X-ray Absorption Edge Studies of the Electronic Structure of Metal Catalysts

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In the year 1912, von Laue proposed that crystals could serve as diffraction gratings for X-rays.[1,2] Shortly thereafter, this proposal inspired the design of the first X-ray spectrometer in 1913 by W. H. Bragg.[3] After the work of Bragg, only a very short time elapsed before Moseley[4] used such an apparatus for his classical investigation of the characteristic X-ray spectra of the elements, which proved to be so important in the ordering of the elements in the periodic table. These monumental events paved the way for many investigations with X-rays, which have provided scientists with some of the most fundamental information available on the atomic and electronic structure of matter. In recent years, the enormous potential of X-ray absorption spectroscopy for the study of catalysts has become increasingly evident. Its main value as a probe of catalysts stems from the fact that it can provide information at a microscopic level which is frequently not obtainable in any other way. In the case of metal catalysts, for example, it can probe features of electronic structure which are intimately related to catalytic activity. In particular, the degree of occupancy of d-electron states of the metal atoms can be determined. The high catalytic activities of the transition metals

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for many reactions have long been attributed to their partially unoccupied d-electron states. Consequently, the experimental investigation of this feature of electronic structure is clearly of interest for advancing our understanding of the catalytic action of metals. The relevant information is obtained from studies of the structures of X-ray absorption edges.

At an absorption edge, the X-ray absorption coefficient increases abruptly with increasing energy, as first observed in 1916 by M. de Broglie.[5,6] In an absorption spectrum for a given element, absorption edges are observed at certain energies characteristic of the element, as is evident from Figure 1. The abrupt change in a spectrum at an absorption edge is illustrated schematically in Figure 2 and with experimental data in subsequent figures in the paper. An explanation for the abrupt rise in absorption was given in 1920 by Kossel,[7] who suggested that it should occur when the energy of the X-ray photons was equal to that required to excite electrons from an inner level of the absorbing atom to the first empty electronic states. Such states may be available within the atoms themselves (as so-called "bound states"), and one commonly speaks of an absorption threshold resonance[8] in referring to an electronic transition in which the electrons are excited to occupy such states. When the energy of the X-ray photons is high enough to eject the electrons from the atoms, one refers to the final states of the electrons as continuum states, since the ejected electrons can have

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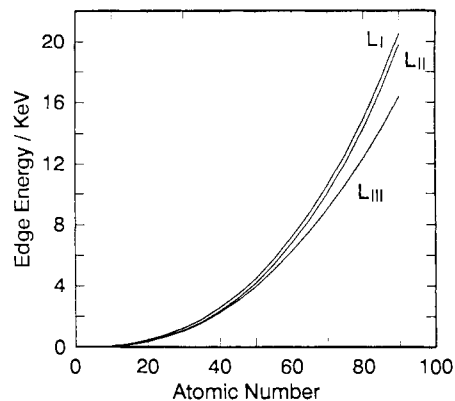(8) Lytle, F. W.; Wei, P. S. P.; Greegor, R. B.; Via, G. H.; Sinfelt, J. H. J. Chem. Phys. 1979, 70, 4849.

Figure 1. Energies of L absorption edges of the elements as a function of atomic number.[36]
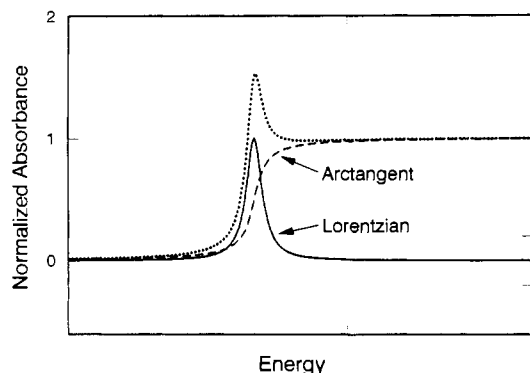

Figure 2. A schematic representation of an L absorption edge (dotted line) as the sum of an arctangent function (dashed line) and a Lorentzian function (solid line).

a continuous range of kinetic energies depending on the energy of the X-ray photons. Edges are identified by the letters K, L, M, etc. to reflect the particular electronic shell from which the electrons are excited by the X-ray photons.

X-ray absorption spectroscopy is now being used extensively for the characterization of catalysts.[8-22] In addition to the information on electronic properties which may be obtained from absorption edges, parameters such as interatomic distances and coordination numbers may be derived from data on the extended

X-ray absorption fine structure (EXAFS) following absorption edges. In this paper we limit our attention to the edges themselves and to the electronic information available therefrom.

X-ray absorption spectra can be obtained from several different types of measurements. One can determine the fraction of the incident X-ray beam which is transmitted through a sample.[23-25] The absorption coefficient is then proportional to the logarithm of the reciprocal of this fraction (Beer's law). The intensity of secondary, or fluorescent, X-rays emanating from a sample can also be determined.[26] The fluorescent radiation is emitted when electrons from outer shells of the atoms occupy vacancies created in inner electronic shells by the X-ray absorption process.[23-25] The intensity of the fluorescent X-rays is proportional to the extent of absorption of the incident radiation. Another measurement is the total emission of electrons from the element of interest in the sample as a consequence of the X-ray absorption process.[27] This quantity, the "total electron yield", is also proportional to the extent of X-ray absorption.

When X-ray absorption spectra are obtained from transmission or fluorescence measurements, one must avoid errors associated with so-called "thickness effects".[28-30] In transmission measurements, there is always some degree of leakage of radiation, where leakage refers to a part of the measured incident radiation which is not absorbed by the sample to the extent expected. Whatever the reason for the leakage,[30] it has the effect of decreasing the measured absorption coefficient, and the effect becomes more pronounced as the sample thickness increases. The problem does not occur if the number of atomic layers of the element of interest in the path of the X-ray beam corresponds to a distance which is no larger than the characteristic absorption length, which in turn is given by the reciprocal of the linear absorption coefficient. For fluorescence measurements, there is a more stringent requirement, namely, that the distance should be small compared to the characteristic absorption length of the incident radiation. In metal catalysts of technical interest, the metal component frequently is present in low concentration in the form of very small clusters or crystallites distributed throughout a porous oxide carrier.[31,32] The thickness criteria for acceptable samples are not too difficult to meet for materials of this type. However, for purely metallic catalyst samples in the form of metal powders, it is generally not possible to obtain particles small enough to eliminate errors due to thickness effects. For such samples, measurements of total electron yields, which eliminate the complications of thickness effects, are recommended.

Experiments in X-ray spectroscopy are generally conducted with synchrotron radiation. Although a

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synchrotron facility is not absolutely necessary for the measurements, it improves the rate of acquisition of data enormously.[33,34] In the analysis of experimental X-ray absorption data, it is common practice to begin by choosing a zero point in the energy scale, generally the energy E_0 corresponding to the point of inflection in the edge. Next, one obtains a value for the so-called "absorption jump" at this energy by taking the difference of absorption values obtained by extrapolation of data from the pre-edge and post-edge regions of the spectrum.[35] The spectrum is then normalized to the absorption jump for quantitative comparisons with spectra for other samples containing the element of interest.

L Absorption Edges of Metals

The absorption of X-ray photons by L shell electrons produces three different absorption edges. The L_I edge is due to excitation of electrons from 2s states (i.e., from L shell states with angular momentum quantum number l equal to 0). The L_{II} and L_{III} edges are due to excitation of electrons from 2p states (L shell states with $l = 1$). For studies of the electronic structures of metal catalysts, the L_{II} and L_{III} edges are of particular interest. The 2p states giving rise to L_{II} edges have their orbital and spin angular momentum vectors opposed to one another and are designated $2p_{1/2}$ (the quantum numbers l and s are 1 and $-^1/_2$, respectively, giving a resultant quantum number $j = l + s = ^1/_2$). The 2p states involved in L_{III} edges have their orbital and spin vectors aligned in the same direction and are designated $2p_{3/2}$ ($l = 1$, $s = +^1/_2$, and $j = l + s = ^3/_2$). The energies of the L edges increase in the order $L_{III} < L_{II} < L_I$. They are shown as a function of atomic number in Figure 1. The plots are based on data tabulated by Bearden and Burr.[36]

Transition probabilities for excitations of 2p electrons to unoccupied d states are very much higher than for excitations to vacant s states.[37] For non transition metals such as copper and gold, which have completely filled d states, the L_{III} and L_{II} edges have the appearance of simple steps. They are attributed to the excitation of 2p electrons to continuum states. The steps can be approximated by arctangent functions, which in turn have a theoretical basis.[38] Transition metals such as nickel and platinum, with incompletely filled d states, have more complex L_{III} and L_{II} edges consisting of peaks superimposed on step functions. The peaks, which are commonly called "white lines" in reference to their appearance in early spectra recorded on photographic film,[39] are indicative of absorption threshold resonances associated with excitation of 2p electrons to unfilled d states in the valence band.[40] When resolved from the step function at the edge, such a resonance has a Lorentzian line shape.[41] In Figure 2 an L_{III} or L_{II} edge

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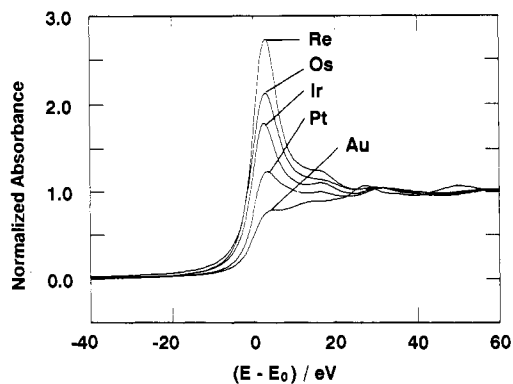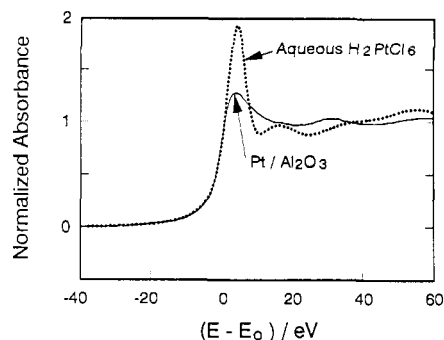(41) Horsley, J. A. *J. Chem. Phys.* **1982**, *76*, 1451.

Figure 3. X-ray spectra comparing the L_{III} absorption edges of the 5d metals rhenium through gold.[35]

(dotted line) is represented schematically as the sum of an arctangent function (dashed line) and a Lorentzian function (solid line).

Spectra comparing L_{III} absorption edges of the series of 5d metals rhenium through gold are shown in Figure 3. As expected, the absorption edge for gold consists simply of a step, since there are no unfilled 5d states available for electronic transitions from 2p states. In contrast, the absorption edge for each of the other metals exhibits a pronounced peak, since these metals all have unoccupied d states. There is a progressive increase in the intensity of the absorption threshold resonance, corresponding to an increase in the number of unoccupied d states, in the order Au < Pt < Ir < Os < Re.[35]

L_{III} Absorption Edges of Dispersed Metals

Catalysts containing metal clusters of the order of 10 Å in size are utilized widely for the production of gasoline components with high antiknock ratings.[42] The first catalysts of this type contained platinum dispersed throughout the pores of alumina.[43] Eventually, catalysts with bimetallic clusters of platinum and a second metallic element (e.g., Pt–Ir and Pt–Re) were introduced.[32,42] The clusters are characterized by a quantity known as the dispersion, which is the ratio of surface atoms to total atoms in the clusters. This quantity approaches unity for clusters which are 10 Å in size. Information on dispersion is obtained largely from chemisorption studies[31] and to a lesser extent from electron microscopy[31] and EXAFS[17,18,44] measurements.

A typical Pt/Al_2O_3 catalyst can be prepared by contacting alumina with an aqueous solution of chloroplatinic acid, H_2PtCl_6. After the material is dried and then heated in air at approximately 825–850 K, it is exposed to hydrogen at 725–775 K prior to use.[31] In Figure 4 we compare the L_{III} X-ray absorption edge of Pt^{4+} in a chloroplatinic acid solution with that of platinum in clusters of the order of 10 Å in size in a Pt/Al_2O_3 catalyst containing 1 wt % platinum. The absorption threshold resonance of Pt^{4+} in the chloroplatinate ion is much more intense than it is for Pt^0 in the metal clusters, owing to the greater number of unoccupied d states. In the various stages of preparation of a Pt/Al_2O_3 catalyst, the state of oxidation of the platinum can be followed by examination of the
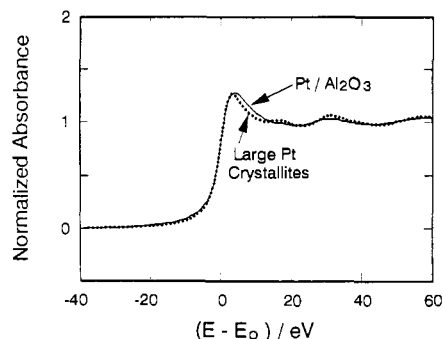
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Figure 4. Comparison of L_{III} absorption edge of platinum in a Pt/Al$_2$O$_3$ catalyst with that of platinum in a chloroplatinic acid solution.


Figure 5. Comparison of L_{III} absorption edge for the platinum clusters in a Pt/Al$_2$O$_3$ catalyst (metal dispersion = 1.0) with that for large platinum crystallites (dispersion = 0.2).[35]

intensity of the resonance. Reduction of a precursor species to the desired metal clusters or crystallites is a key step in the preparation of a metal catalyst.[31,45]

Metal Dispersion Effects. In Figure 5, L_{III} absorption edges of platinum are shown for a Pt/Al$_2$O$_3$ catalyst with a metal dispersion approaching unity and for a sample with "large" platinum crystallites having a metal dispersion of 0.2. A very careful comparison indicates that the resonance may be slightly more intense for the small metal clusters in the Pt/Al$_2$O$_3$ catalyst, but the difference is close to the limits of uncertainty in the determination.[35] Similar results on the effect of dispersion are obtained for iridium and osmium. Some previous reports of larger effects[8,9] appear to have been confounded by sample thickness effects. Thus, we conclude that clusters of platinum, iridium, or osmium of the order of 10 Å in size (with a ratio of surface atoms to total atoms approaching unity), supported on either alumina or silica, exhibit electronic properties not very different from what they are in much larger crystallites representative of the metal in the bulk. Apart from indicating that intrinsic size effects are small down to a size of about 10 Å, the results also show that the extent of electronic interaction of the metal clusters with alumina or silica is minimal.

When alumina or silica is used as a support for a number of metals, the metal–support interaction is not strong enough to affect the metallic nature of the cluster significantly. Consequently, these oxides are excellent supports for metals in catalytic applications where metallic properties are important. In such applications the interaction of the metal with the support is ideally only strong enough to limit the mobility of the small metal clusters, thereby inhibiting their growth.[35]

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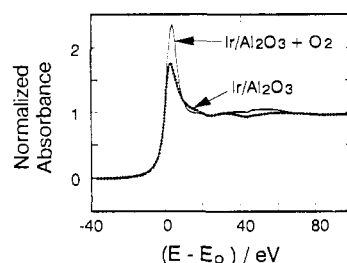
Figure 6. Effect of chemisorbed oxygen on the iridium L_{III} absorption edge of an Ir/Al$_2$O$_3$ catalyst.[8]

Effect of Chemisorbed Oxygen. When a monolayer of oxygen is chemisorbed on highly dispersed clusters of platinum, iridium, or osmium, the intensity of the resonance at the L_{III} edge increases substantially.[8,35] Typical data are shown in Figure 6 for an Ir/Al$_2$O$_3$ catalyst containing 1 wt % Ir, with iridium clusters of the order of 10 Å in size.[8] The dotted line is the L_{III} edge for the catalyst after it is cooled in a stream of helium from 675 K to the temperature of the measurement. The solid line is the edge after exposure of the catalyst to a helium stream containing 1 mol % oxygen at room temperature. We conclude that the number of unoccupied d states of the metal increases as a result of the interaction with the oxygen, i.e., the metal clusters become more electron deficient. The chemisorption does not lead to bulk oxidation, as shown by the fact that the L_{III} edge is much less intense than the edge for the bulk oxide.[8] Thus, the metal clusters are not destroyed by the interaction with chemisorbed oxygen.

L Absorption Edges of Bimetallic Catalysts

Bimetallic Clusters. Studies of L_{III} X-ray absorption edges have been very useful in the characterization of bimetallic catalysts. Data obtained on a Pt–Re/Al$_2$O$_3$ catalyst (1% Pt, 1% Re) provide a good example.[11] This catalyst system is used for hydrocarbon reactions in a hydrogen-rich gaseous environment at pressures of 10–20 atm and temperatures of 725–775 K. When the catalyst first attracted interest, there was a question about the state of oxidation of the rhenium after exposure to hydrogen at operating temperatures,[46–48] specifically, whether or not the oxidation state is 0. In Figure 7, L_{III} edges of rhenium are compared for bulk rhenium (a foil), for a Pt–Re catalyst, and for an aqueous NaReO$_4$ solution.[11] The L_{III} edge of the rhenium in the catalyst is insignificantly different from that of the rhenium foil and much less intense than the edge for the rhenium in the +7 oxidation state in ReO$_4^-$. This result indicates that the rhenium in the catalyst has an oxidation state of 0. The same conclusion is reached from analysis of EXAFS data, which also provide evidence for the existence of bimetallic clusters of platinum and rhenium.[11]

Another issue of interest in the use of Pt–Re catalysts is concerned with the effect of sulfur on the state of rhenium in the catalyst. Prior to its use in the reforming of petroleum fractions, the catalyst is exposed to a gas containing H$_2$S to suppress the high activity of rhenium

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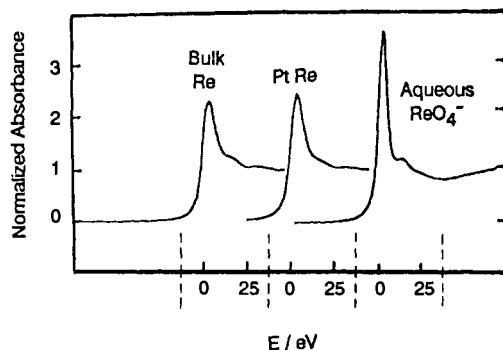(48) Johnson, M. F. L. *J. Catal.* **1975**, *39*, 487.

Figure 7. Comparison of L_{III} absorption edges of rhenium in a pure rhenium foil, in a Pt–Re/Al$_2$O$_3$ catalyst, and in an aqueous NaReO$_4$ solution.[11]
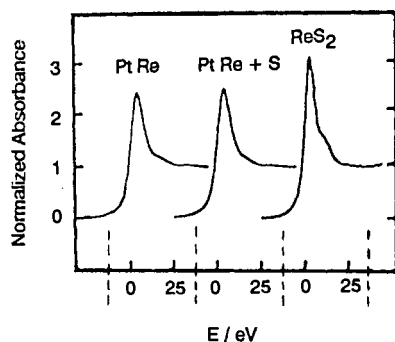

Figure 8. Comparison of L_{III} absorption edges of rhenium in ReS$_2$, in a Pt–Re/Al$_2$O$_3$ catalyst, and in the same catalyst containing sulfur.[11]

for hydrogenolysis of C–C bonds in hydrocarbons.[49,50] Since the sulfur interacts strongly with the rhenium in the catalyst, one may well inquire about its possible effect on the Pt–Re clusters originally present. Thus one might wonder about the possibility of formation of ReS$_2$. Data with a bearing on this question are given in Figure 8, which shows the L_{III} edges of rhenium in ReS$_2$ and in a Pt–Re catalyst before and after exposure to a gas stream containing H$_2$S.[11] The edge of rhenium in the catalyst after exposure to H$_2$S is insignificantly different from what it was before the exposure, but is much less intense than the edge of rhenium in ReS$_2$. These data, coupled with EXAFS data, indicate that the Pt–Re clusters in the catalyst are not disrupted by the treatment with H$_2$S. Sulfur incorporated in the catalyst during the treatment appears in the form of sulfur atoms chemisorbed on exposed rhenium atoms in the Pt–Re clusters, in agreement with a conclusion reached by Biloen et al.[51] from other types of measurements.

Nickel–Copper Alloys. The evolution of ideas concerning the "electronic factor" in catalysis by metals has involved many studies with nickel–copper alloys.[52–57] According to an early theory of their electronic structure known as the "rigid-band" model, there is a single d band which becomes increasingly filled as the copper

content of the alloy increases.[58,59] The theory predicts that the d band is completely filled at a composition of approximately 60 atom % copper. Therefore, ferromagnetism should disappear at this composition, as is actually observed.[56,60] From the standpoint of catalysis, the model leads one to expect changes in catalytic activity in relation to the expected change in filling of the d band as the alloy composition changes. Although the rigid-band model was widely accepted by solid-state physicists when it was originally proposed, questions about the validity of the model were eventually raised.[61–63]

Measurements of intensities of absorption threshold resonances at L_{III} and L_{II} absorption edges provide a direct way of probing the number of unfilled d states of nickel atoms in the alloys.[64–66] Recently, the present authors, in collaboration with D. A. Fischer, have obtained data on the L_{III} and L_{II} absorption edges of a series of nickel–copper alloys from measurements of total electron yields.[65,66] The alloys were powders which had previously been the subject of an extensive catalysis study.[56] The approach of measuring electron yields avoids experimental artifacts due to sample thickness effects. Since the depth of escape of electrons from a sample is limited, one might have thought that the spectra for the alloys would be characteristic of only the surface, which is well-known to be rich in copper relative to the bulk.[56,67,68] However, the relative magnitudes of the absorption jumps for the nickel and copper edges clearly indicated that the spectra were representative of the bulk compositions of the alloys. Apparently, the region of composition different from that of the bulk was very thin compared to the escape depth of the electrons.

The L_{III} and L_{II} edges of pure copper do not exhibit the absorption threshold resonances observed with pure nickel, since the d states of copper are completely filled. The edges for the two metals are compared in the upper section of Figure 9. An approximate method for isolating the resonances for the nickel consists of a simple subtraction of the spectrum for copper from that for nickel, as illustrated in the lower half of Figure 9. This procedure, adopted from a suggestion of Lytle[69] with a modification of Cordts et al.,[70] assumes that the edges for copper are good approximations of the steps underlying the edges for nickel, the element immediately preceding copper in the periodic table. In the subtraction, the energy corresponding to the point of inflection in the L_{III} edge of copper is aligned with the energy corresponding to the maximum in the peak in the nickel L_{III} edge. As discussed by Cordts et al.,[70]

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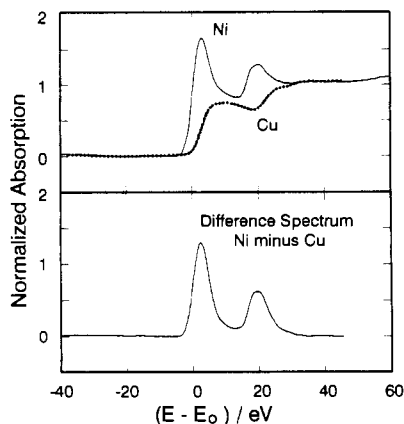(52) Dowden, D. A.; Reynolds, P. *Discuss. Faraday Soc.* **1950**, *8*, 184.
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Figure 9. Comparison of X-ray absorption spectra of nickel and copper in the region of the L_{III} and L_{II} edges (upper section of figure). The point of inflection in the L_{III} edge of copper is aligned with the maximum in the peak at the L_{III} edge of nickel. A difference spectrum is shown in the lower section of the figure. It is assumed to represent the L_{III} and L_{II} absorption threshold resonances of nickel.[66]

this procedure serves to align the two components of the spectrum with respect to the Fermi energy.

The total spectral area under the nickel L_{III} and L_{II} edges for each of the nickel–copper alloys is slightly smaller than the corresponding area for pure nickel. When the difference in areas is normalized to the spectral area of the combined L_{III} and L_{II} resonances of pure nickel shown in the lower section of Figure 9, one has a value for the fractional decrease in the number of unfilled d states of nickel as a consequence of its association with copper in the alloy. The number of unfilled nickel d states for a nickel–copper alloy relative to the number for pure nickel is shown as a function of alloy composition in Figure 10 (the solid line through the data points). For comparison, the prediction of the rigid-band theory of the electronic structure is shown as the broken line in the figure. The measured effect is an order of magnitude smaller than the predicted one. Thus, the rigid-band theory does not provide a satisfactory description of the electronic structure of nickel–copper alloys and, therefore, does not provide a rigorous basis for the use of such alloys to probe the electronic factor in catalysis.
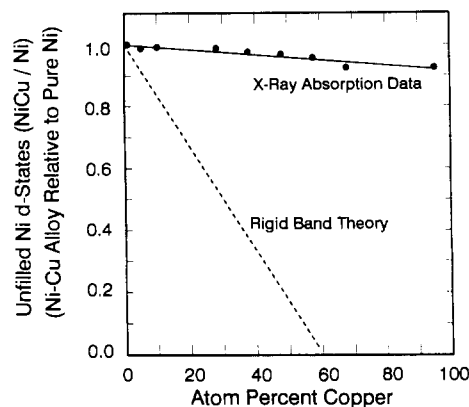
Figure 10. Electronic structure of nickel–copper alloys as a function of alloy composition: comparison of results of X-ray absorption experiments with the prediction of the rigid band model. The ordinate represents the number of unfilled d states per nickel atom in an alloy relative to the number in pure nickel.[66]

Concluding Remarks

Studies of X-ray absorption threshold resonances at L_{III} and L_{II} absorption edges can provide useful information on the electronic structure of a metal catalyst, if complications associated with sample thickness effects are recognized and corrected. One can measure the d-band occupancies of various metals of interest in catalysis, thereby providing a quantitative basis for relating catalytic activity to this parameter. One can also determine whether or not this parameter is influenced by the state of dispersion of the metal on a support, by the chemical nature of the support itself, or by alloying. Moreover, the resonances are useful for probing the oxidation states of precursor species during various stages in the preparation of a metal catalyst. Such information can be used in the optimization of a preparation procedure. For these reasons, among others, absorption edge studies provide a valuable probe for the characterization of metal catalysts.