9	9
Interatomic distances, Å												
R_{aa}	2.53	2.55	2.58	2.65	2.61	2.62	2.63	2.55	2.72	2.71	2.75	2.74
R_{bb}	2.73	2.68	2.69	2.72	2.80	2.68	2.68	2.89	2.72	2.75	2.73	2.72
R_{ab}	2.64	2.67	2.64	2.66	2.68	2.64	2.64	2.71	2.72	2.71	2.63	2.67
Composition of first coordination shell, % *a*												
About *a*	55	49	52	42	73	50	44	92	40	60	65	92
About *b*	46	17	37	39	29	21	8	12	27	43	44	37
Number of nearest neighbor metal atoms												
Total, about *a*, N^a	5	9	6	12	12	–	–	12	10	5	–	7.0
Total, about *b*, N^b	3	12	10	11	11	–	–	8	11	7	–	7.5
Type *b*, about *a*, N^{ab}	2.2	4.6	2.9	7.0	3.2	–	–	0.96	6.0	2.0	–	0.56
Type *a*, about *b*, N^{ba}	1.4	2.0	3.7	4.3	3.2	–	–	0.96	3.0	3.0	–	2.8

atoms of a coordinated to an atom of b (from EXAFS data for component b). Although N^{ab} and N^{ba} are readily obtainable from other data given in the table, they are included for purposes of the following discussion.

There is a simple condition which is necessarily satisfied concerning the number N^{ab} of nearest neighbor atoms of b about a and the number N^{ba} of nearest neighbor atoms of a about b,

$$N^{ab} = (X_b/X_a)N^{ba} \tag{5}$$

where X_a and X_b are the atomic fractions of a and b in the bimetallic cluster catalyst. While the values of the parameters N^{ab} and N^{ba} are dependent on the structural details of the clusters, the condition embodied in eq. (5) is independent of structure. For a catalyst in which the atomic ratio of b to a is one, the values of the parameters should be equal. While adherence to this criterion is good to excellent for some of the results of table 1 (for the Au-Cu, Ag-Cu, and Ir-Cu clusters, in particular), it is generally only fair and sometimes rather poor. Thus, there can be a high degree of uncertainty in the value of the parameter when the EXAFS data for the two absorption edges are fitted separately.

In the analysis of EXAFS data on bimetallic clusters, one occasionally experiences difficulty in obtaining a satisfactory set of absolute values of coordination numbers, i.e., N^{aa} (a about a), N^{bb} (b about b), N^{ab} (b about a), and N^{ba} (a about b). There may be more than one set of values which describe the data equally well, or the values may not be physically reasonable (e.g., the total coordination number may be substantially higher than is physically possible). The difficulty is traced to a high degree of correlation between a given coordination number and a corresponding value of the parameter $\Delta\sigma^2$ referred to earlier. In such cases, however, one may find that the ratio of N^{aa} to N^{ab} (or of N^{bb} to N^{ba}) does not exhibit much variability among different sets of values giving about the same quality of fit to the data. Consequently, it is possible to obtain a reasonable estimate of the composition of the first coordination shell of metal atoms without being able to determine absolute values of coordination numbers. This situation was encountered with the Rh-Cu and Pt-Re clusters, for which values of coordination numbers are not given in table 1.

Recently, we have modified our method of analysis so that all of the EXAFS data are fitted simultaneously. This has been made possible through extensive modification of the computer program used in our analysis of EXAFS data. The new method has the feature that *all* of the EXAFS data are used in the determination of *all* of the structural parameters. In this method, eq. (5) is incorporated into the computer program, and there is a single value of the interatomic distance R and disorder parameter σ for the unlike pair of atoms ab. Consequently, the EXAFS data are fitted with fewer adjustable parameters, and there is generally a modest sacrifice in the quality of fit obtained. However, one has greater confidence in the physical significance of the information obtained from the analysis. An earlier example of a structural study involving the simultaneous fitting of EXAFS data for two different absorption edges, with the application of a relationship such as eq. (5), has been described by Zschech et al. [18] for metallic glasses.

A summary of the results obtained by the new method of analysis for the various bimetallic cluster catalysts investigated previously, including Ru-Cu, is given in table 2. The EXAFS data used in obtaining these results, along with the associated Fourier transforms and filtered inverse transforms, were the same as those from which the results in table 1 were obtained. They are given in detail in the original publications (refs. [3–9]). With regard to phase shift functions for the combinations *ab* and *ba* of unlike atoms, an initial function for one of the combinations, say *ab*, is obtained from Teo and Lee [16], as in the previous method of analysis. An initial phase shift function utilizing recent results of a more rigorous curved wave treatment of EXAFS by McKale et al. [19] could also have been used. Since the fitting algorithm makes provision for treating the theoretical threshold absorption energy E_0 as a variable, it thereby provides a way to vary the initial phase shift function for the combination *ab* in the fitting process. Simultaneous variation of the phase shift function for the other combination *ba* is achieved through the incorporation of eq. (4) in the fitting algorithm.

As a consequence of the incorporation of eq. (5) into the analysis, the values of N^{ab} and N^{ba} are identical for all of the catalysts with $X_a = X_b$ and differ by a factor of two for the one catalyst with $X_b = 2X_a$. A comparison of values of interatomic distances given in tables 1 and 2 reveals that in almost all cases (more than 90%) a value of a particular distance obtained by the new method agrees with that obtained by the previous method within 0.02 Å. However, more significant differences between the two methods are noted for results on compositions of first coordination shells. In particular, for the catalysts containing Os-Cu, Ir-Cu, and Pt-Cu clusters, which represent one fourth of the catalysts for which comparisons can be made from tables 1 and 2, the parameters obtained by the new analysis indicate a degree of segregation of the components which is significantly higher than that indicated by the previous analysis. For the Os-Cu and Ir-Cu systems, the degree of miscibility of the components in the bulk is very small, and the greater segregation indicated by the new, improved analysis seems more reasonable. In the case of the Pt-Cu clusters, the components of which are completely miscible in the bulk, the substantial segregation of components indicated by the new analysis might at first glance appear to be highly questionable. However, for bimetallic systems in general, there is a tendency for the surface to be enriched in one of the components, even if the components are completely miscible in the bulk [20]. If the surface atoms in a bimetallic cluster represent a substantial fraction of the total atoms present, as is frequently the case, extensive enrichment of the surface with one of the components has the consequence that the component in question is present almost entirely in the surface. It is to be noted that the analysis of the EXAFS data on the Au-Cu system, which resembles the Pt-Cu system with regard to the complete miscibility of the components in the

Table 2
Summary of structural parameters obtained by simultaneous fitting of EXAFS for both components of bimetallic clusters

Bimetallic cluster system	Re-Cu	Os-Cu	Ir-Cu	Pt-Cu	Au-Cu	Ru-Cu	Rh-Cu	Rh-Cu	Ag-Cu	Ir-Rh	Ir-Rh	Pt-Re	Pd-Re
Component *a*	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Rh	Rh	Pt	Pd
Component *b*	Re	Os	Ir	Pt	Au	Ru	Rh	Rh	Ag	Ir	Ir	Re	Re
Support	SiO$_2$										Al$_2$O$_3$		
b: *a* atomic ratio	1	1	1	1	1	1	1	2	1	1	1	1	1
Interatomic distances, Å													
R_{aa}	2.55	2.57	2.60	2.63	2.60	2.57	2.62	2.65	2.54	2.72	2.69	2.75	2.73
R_{bb}	2.74	2.68	2.69	2.71	2.82	2.66	2.65	2.67	2.88	2.72	2.74	2.74	2.73
R_{ab}	2.62	2.67	2.65	2.66	2.69	2.65	2.62	2.65	2.68	2.71	2.70	2.63	2.71
Composition of first coordination shell, % *a*													
About *a*	69	80	62	67	70	80	59	48	86	61	52	64	70
About *b*	55	11	16	23	26	8	21	14	15	37	44	52	47
Number of nearest neighbor metal atoms													
Total, about *a*, N^a	5.1	7.2	4.7	7.6	10.9	3.9	6.3	6.9	9.8	9.5	6.3	9.5	8.1
Total, about *b*, N^b	2.9	12.3	11.3	11.0	12.7	9.6	12.6	12.5	9.1	10.1	6.8	6.5	5.1
Type *b*, about *a*, N^{ab}	1.6	1.4	1.8	2.5	3.3	0.8	2.6	3.6	1.4	3.7	3.0	3.4	2.4
Type *a*, about *b*, N^{ba}	1.6	1.4	1.8	2.5	3.3	0.8	2.6	1.8	1.4	3.7	3.0	3.4	2.4

bulk, also indicates extensive segregation of the components. For the Au-Cu clusters, however, nearly the same degree of segregation of the components is indicated by either the new or the previous method of analysis of the EXAFS data.

In conclusion, the new method of analysis of EXAFS data on bimetallic clusters is a significant improvement over the previous one, since certain necessary physical conditions regarding the system can be imposed in a direct manner when the EXAFS for the two components are fitted simultaneously.

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