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The Study of Heterogeneous Catalysts by the EXAFS Method

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The principles of the EXAFS method, which makes it possible to determine the structure of the local environment of a chemical element being studied within a radius of 4 Å, are described. Information on the experimental apparatus, the fields of application, and the accuracy of the determination of the structural parameters (interatomic distances, coordination numbers, Debye-Waller factors) are given. Examples of the use of the method to study catalysts are described.
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I. INTRODUCTION

In the last ten years, a fundamentally new method has been developed for determining the local structure of the environment of a given chemical element in any state of aggregation, namely the EXAFS method. (EXAFS is an abbreviation for Extended X-Ray Absorption Fine Structure, or DTSRSP in Russian). Unlike traditional diffraction methods, which make use of the phenomenon of the elastic scattering of the probing radiation (X-rays, electrons, neutrons) on a crystal lattice, the EXAFS method makes use of the characteristic absorption of X-rays by the chemical element being studied, which is independent of the existence of a crystal lattice. Thus the EXAFS method can be used to study materials amorphous towards X-rays, such as, for example, highly dispersed deposited catalysts. The present review describes the principles of the EXAFS method and describes its possible applications in the study of catalysts.

II. PRINCIPLES OF THE METHOD

In X-ray absorption spectroscopy, use is made of processes involving the transfer of an electron from an inner level, usually 1*s*, 2*s*, and 2*p*, to higher unoccupied levels or to the free state, that is ionisation. Fig.1 shows the hypothetical X-ray absorption spectrum of an isolated atom. When the X-ray quantum reaches an energy E_0 sufficient to ionise the electrons of one of the inner levels, a sudden jump is observed. Before this point, absorption involves higher-lying levels and is described by an expression of the form $A.E^{-3} + B.E^{-4}$ (where E is the energy of the X-ray quantum, and A and B are parameters specific for each chemical element). When the energies of the quanta are greater than the ionisation potential of this level, a regular decrease in the absorption coefficient according to the same law should be observed.

For a real specimen, where there are other atoms in the local environment of the absorbing atom, the absorption spectrum has a different appearance. Fig.2 gives the X-ray absorption spectrum of metallic platinum with ionisation of the $2p_{3/2}$ level; the spectrum shows a complex structure close to the absorption edge and oscillation over a very wide range, from 50 eV to ~1000 eV. These oscillations have been called the extended X-ray absorption fine structure.

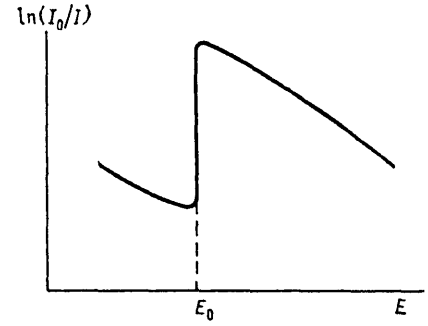


Figure 1. Assumed X-ray spectrum of an isolated atom: I_0 is the intensity of the incident radiation, I the intensity of the radiation passed through the specimen, E the energy of the X-ray quantum, and E_0 the ionisation potential of one of the inner levels of the atom.

The phenomenon was discovered[1] in the nineteen-thirties. In the nineteen-fifties, the following model was developed[2,3] to explain the nature of the phenomenon; for an isolated atom, a photoelectron ejected by an X-ray quantum is described by a spherically symmetrical divergent wave-function. When there are other atoms close to the absorbing atom, the photoelectron will be partly scattered backward

on these atoms, and its state will be described by the superposition of the emitted and scattered wavefunctions. This leads to a change in the absorption coefficient. The absorption coefficient will increase or decrease, depending on the phase in which the wave front of the scattered photoelectron returns to the absorbing atom. If the wavelength of the ejected photoelectron is changed by changing the energy of the incident quantum, sinusoidal fluctuations will be observed in the absorption spectrum, with a period equal to twice the distance between the absorbing and scattering atoms.

The total spectrum will contain oscillations of this kind from all surrounding atoms. By determining the period of the oscillations in the absorption spectrum, it is possible in principle to measure the distance from the absorbing atom to the scattering atom, and, by determining the amplitude of the oscillations, to measure the number of scattering atoms. The determination of interatomic distances by this method has an important advantage, since it is possible to measure the distances around the atom of one chemical element. The atoms of other chemical elements, which are present, for example, in multicomponent systems such as catalysts, do not interfere in these measurements, since as a result of the large energy range over which the absorption edges of the inner levels of the atoms of different chemical elements are distributed, the superposition of the absorption edges of different elements is fairly infrequent.

The first attempts to determine interatomic distances by this method were unsuccessful,[4] however, because in the emission and scattering of photoelectrons, additional displacements of the phase of their wavefunction may occur, and it became possible to calculate these displacements, and also the amplitudes of the probability of the scattering process, only in the mid nineteen-seventies.

With the development of computing techniques, the model was refined, the forms of the interatomic potentials were selected, and numerical calculations were carried out to determine the amplitudes of the probability of the scattering of the photoelectron and the magnitude of the phase displacements in the emission and scattering of the photoelectron.[5-9] Experimental verification showed that the model chosen for the phenomenon is correct, and confirmed that the accuracy attained in the calculations and the fact that the phase displacements are independent of the chemical state of the scattering and absorbing atoms make it possible to determine interatomic distances by means of a Fourier analysis of the fine structure of the X-ray absorption spectrum.[10] The limitations of the model lead mainly to uncertainty in the determination of the coordination numbers and the amplitudes of the thermal vibrations of the atoms, and have little influence on the accuracy of the determination of interatomic distances. Nevertheless, the complexity of the experiment (the recording of a single spectrum on a laboratory instrument even at the present time can take days) would have prevented EXAFS spectroscopy from developing into an analytical method if the synchrotron emission from electron storage rings had not begun to be more widely used in X-ray spectral studies.

III. APPARATUS AND FIELDS OF APPLICATION

Synchroton emission (SE) is the emission by relativistic electrons in their movement along the annular orbit of the storage ring. The spectral range of SE extends from the infrared to the X-ray region. The intensity of SE is hundreds of times that of the emission of the resonance lines of the X-ray tubes usually employed for structural analysis; SE is continuous throughout its spectral range. This makes it possible to carry out experiments over a wide range of energies, to change easily from one element to another, and to work with lower concentrations of absorbing elements. Moreover, the SE beam has a very low angle of divergence (10^{-3} rad) and a high degree of polarisation.[11,12]

Because of these advantages of SE, and in spite of the need to construct special apparatus, an increasing proportion of X-ray spectral studies are being carried out using it. The first studies were carried out in parallel with experiments on high-energy physics, but many countries, such as the USA, Britain, France, West Germany, Italy, and Japan, now have electron storage rings that are used only to generate SE as

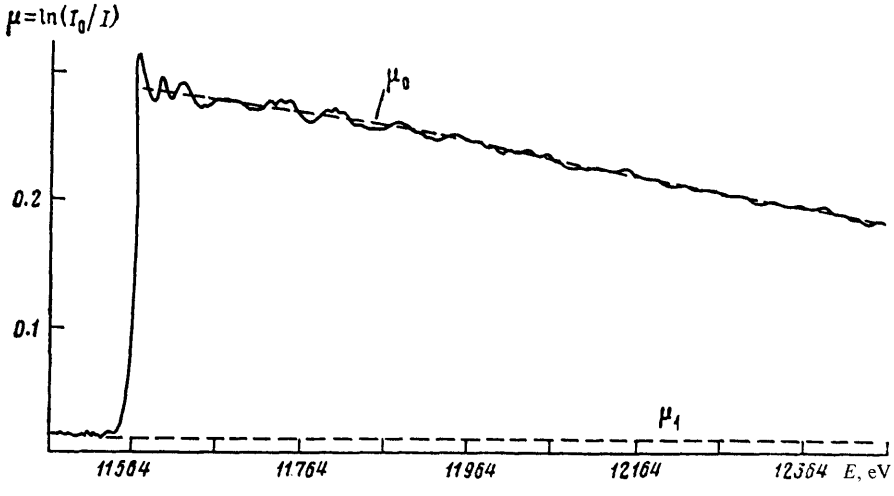


Figure 2. X-Ray absorption spectrum of the L_{III} level of metallic platinum: μ is the absorption coefficient, μ_0 the smooth part of the absorption coefficient, and μ_1 the absorption of other electron levels in the atom.

a source for X-ray studies. The use of SE for EXAFS spectroscopy has made it possible to decrease the time taken to record the spectrum from days to 10–20 minutes and to work at concentrations of the element being studied reaching 0.1 M in a weakly absorbing matrix.

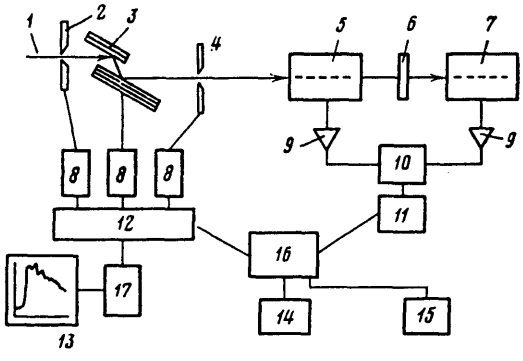


Figure 3. Block diagram of an EXAFS spectrometer: *1*) beam of synchrotron radiation, *2*) inlet slit of the monochromator, *3*) single-block crystal double monochromator, *4*) outlet slit of the monochromator, *5*) flow-through ionisation chamber, *6*) specimen, *7*) total absorption ionisation chamber, *8*) stepped motor control blocks, *9*) pre-amplifier, *10*) commutator, *11*) digital voltmeters, *12*) KAMAK box, *13*) display, *14*) video terminal, *15*) digital printer, *16*) ODRA-1305 computer, *17*) display control block.

In the USSR, EXAFS spectroscopic studies are being carried out using the electron storage rings of the Institute of Nuclear Physics of the Siberian Branch of the Academy of Sciences of the USSR in the Siberian Collective Centre for the Use of Synchrotron Emission. An EXAFS spectrometer (Fig.3) has been constructed for this purpose, and is in regular operation.[13] A general description of the principles of the construction of spectrometers for use with SE can be found in Ref.12. It should be noted only that when the generally employed two-crystal monochromator scheme (with Ge(111) and Si(220) crystal monochromators) is used to record the spectrum, no change takes place in the direction of the propagation of the X-ray beam after passing through the monochromator. Only a lateral displacement of the X-ray beam takes place, leading to a displacement of the beam along the specimen when the spectrum is recorded (by ~0.02 mm).

The recording system should ensure the measurement of the intensity of the quantum flux with an uncertainty of not more than 10^{-4} and the measurement of the absorption coefficient with an uncertainty of not more than 0.1% for an intensity of the incident radiation of 10^{13} photon $rad^{-1}\,s^{-1}$ with $\Delta\lambda/\lambda \cong 3 \times 10^{-4}$.

EXAFS spectrometers of different types have now been developed. They differ in the construction of the monochromator system and mainly in the recording system. Changes in the monochromator system are made to give a "purer" signal at the outlet by decreasing the scattered background and the contribution from higher harmonics. The choice of the method of recording the spectrum depends on the problem being studied. A whole set of procedures has now been developed. The most widely encountered scheme for operating the instrument "in transmission" makes it possible to record the EXAFS spectra from an element in a matrix whose absorption is slight compared with that by the element being studied in the range of quanta energies used, for example the spectra of Pt/SiO_2 and Pd/TiO_2 catalysts. The concentration of the element being studied may reach 1 mass %.

When the absorption by the matrix is strong compared with that of the element being studied close to its ionisation potential (Ti/SiO_2, Pt/TiO_2), the EXAFS spectra cannot be obtained by this method, since the strong absorption by the carrier leads to a decrease in the accuracy of the measurement of the absorption coefficient. For the study of these materials or for the study of surfaces, other methods are employed, which make use of the fact that the primary process in the absorption of X-rays is accompanied by secondary processes of X-ray and optical fluorescence or the emission of Auger electrons. The system of recording X-ray fluorescence[14] makes it possible to increase the sensitivity with respect to the element being studied by factors of 10–100 and to work with strongly absorbing matrices.

The recording of Auger electrons,[15,16] the total electron photocurrent,[17,18] or the X-ray-induced desorption of ions[19] makes it possible to study the structure of a surface and the coordination of molecules adsorbed on a surface. The thickness of the surface layer that can be studied reaches 100 Å for the total-photocurrent method, and 2–10 Å for methods using the recording of Auger electrons or the X-ray-induced desorption of ions.

Other methods are now being developed, which make it possible to study the structure of the surface of a catalyst not in a vacuum but in the presence of a reaction medium (the total external reflectance method[20]) or to carry out a selective study of the structure of the environment of the atoms of an element in states which luminesce in the optical range of the spectrum under the influence of X-rays.[21]

IV. METHODS OF EXTRACTING STRUCTURAL DATA

In the model described above, the extended X-ray absorption fine structure is described by the function[10]

$$\chi(k) = \frac{1}{k}\sum_i \frac{N_i}{R_i^2} f_i(k)\, e^{-\sigma_i^2 k^2} e^{-R_i/\lambda} \sin(2kR_i + \varphi_i(k)) \qquad (1)$$

where k is the modulus of the wave vector of the photoelectron, $k = [2m_e \times (E_0 - E)/\hbar^2]^{1/2}$, E_0 the ionisation potential of the absorbing electron level, N_i the number of atoms in the i^{th} coordination sphere, R_i the radius of the i^{th} sphere, σ_i^2 the Debye–Waller factor, λ the free path of the photoelectron, $f_i(k)$ the amplitude of the probability of the scattering "backward" and $\phi_i(k)$ the change in phase during emission and scattering. The summation is carried out over all coordination spheres.

$\chi(k)$ is determined from the experimentally measured absorption spectrum using the equation

$$\chi(k) = (\mu - \mu_0)/(\mu_0 - \mu_1)$$

where μ is the absorption coefficient of the atom being studied in the specimen, μ_0 the absorption coefficient of the same atom in the isolated state, and μ_1 the absorption coefficient of the atoms of other elements present in the specimen, and of other levels of the atom being studied (see Fig.2).

There are several methods for analysing $\chi(k)$. The simplest is the Fourier transformation of $\chi(k)$, which gives a series of maxima displaced relative to the origin of coordinates by an amount $2R_i + \delta_i$, where δ_i is the linear part of

$\phi_i(k)$.[10] If the summation with respect to i in Eqn.(1) is replaced by integration with respect to the distribution function $\rho(R)$,[22] it is possible to find a direct solution of the integral equation obtained. In addition, extensive use is made of modelling, where the parameters to be determined are varied to give best agreement between the experimental and model spectra.[23]

All these methods have advantages and disadvantages, and preference cannot yet be given to any one of them. The direct solution of the integral equation is possible only for one-component systems, and the results depend markedly on the uncertainty in the determination of the experimental data. This method therefore finds only limited application, and is unsuitable for the study of catalysts.

The methods of Fourier analysis and modelling are most widely used. Fourier analysis is applicable to all systems, does not require the introduction of additional assumptions, and gives reliable information. Its main unsatisfactory feature is that the analysis is carried out over a limited range of wavenumbers, 12–15 Å^{-1}. The narrowness of the range leads to a large apparatus width in the Fourier transformation for the atom radial distribution function being sought, and this makes it difficult to analyse complex systems, because of the overlap of the peaks. The necessary restriction of the range of integration at low wavenumbers to 3–4 Å^{-1}, below which the photo-ionisation model used is inapplicable, leads to the appearance of additional interference distortion on the atom radial distribution curve, as a result of which additional splitting and displacement of the peaks are possible. Moreover, Fourier analysis does not make it possible to determine the nature of the scattering atoms, and it is necessary to seek a correction for the phase displacement δ_i, by making assumptions about the nature of the scattering element on the basis of additional information about the material being studied.

In the modelling method, the nature of the scattering atom and, usually, the functions $f_i(k)$ and $\phi_i(k)$ for this atom are given. The experimental spectrum and the Fourier filtration procedure are then used to separate the oscillations corresponding to the distance being analysed. The parameters R_i, N_i, σ_i^2, E_0, and, in individual cases, λ are varied. This method gives a higher accuracy of the determination of the interatomic distances, compared with Fourier analysis, and makes it possible to find the atomic number of the element to within ±5. The parameters being varied are correlated (E_0 and R_i, N_i and σ_i^2), however, because of the internal characteristics of the approximation used and the narrowness of the wavenumber range for which it is possible to obtain experimental data. The existence of this correlation may lead to errors in the determination of the parameters. The most reliable results are therefore obtained by a combination of both methods, where the primary analysis is carried out by the Fourier method, after which the results obtained are refined by modelling.

Fig.4 gives the results of a Fourier analysis of the function $\chi(k)$ for the absorption spectrum of the L_{III} level ($2p_{3/2}$ level) of metallic platinum, given in Fig.2. Fig.4 shows that, in accordance with Eqn.(1) with increase in R the intensity of the peaks decreases rapidly (as R^2). This feature, and also the damping of the function $\chi(k)$ as a result of the loss of energy by the photoelectrons with long free paths in inelastic scattering processes, restricts the range of interatomic distances that can be measured to 1.5–4.0 Å. The lower limit is determined by the need to have several oscillation periods on the experimental curve. The positions of the peaks in Fig.2 also do not correspond to the true distances between the atoms in metallic platinum. This difference is determined by the change in phase $\phi(k)$. Special studies have shown[24,25] that the observed displacement δ_i depends only on the nature of the absorbing and scattering elements, and not on their chemical state. The fact that $\phi_i(k)$ is independent of the chemical state makes it possible to determine interatomic distances with a high accuracy (from 0.04 Å to 0.01 Å for different methods). Tables of functions $f_i(k)$ and $\phi_i(k)$ for the ionisation of the K and L levels have now been published[9] for practically all chemical elements.

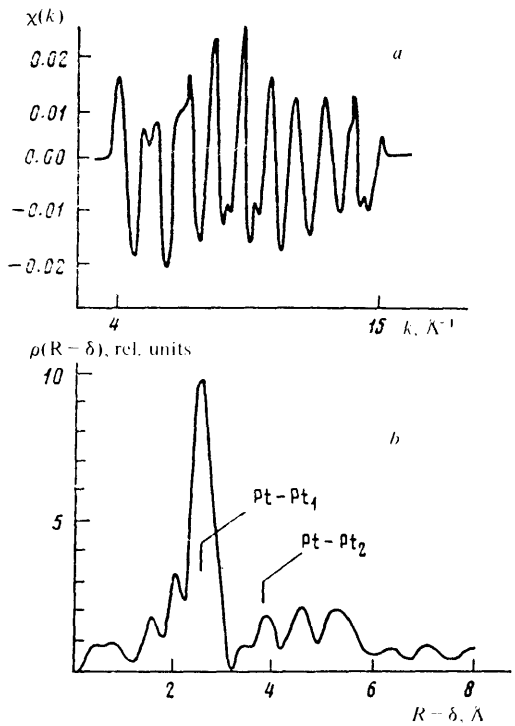


Figure 4. Extended X-ray absorption fine structure of the L_{III} level of metallic platinum (a) and the radial distribution function of the atoms obtained from it (b).

The accuracy of the determination of coordination numbers is much lower than that for distances. There are several reasons for this. Firstly, the amplitude of a peak on the experimental curve is determined by the integral magnitude of $f_i(k)$ in the range in which the experimental data are analysed. A large contribution to the amplitude is therefore made by the scattering of low-energy photoelectrons, and the amplitude for a given coordination number depends markedly on the chemical state of the scattering atom.[25,26] Secondly, all the effects which are present in photo-ionisation and scattering processes and which are not taken into account in the model used also influence primarily the amplitudes of the peaks. Processes such as inelastic scattering give a value of the coordination number being determined which is too low,[27] whereas multiple scattering may give a value of the coordination number which is too low or too high[28] and may even lead to the appearance of spurious peaks.[29] At the present time it is considered that the EXAFS method can be

used to determine coordination numbers of the first coordination sphere to within 20%; for subsequent spheres the uncertainty may reach 100%.[23]

A systematic analysis of the accuracy of the determination of the Debye–Waller factor by the EXAFS method has not been carried out, although the method is used for this purpose.[23] It has been shown that the possibility of using the EXAFS method to determine interatomic distances and coordination numbers depends markedly on the magnitude of σ_i^2.[30] For values of $\sigma_i^2 > 0.04$ Å^2, oscillations are not observed in the EXAFS spectrum. In some cases this leads to a situation in which any changes in the environment of the ligand atom being studied are not reflected in the spectrum.[31]

The treatment of the spectra is now being carried out everywhere by practically identical methods using similar computer programs. Work is being carried out to extend the possibilities provided by the programs. Thus an attempt has been made,[28,29] by estimating the influence of double scattering on the amplitude of the peaks in the EXAFS spectrum, to determine the angular distribution of the atoms in the second and higher coordination spheres.

V. APPLICATIONS IN THE STUDY OF CATALYSTS

The number of publications devoted to the study of catalysts by the EXAFS method has now reached several hundreds. The first reviews of these studies have been published.[23,32] The present section will examine mainly studies of deposited metallic catalysts, which make up a large proportion of the work carried out. This is related both to their extensive practical application and to their relative simplicity. These catalysts are distinguished by the ease of selecting model compounds, for which metals are used. In view of the practical importance of deposited platinum catalysts, most studies deal with these materials. Most studies have dealt with the effect on the structure of small metal particles of the adsorption of various molecules and of the interaction of the deposited metal with the support.

For platinum particles with dimensions of 20 Å or less, a significant change in the radius of the first coordinations sphere, normally a decrease, has been observed. The effect is observed on different supports, such as SiO_2, Al_2O_3, and HY zeolite.[33–36] The decrease in the metal–metal interatomic distances compared with metal foil reaches 0.2 Å. The reason for this effect is not yet clear. It is suggested that it is due to a change in the electron density in the metal as a result of surface effects, for example chemisorption. In contrast to this, in a study[37] of the dependence of the structure of platinum deposited on γ-Al_2O_3 on its degree of dispersion, an increase in the length of the Pt–Pt bond by 0.14 Å compared with platinum foil was observed in the most highly dispersed particles reduced at 470 K (see Fig.5). Estimation of the coordination numbers by comparing the intensities of the peaks in the catalyst and in Pt foil made it possible to establish with an uncertainty of 20% that the coordination number for the Pt–Pt distance is 3. This indicated that in this system, nuclei of metallic clusters are produced in the form of tetrahedra of platinum ions, stabilised in aluminium atom vacancies in the γ-Al_2O_3 lattice.

It should be noted, however, that the coordination number determined by the EXAFS method is averaged over all atoms of the element being studied. It is not excluded, therefore, that some of the platinum atoms are in the monoatomic form (coordination number for the Pt–Pt distance equal to zero), while the rest are present as large particles (coordination number 9–12). This apparently explains the fact that increasing the temperature of treatment to 670 K leads to the appearance of particles in which the Pt–Pt distance is the same as in the massive metal, while the coordination number is very small and equal to 3 (Fig.5*b*).

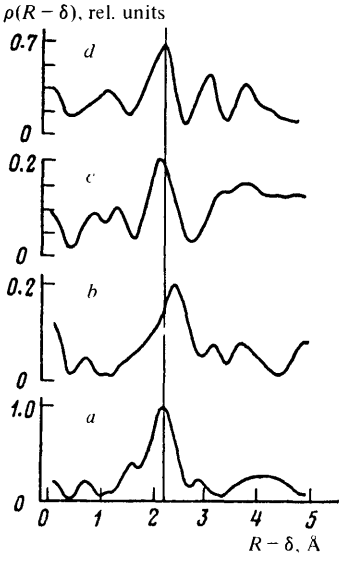


Figure 5. Radial distribution function of the atoms of metallic platinum (*a*) and catalysts with the composition 2.5 mass % Pt/Al_2O_3, reduced at 470 (*b*), 670 (*c*), and 870 (*d*) K.

A number of authors have studied the influence of the adsorption of various gases on the structure of the platinum particles. The adsorption of oxygen on highly dispersed catalysts at room temperature leads to a decrease in the Pt–Pt distance.[34–36] For catalysts deposited on γ-Al_2O_3 (particle size ~20 Å)[36] and on HY zeolite (particles 12 Å),[35] the decrease is 0.2 Å, and for catalysts deposited on SiO_2 (20 Å) it is 0.12 Å.[34] The adsorption of hydrogen leads to an increase in the length of the Pt–Pt bond to the value characteristic of the massive metal.[34] The adsorption of CO does not lead to a change in the interatomic distances.[35]

The possibility of following the phase composition of deposited catalysts by the EXAFS method has been demonstrated for deposited platinum catalysts treated with oxygen at high temperatures. In addition to metallic platinum, the phases PtO,[36] β-PtO_2,[38,39] and Pt_3O_4 [40] were observed. The change in the ratio of the intensities of the peaks corresponding to the Pt–O distances in the oxide and the Pt–Pt distances in the metal was used to determine the dependence of the ratio between the phases on the method of treatment of the specimen. Reaction with oxygen gives a range of oxides whose structure is perturbed by the interaction with the carrier, and which are very difficult to reduce.

The advantages of the EXAFS method are most clearly revealed in the study of multicomponent catalysts, if it is possible to study separately the environment of the atoms of each of the chemical elements making up the active fraction of the catalyst. An analysis of the environment of the Pt and Re atoms in platinum–rhenium reforming catalysts has been carried out.[41] The study of the absorption spectra of the L_{III} level of the rhenium atoms established that when

platinum is deposited on rhenium catalysts obtained by reducing $[Re(OC_2H_5)_3]_3$ with hydrogen at 870 K, the platinum (at ratios Pt/Re = 1/3 and 2/3) is adsorbed on Re_3^{n+} trimers, reoxidizing them. This is revealed by a decrease in the Re–Re distance. On subsequent reduction of Pt, the Re–Re distance increases, but comparison of the EXAFS spectra for Re and Pt indicates that the length of the Re–Pt bond remains unchanged and that platinum is stabilised not on SiO_2 but on rhenium ions. This effect is not observed with an excess of platinum relative to rhenium.[42]

Among non-metal systems, the EXAFS method has begun to be used to study oxide[32] and sulphide W and Mo hydrodesulphurization catalysts.[43,44] When W and Mo are deposited on SiO_2 and then treated with sulphur, surface oxide sulphides are formed, leading to a marked change in the nature of the metal–metal bond.[44] The metal ions are separated into pairs, within which the distance between the atoms is shorter than in tungsten and molybdenum disulphides, and the pairs themselves are separated from one another by larger distances. The position of the promoter (nickel) in W–Ni catalysts relative to the atom of the main element, which forms W–S–Ni bonds, has also been determined.

Thus the EXAFS method has now passed through the stage of methodological development, and is beginning to produce its first results. Its further application, particularly in the study of catalyst surfaces, will undoubtedly provide fundamentally new information.

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