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Application of Photoelectron Spectroscopy in the Study of Catalysis and Adsorption

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Problems associated with the application of photoelectron spectroscopy (PES) in the study of catalysis and adsorption are examined, the physical principles of PES and the experimental technique are briefly described, and an account is given of the results of the application of the method to the study of metallic, alloy, oxide, deposited, and zeolite catalysts. It is shown that the method can be used successfully to investigate the valence and physical states and the surface concentrations of elements in catalysts, the nature of the adsorption complexes, and the mechanism of surface reactions.
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I. INTRODUCTION

Since the 1970s, X-ray photoelectron spectroscopy (XPES) has been widely used in chemical research. The method is based on the phenomenon of the photo-electric effect. The energy distribution of the inner and valence electrons of the test substance is analysed in the spectra excited by monochromatic X-rays. The practical application of the method became possible when a group of Swedish workers headed by Siegbahn developed in the middle 1950s apparatus which made possible the analysis of photoelectrons with a high resolution and sensitivity. Their studies showed that XPES is extremely sensitive to changes in the electronic structures of substances which occur on chemical reaction [1,2]. During the same years, Vilesov et al.[3] developed the practical principles of the application of ultraviolet photoelectron spectroscopy (UPES) in the study of gases. At the present time both these methods have been constructively combined and are used successfully to investigate the gaseous and solid states.

Because of the universality of the information obtained with the aid of XPES, the method has been used to solve various physical and chemical problems. During a short period, more than a thousand studies on complex and organoelemental compounds [4-8] and the electronic structures of solids [8-11] were carried out. Recently a tendency has arisen towards a more vigorous employment of XPES and UPES in the study of surface phenomena: adsorption, catalytic, corrosion, oxidation, etc. processes. In view of a number of its characteristic features, this field of application of the method appears to be the most promising.

1. The photoelectron spectra excited by X-rays record electrons leaving the specimen without loss of energy in non-elastic collisions with lattice elements. Theoretical calculations [12] and numerous experimental studies [13-15] have

shown that the depth of the surface layer from which electrons are emitted for $E_{kin} \simeq 1000$ eV in most cases does not exceed 20–30 Å. In ultraviolet or synchrotron excitation of the spectra and in the measurement of low-angle photoemission the depth of the analysed layer may be equivalent to several atomic layers[16-18].

2. The energies of the lines and the structure of the spectra of the inner levels characterise the valence state of the elements and the nature of their interaction with the immediate environment; the valence bands characterise the band structure of the solid.

3. The spectra of the inner and valence levels of adsorbates serve as a basis for the determination of the type and geometry of the adsorption bond.

4. The PES method permits a quantitative analysis of the composition of the surface and the adsorption layer.

5. The method is applicable to the study of all the elements in the Periodic System.

There are many reviews devoted to problems of the study of the surfaces of solids[19-27], including heterogeneous catalysts[22-28]. Problems of the study of adsorption on clean surfaces have been repeatedly and most fully discussed[24,27,29-37], but the majority of the reviews have been published abroad and do not deal with studies carried out recently in the USSR. Furthermore, owing to the vigorous development of this field of study, even reviews published in recent years cannot claim to give a complete survey and do not include recently published fundamentally new results, acquaintance with which would promote a rapid adoption of the method in practical catalytic research.

Within the framework of the present review, the authors have considered the results of studies on heterogeneous catalysts, as well as adsorption and catalysis by methods of photoelectron spectroscopy.

II. PHYSICAL PRINCIPLES OF THE METHOD OF PHOTOELECTRON SPECTROSCOPY

Bearing in mind that the physical principles of the PES method and the problems concerned with the interpretation of the spectra have been described in detail in a number of monographs and reviews[1,4,11,22,23,25,30], we shall confine ourselves to a very brief consideration of the main principles of the analysis of the spectra. The binding energy of an electron emitted from a conducting solid is defined by the equation

$$h\nu = E_{kin} + E_b^F + \varphi_{sp}, \qquad (1)$$

where $h\nu$ is the energy of the quantum (the emission energies of the Al $K\alpha$ and Mg $K\alpha$ lines are 1486.6 and 1254.6 eV and the energies of the He I and He II lines are 21.2 and 40.8 eV respectively), E_{kin} is the experimental kinetic energy of the electrons, E_b^F is the electron binding energy relative to the Fermi level of the material of the spectrometer, and φ_{sp} is the electron work function of the material of the spectrometer. For non-conducting specimens, the determination of E_b is complicated for two reasons: (a) an effective electrical contact with the spectrometer is absent; (b) the specimen is charged under the influence of the radiation. (The charging is taken into account using external and internal standards[38-41]; various devices have been suggested to compensate the charge[42,43].)

The determination of the change in E_b for the inner levels (chemical shifts) constitutes the main source of information about the change in the valence state of elements, the nature of the chemical bond, coordination, etc. ΔE_b is described by the formula[1,5,11,44-46]

$$\Delta E_b = \Delta E(q) + \Delta V + E_{rel}, \qquad (2)$$

where $\Delta E(q)$ is the change in bond energy caused by the change in the charge of the free ion, ΔV the change in the crystal field potential near the atom investigated, and E_{rel} the relaxation energy of the system caused by the formation of a vacancy at an inner level. The second and third terms of Eqn. (2) in general have the opposite sign to the first term. Allowance for only the first term in Eqn. (2) leads to larger calculated shifts compared with experimental values[1,5,11,44,45]. At the same time there is a correlation between the effective charge on the ion in the compounds and E_b.[5,8]

The chemical shift in the spectra of adsorbed molecules is defined by the expression

$$\Delta E = E_{ads} - E_{gas} = \Delta E_b + \varphi_{sp} + \Delta E_{rel}, \qquad (3)$$

where ΔE and ΔE_{rel} are the overall change in the energy of the level and the change in relaxation energy when the molecule passes from the gas phase to the adsorbed state (the "interatomic" relaxation is of decisive importance in chemisorption[46]).

The following method for separating the chemical and relaxation shifts in the spectra of adsorbed molecules has now been adopted. It is suggested that the changes in relaxation energy for non-bonding orbitals, bonding orbitals, and the inner levels are approximately equal. ΔE_{rel} can be determined by studying the physical adsorption of condensation of molecules on inert carriers.

The spectra of the inner levels frequently consist of a set of lines and not singlets, which is due to the multiplet splitting of the inner levels[5,8,47-49], the emission of Auger electrons[1,5,11], and many-electron processes[5,8,48,50-59], arising owing to the instability of the photoionised state of the atom. The mechanism of the formation of satellite lines owing to many-electron processes has not been fully elucidated. Some workers attribute their appearance to the intra-atomic transitions from the valence band to the conduction band[50-53] or to monopole transitions with charge transfer[54-56]. According to other workers, the satellites arise owing to the interaction of the emitted and outer unpaired electrons, leading to the inversion of the spin of the latter[57,58]. The parameters of the satellite structure change when the valence state[54-56], the spin density[57,58], the coordination of the atom[54-56], etc. are altered.

The intensity of the peak in the photoelectron spectrum is described by the formula[1,5,8,60]

$$I_i = FGS_i\sigma_i \lambda_i(E_i)\, N_i, \qquad (4)$$

where F is the intensity of the photo flux, G the fraction of the overall electron flux measured by the spectrometer (it depends on the geometry of the specimen), S_i the sensitivity of the analyser and the detector, σ_i the atomic photoionisation cross-section of the ith level, $\lambda_i(E_i)$ the average path traversed by electrons (with $E_{kin} = E_i$) without undergoing non-elastic collisions in the specimen, and N_i the number of electrons emitted from the ith level of the element investigated. In practice, when the concentrations of elements are determined, one measures the relative intensities[1,5,8,12,61-64]. For two elements, the intensity ratio can be expressed thus:

$$I_1/I_2 = T_{1,2}\frac{\sigma_1}{\sigma_2}\frac{N_1}{N_2}, \qquad T_{1,2} = \frac{S_1(E_1)\cdot\lambda_1(E_1)}{S_2(E_2)\cdot\lambda_2(E_2)}. \qquad (5)$$

There are now fairly reliable calculated and experimental data for σ_i[61-64] and λ_i[13-15,36,60]; the problem of the quantitative analysis of "thick" homogeneous specimens is

therefore solved successfully. However, analysis of heterogeneous systems requires allowance for many additional factors (see Section III).

Studies on the angular distribution of photoelectrons [16, 17, 32, 33, 65, 66], which it is hoped will increase the surface sensitivity of PES and will make possible the investigation of the geometry of adsorption bonds, have begun recently.

Table 1 presents certain parameters of standard and modernised commercial spectrometers, which illustrate the technical scope of the PES method [87]. Certain types of unique laboratory apparatus have additional possibilities: additional monochromatisation of the X-rays makes it possible to obtain the line width (~ 0.2 eV) [68]; the employment of a synchrotron as the source of radiation makes it possible to alter continuously the energy of the quanta from 5 to 450 eV and to investigate systematically the dependence of the intensity on $h\nu$. [18] Table 1 shows that the analytical possibilities of XPES are small; however, when surfaces are investigated, this method is irreplacable. The employment of combined apparatus, involving several methods (UEPS–AES–LEED, XPES–APES–UPES, and UPES–SIMS–LEED†) has incontrovertible advantages in combined studies of surfaces, but the intrinsic possibilities of each method are then restricted.

Table 1. Parameters of electronic spectrometers*.

Name of firm and instrument	Limiting resolution on X-ray excitation, eV	Sources of excitation of spectra	Limiting sensitivity w.r.t. Au(4f) line, counts s^{-1}	Limiting vacuum, mmHg	Devices for treatment of specimens
Hewlett-Packard, HP 5950 A	0.5	AlK_α, MgK_α, AlK_α monochr.	10^5	10^{-8}	treatment camera, ion gun,
Vacuum Generators, ESCA-3 MK II	0.9	AlK_α, MgK_α, He I, He II, electron flux	10^5	$5\cdot10^{-11}$	ditto
A. E. I. ES-300	0.5	AlK_α, MgK_α, He I, He II AlK_α monochr. electron flux	10^5	10^{-10}	»
Physical Electronics, SAM/ESCA-549	0.9	AlK_α, MgK_α	—	10^{-10}	»
McPherson, ESCA-36	0.9	ditto	—	10^{-10}	»

*The average sensitivity with respect to elements is 0.1–1.0 wt.%; the minimum amount of adsorbate on the surface is 0.05–0.1 of a monolayer.

The method of preparation of the catalyst specimens and their treatment and the procedures used in the measurement of the spectra have been examined in a number of reviews [23, 25, 26]. One should note that the most effective elimination of impurities from the surface and dehydration are achieved when the catalysts are treated *in situ*. After the reaction the catalyst studied must be transferred to the spectrometer without any external influences on the specimen. Unfortunately these self-evident requirements were not fulfilled in all experimental studies.

†AES = Auger-electron spectroscopy, LEED = low-energy electron diffraction, and SIMS = secondary ion mass spectrometry.

III. RESULTS OF THE STUDY OF CATALYSIS AND ADSORPTION BY PHOTOELECTRON SPECTROSCOPY

1. Metals and Alloys

It has been shown [9–11, 69–79] that the stretching vibration band spectra reproduce fairly effectively the principal characteristics of the distribution of the density of the states of valence electrons in metals and alloys. Studies on many transition (Mn, Fe, Co, Ni, Cu) and noble (Ag, Pd, Au, Rh, Ir, and Pt) metals and their alloys [11, 69, 72] led to the conclusion that the *d*-states of both components in non-ordered binary alloys to a large extent retain the localisation characteristic of the pure metal; when an alloy is formed, the inner levels of the metals undergo only a slight perturbation [11]. Studies have been made recently to investigate the band structure of metals and alloys, using monochromatised sources of X-rays and UPE spectroscopy [11, 76, 77, 79].

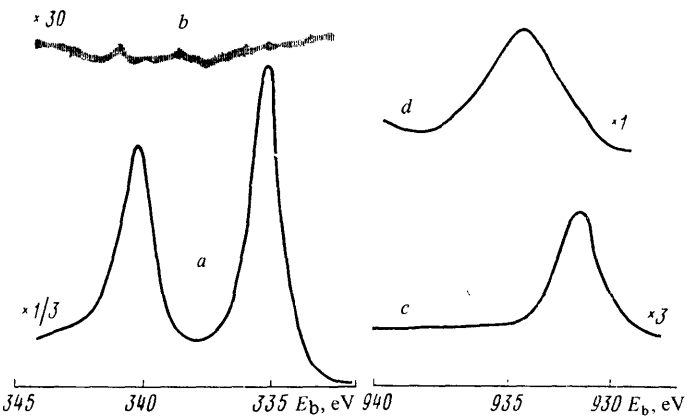


Figure 1. The surface composition of Pd–Cu alloys (40 wt.% Cu) [82]: *a*) and *c*) Pd($3d_{5/2}$) and Cu($2p_{3/2}$) spectra after reducing the specimens with hydrogen at 500°C; *b*) and *d*) Pd($3d_{5/2}$) and Cu($2p_{3/2}$) spectra after treating the alloys in air at 450°C. The numbers against the curves indicate the spectrometer amplification factors.

The composition of the surface layer of alloys in many instances differs from the bulk-phase composition: on treatment with hydrogen, the surfaces of Pt–Sn, Pt_3–Sn, [80] Ni–Al, [81] and Pd–Al [82] alloys become enriched in the second component. On treatment of the Pd–Cu (40 wt.% Cu) alloy with hydrogen at 400°C, the surface concentration of copper also increases (Fig. 1) [82]. The most marked changes in the surface layer occur in the oxidative regeneration of Pd–Cu catalysts. The spectra show that the surface layer is coated by a CuO film whose thickness exceeds 50 Å according to approximate calculations [82]. By employing synchrotron radiation or Auger electron spectroscopy, it is possible to analyse the composition of alloys in depth, starting from a monolayer and continuing up to several tens of atomic layers [80, 83].

2. Simple Oxides

Studies devoted to oxides can be divided by convention into three groups: (1) the study of thin oxide films; (2) the study of bulky oxide specimens; (3) the study of two- and multi-component oxide catalysts. Table 2 presents the principal results of studies on oxide films and bulky oxide specimens.

Table 2. Results of the study of oxides by the PES method.

Element	Main results	Changes in spectra; method of determination	References
	Thin oxide films		
Ti	formation of monolayer oxide film observed for exposures to O_2 not less than 7–10 L*	change in the form of valence bands	84
Fe	Fe_3O_4 structure studied	ditto	85
Ni	formation of NiO demonstrated in oxidation of Ni foil	shift in the Ni($2p_{3/2}$) spectrum	86
Ni	structural differences observed in thin oxide films	position of 3d levels of Ni	87
Pt	formation of PtO and higher oxides demonstrated in oxidation of sputtered Pt	shifts in Pt(4f) spectrum	88
Pt, Au	thin films obtained by anodic oxidation investigated	shifts in spectra of 4f levels of Pt and Au	89
Mo	formation of F-centres in substoichiometric amorphous MoO_3 films demonstrated; oxygen vacancies found in surface MoO_2 layer	peak near Fermi level; O(1s) peak with E_b = 532.2 eV	90,91
Pb	formation of orthorhombic and tetragonal PbO demonstrated	Pb(4f) and O(1s) spectra	92–94
r.e.	formation of lanthanide (from Tb to Lu-) oxide films demonstrated	shifts in spectra of inner levels	95
Si	stoichiometry and structure of thermally grown SiO_2 films investigated	analysis of Si(2p), Si(2s), and O(1s) spectra	96
–	stability of oxide films in vacuum heat treatment investigated	spectra of inner levels	97
	Bulk-phase oxide specimens		
V	reduction of V_2O_5 to V_4O_9 and V_6O_{11} observed	appearance of 3d states in valence band	98
Mn	reduction of α-MnO_2 and β-MnO_2 investigated; only one oxidation state of Mn found in Mn_3O_4	changes in the spectra of the 2p level of Mn	99
Fe	the occurrence of reaction $Fe_2O_3 \xrightarrow{CO,\ 300-460^\circ C} Fe_3O_4$ demonstrated	–1.0 eV shift of Fe(2p) line	100
Co	the reaction $Co(CO_3)_2 \xrightarrow{250^\circ C,\ vacuum} Co_2O_3$ (surface layer contains only Co^{3+} ions) investigated	no satellite in Co($2p_{3/2}$) spectrum	101
Co	Co_3O_4 surface layer found to contain Co^{3+} and Co^{2+} ions	spectra of inner levels and stretching vibration bands	102
Co	Co^{2+} and Co^{3+} ions identified in Co oxides	$2p_{1/2}$ – $2p_{3/2}$ spin-orbital splitting of Co levels	103
Co	quantitative determination of degree of reduction of Co in $Co_2O_3 \rightarrow Co_3O_4 \rightarrow CoO$ transitions	intensity ratio $I_{cat}/[I_{cat} + I_{Co}.(2p_{3/2})]$	104
Ni	formation of Ni_2O_3 on Ni and NiO surfaces observed	the shift of Ni($2p_{3/2}$) level is + 1.5 eV in the transition $Ni^{2+} \rightarrow Ni^{3+}$	54
Ni	the formation of Ni–O_{ads} and NiO–O_{ads} on bombardment with O_2^+ ions demonstrated	Ni($2p_{3/2}$) and O(1s) spectra	54,105
Cu	$CuO \rightarrow Cu_2O \rightarrow Cu$ reduction investigated	satellite disappears from Cu($2p_{3/2}$) spectrum in the $Cu^{2+} \rightarrow Cu^+$ transition	55, 106–108
Ag	$Ag \rightarrow Ag_2O \rightarrow AgO$ oxidation investigated	negative shift observed in Ag(3d) spectrum	109
Pb	Pb in two oxidation states not detected in Pb_3O_4	Pb(4f) spectra	110
Pb	surface composition of Pb_3O_4 found to correspond to $2PbO.PbO_2$	Pb(4f) and O(1s) spectra	92
Cr	$CrO_3 \rightarrow Cr_2O_3$ reduction observed	shift of 2p level of Cr	111
Mo	quantitative analysis of MoO_3–MoO_2 mixture	analysis of intensities in Mo(3d) and O(1s) spectra	112
Mo	reduction process $MoO_3 \xrightarrow{400^\circ C,\ H_2} Mo^{6+}, Mo^{5+}, Mo^{4+}$ observed	shifts in Mo(3d) spectra	113,114
Mo	reduction process $Mo^{6+}(MoO_3) \xrightarrow{400^\circ C,\ H_2} Mo^{n+}\ (n<4)$ observed	ditto	115
Mo	reduction process $Mo^{6+}(MoO_3) \xrightarrow{400^\circ C,\ H_2} Mo^0$ observed	"	116
Ru	RuO_2 and $RuOCO_3$ detected on the surfaces of RuO_2 and hydrated specimens respectively	analysis of Ru(3d), O(1s), and C(1s) spectra	117
W	$WO_3 \rightarrow WO_2$ reduction observed	analysis of W(4f) spectra	118,119
Re	surfaces of the oxides Re_2O_7, ReO_3, and ReO_2 investigated	analysis of Re(4f) spectra	120
Re	distribution of the density of states in the valence band of ReO_3 investigated	analysis of valence band	121
Al	differences observed in the energies of levels of different modifications of aluminium oxide and hydroxide	analysis of Al(2p) and O(1s) spectra	122
Al	correlation found between E_b for 2p level of Al and Al–O distance in aluminosilicates	analysis of Al(2p) spectra	123
–	correlation established between E_b for O(1s) and 1/r for M–O bond in 50 oxides	analysis of O(1s) spectrum	124,125
Co, Ni	decrease of E_b for O(1s) with increasing oxidation state of the cation in oxides observed	analysis of O(1s) spectra	126
Fe, Zn	three types of oxygen observed in oxide minerals	analysis of O(1s) spectra	127
–	dependence of shifts of inner levels of metals on the nature of their bond with oxygen in oxides investigated	analysis of O(1s)spectra and inner levels of metals	47

*1 L (1 Langmuir) = 10^{-6} mmHg s^{-1}.

Generalising the experimental data, one may conclude that the most significant information has been obtained about the state of transition metals in the surface layer of oxides. Further studies are probably required to identify the different forms of surface oxygen, using methods sensitive to the nature of the surface oxygen, such as, for example, EPR, optical spectroscopy, etc.

3. Complex Oxides

Regions of homogeneity (solid solutions or chemical compounds) and heterogeneity are as a rule present in two-component variable-composition oxide catalysts. The study of the state of the components in such catalysts and the estimation of surface concentrations are therefore of considerable interest. Quantitative analysis of CuO–MgO, CoO–MgO, CuO–ZnO, and CoO–ZnO systems has been carried out [128,129]. It follows from Fig. 2*a* that in the region of solid solutions in the CuO–MgO system, there is a linear relation between the intensity ratio and the atomic ratio of the components in the bulk of the catalyst. The agreement between the slopes of the experimental and calibration (not shown in Fig. 2) lines indicates the similarity of the surface and bulk-phase compositions [128]. On passing to the heterophase system, the straight line shows a break. Enrichment of the surface in the region of solid solutions has not been observed for CoO–MgO specimens, whereas in CoO–ZnO the surface concentration of cobalt is somewhat higher than the bulk-phase value. No changes in the spectra of the inner levels of the metals after the alteration of the concentrations of the components have been observed [128,129]. It has also been noted [130] that the E_b for the $2p_{3/2}$ levels of cobalt, copper and nickel in

the $M_xMg_{1-x}O$ systems do not change, but the ratio of the intensities of the satellite and the peak and the half-widths of the Co^{2+} and Cu^{2+} levels in the catalyst are smaller than in CoO and CuO respectively. In contrast to the above studies, an increase of E_b for the $2p_{3/2}$ level of cobalt by 0.5–0.6 eV has been observed [131] at the 11.3% CoO–MgO concentration, which was accompanied, according to magnetic susceptibility measurements, by an increase of the magnetic moment of cobalt ions. The authors believe that this is caused by the absorption of oxygen in a paramagnetic form, which results in electron transfer from Co^{2+} to O_2.

In $Li_xNi_{1-x}O$ catalysts ($0 \leq x \leq 0.3$) the addition of lithium leads only to a change in the profile of the Ni($2p_{3/2}$) and O($1s$) lines [132]. More significant changes in the spectra were observed for NiO–Al_2O_3 specimens (Fig. 2*b*). In catalysts with a high NiO content (97.5 and 95%) E_b for Ni($2p_{3/2}$) is close to the value observed in NiO. However, the shoulder in the spectrum characterising the multiplet splitting is absent for these specimens. With decrease of the NiO concentration to 40 mole %, E_b increases by 1.6 eV and becomes close to the value for the $NiAl_2O_4$ spinel. In the region of solid solutions (0–15 mole % NiO), there is a further increase of E_b, apparently characterising the increase of the effective charge of Ni ions. As in the study of Boreskov and Zhdan [128], the dependence of the line intensity ratio on concentration was obtained in the form of a broken straight line with the break point in the region of the transition to the heterophase system (Fig. 2*b*). A change in the slope of the straight line may be caused by the change in the surface concentrations of the components or the ratio of the particle sizes.

Catalysts obtained by the joint treatment of the La_2O_3–Cr_2O_3 oxides at 750°C have been investigated [133]. For the ratio $La_2O_3 : Cr_2O_3 = 3:1$, chromium is almost completely oxidised to Cr^{6+}, while for the 1 : 1 ratio approximately 50% of chromium remains in the form of Cr^{3+}. The $Mg_{1-x}Cu_x.Al_2O_4$ three-component system has been studied by a number of methods: XPES, secondary ion mass spectrometry (SIMS), EPR, and others [134]. It follows from SIMS data that, after heat treatment at 900°C in air, the system has only the spinel structure. In the spectra of specimens with a low copper content, the O($2p$) signal is split into two peaks and, with increase in the copper content, the higher energy peak remains unchanged either as regards energy or intensity, while the intensity of the lower energy peak increases and it is displaced towards lower values of E_b. The set of data obtained led to the conclusion that an increase of the copper content results in a delocalisation of the copper electrons, which is the cause of the decrease of the activity of the catalyst in the oxychlorination of ethylene.

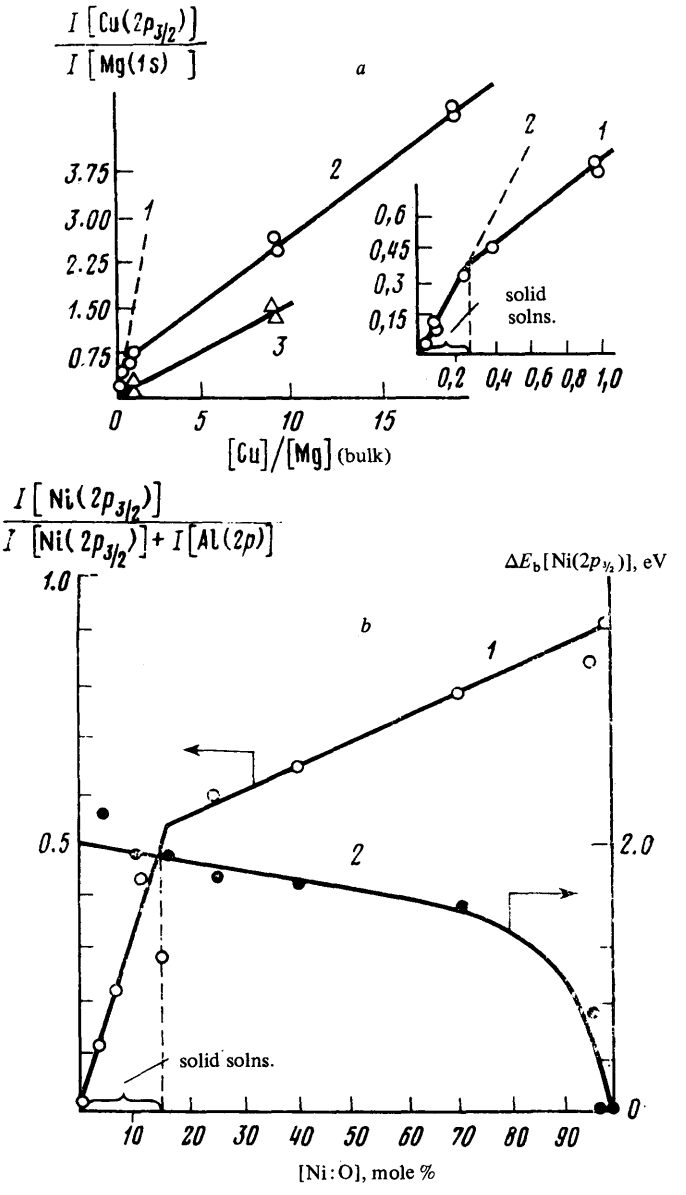


Figure 2. Dependence of the spectroscopic characteristics of the elements (the intensity ratios and the inner level bond energies) on the composition of oxide catalysts: *a*) CuO–MgO [128] [1) and 2) catalysts (curves *1* and *2* represent the solid solution and heterogeneous regions respectively); 3) mechanical mixture]; *b*) NiO–Al_2O_3 [1) dependence of the intensity ratio on composition; 2) dependence of the Ni($2p_{3/2}$) line shift (relative to the NiO line) on composition].

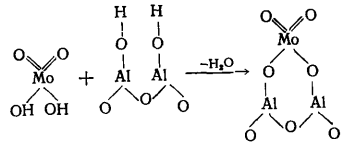
4. Deposited Catalysts

In the study of catalysis on deposited catalysts, information about the nature of the interaction of the active components with one another and with the carrier, about the surface compounds, and about the valence state and concentration of the deposited component is of significant interest for investigators. Depending on the state of the deposited component in the active form, deposited catalysts may be divided into two groups: oxides on carriers and metals on carriers.

(a) Oxides on carriers. Starting with the study of Miller et al. [135], investigators drew attention to the fact that the spectra of deposited cations giving rise to oxides or oxide compounds after heat treatment differ from those of the cations in the corresponding individual compounds. The lines due to the elements in the spectra of catalysts are appreciably broadened and in certain cases chemical shifts are also observed. The magnitude of the observed

effects depends on the type of cation and carrier and the method of preparation and treatment of the specimen. The usual scheme followed in the study of such catalysts therefore involves a comparison of the spectra of the catalysts, after various types of treatment or catalysis, with the spectra of the individual oxides, and with those of the postulated bulk-phase analogues of the surface phases and the estimation of the relative surface concentrations.

The most important results were obtained in a study of molybdenum catalysts, which have practical importance. These include in the first place data obtained in the investigation of the alumina–cobalt–molybdenum catalyst for the elimination of sulphur from petroleum, the binary deposited Co/Al_2O_3 and MoO_3/Al_2O_3 catalysts, and the non-deposited cobalt and molybdenum sulphide catalysts, which to some extent simulate the structure of the Co–Mo–Al_2O_3 surface layer, after various types of treatment, or the hydrodesulphurisation reaction in hydrocarbons. In a study of MoO_3/Al_2O_3 Miller et al.[135] observed for the first time a broadening of the Mo(3*d*) line, which was attributed to a donor–acceptor interaction of MoO_3 with the carrier. Other workers reached the same conclusion[114,115,136]. When (3% MoO_3)/Al_2O_3 was reduced, Mo^{6+}, Mo^{5+}, and Mo^{4+} ions were detected[114], oxidation in air resulting in a decrease in the concentration of Mo^{5+} ions, while that of Mo^{4+} ions remained unchanged. The reduction of Mo^{6+} ions in MoO_3/Al_2O_3 proceeds with much more difficulty than in the MoO_3/SiO_2 catalyst owing to the stronger interaction of molybdenum with Al_2O_3. The intense interaction of molybdenum with the carrier persists also in the ternary system[115,136–138]. This is indicated particularly by the finding that the reduction of MoO_3 at 400–500°C in hydrogen leads to the formation of metallic molybdenum, while only Mo^{5+} and Mo^{4+} ions are formed in the Co–Mo–Al_2O_3 system[115,136,138], and, even after prolonged treatment in hydrogen[138] at 500°C, approximately 25% Mo^{6+} remains unreduced. A study of the reduction kinetics showed[138] that Mo^{5+} ions behave as intermediate species in the $Mo^{6+} \rightarrow Mo^{4+}$ transition; the Mo^{5+} concentration on the surface exceeded by a factor of 5 that observed by EPR. The similarity of the Mo(3*d*) bond energies in Co–Mo–Al_2O_3, $Al_2(MoO_4)_3$, and MoO_3 precludes a conclusion in favour or against the formation of aluminium molybdate on the surface. It is noteworthy that XPES data do not appear to conflict with the reaction mechanism adopted in the literature[138].



The Co($2p_{3/2}$) signals in the Co/Al_2O_3 and Co–Mo–Al_2O_3 catalysts are similar in both the initial specimens and after heat treatment at 600°C and apparently correspond to Co^{2+} ions[136,138,139]. We may note that the peaks with E_b = 781.4 and 780.5 eV for Co($2p_{3/2}$) were assigned to cobalt in Co_2AlO_4 and CoO respectively, while the satellite peak with E_b = 784.9 eV was erroneously assigned to Co^{2+} ions coordinated to H_2O molecules. The decrease of the spin–orbit splitting of the $2p_{1/2}$ and $2p_{3/2}$ cobalt sublevels[103] after the heat treatment of (5–10% Co)/Al_2O_3 led to the hypothesis that the cobalt on the surface exists in the tervalent state, although X-ray diffraction revealed the presence of the $CoAl_2O_4$ phase. Analysis of the satellite structure of the spectra of the variable-composition Co–Mo–Al_2O_3 system[140] (0.5–0.6% Co, 2–10% Mo) led to the conclusion that at low concentrations the tetrahedral centres in Al_2O_3 are occupied solely by Co^{2+} ions, while after the formation of the monolayer the Co_3O_4 phase appears. Although, in view of some discrepancy between the results, one cannot postulate an unambiguous form of the surface compound of cobalt and alumina, it is evident that such a complex exists. This is also indicated by the difficulty of reducing Co^{2+} by hydrogen in deposited catalysts.

The problem of the interaction of cobalt and molybdenum in the cobalt–molybdenum–alumina catalyst is no less complex. The authors[141] believe that, with increase of the cobalt concentration to 1% (to give a ratio Mo : Co $\leq$ 4), a phase designated as Mo_4Co is formed on the surface. When the ternary system is heat-treated in air at 600°C, the ratios of the integral intensities of the Co and Al, Mo and Al, and Co and Mo pairs of signals change, which indicates an enrichment of the surface in molybdenum ions and a decrease of the surface concentration of cobalt ions[136]. Reduction of the specimen leads to the opposite effect[115,136]. A smaller cobalt and molybdenum signal intensity ratio in Co–Mo–Al_2O_3 compared with CoO/Al_2O_3 for the same bulk-phase CoO concentrations may be attributed to the fact that cobalt ions are located in deeper layers of the catalyst than molybdenum ions[115,136]. Thus the different conditions for the reduction of cobalt and molybdenum ions and the variation of their surface concentrations when different types of treatment are employed, as well as the differences between the energies in the $CoMoO_4$ and Co–Mo–Al_2O_3 spectra, show that cobalt and molybdenum interact mainly on the carrier. At the same time, according to some data, molybdenum ions prevent the penetration of cobalt ions into the lattice and the formation of a phase resembling a bulk-phase spinel[136].

It has been found that the state of cobalt and molybdenum changes significantly in the interaction of the catalyst with model mixtures: thiophen–H_2,[138,142] H_2S–H_2,[138,139] and CS_2–H_2.[143] A general conclusion arrived at in these studies is that cobalt and molybdenum are vigorously, although not completely, converted into sulphides. As regards the identification of the surface sulphides, reliable data on E_b for the electrons of cobalt and molybdenum in sulphides of different composition are necessary. It has been found[143–145] that in contrast to the oxides MoO_2 and MoO_3 the transition from the lowest to the highest molybdenum sulphide entails a negative shift of the Mo(3*d*) line. Furthermore, two S($2p$) components (with an intensity ratio of 1 : 2), having E_b = 162.9 (S^0) and 161.8 eV (S^{2-}) were observed in MoO_3. This shows that MoS_3 is formed by the association of subcrystalline MoS_2 and amorphous sulphur. A similar conclusion was reached in another study, where Co–Mo–Al_2O_3 deposited catalysts were investigated. Reliable information[146,147] for the Co–S systems was not obtained in the above investigations, because specimens with low cobalt contents were studied [Co/(Co + Mo) < 0.1].

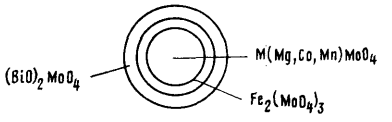
The NiO–WO_3–Al_2O_3 catalyst, which is an analogue of the cobalt–molybdenum–alumina catalyst, has been studied in detail[148]. In the oxide form of the specimen nickel is present as Ni_2O_3 and $NiAl_2O_4$, while W forms a stable complex with γ-Al_2O_3. Nickel is comparatively readily reduced in H_2 to zerovalent nickel, while tungsten remains in the form of W^{6+}. Treatment with thiophen–H_2 and particularly H_2S–H_2 mixtures leads to the formation of sulphides: WS_2 and Ni_3S_2 and NiS. Since the ratio of the nickel and aluminium signal intensities increases under these conditions, it is suggested that nickel sulphides are

dispersed on the alumina surface and possibly on the surface of WS_2. We may note that, in contrast to $Co-MoO_3-Al_2O_3$, the $NiO-WO_3-Al_2O_3$ system is almost completely converted into sulphides under these conditions.

Thus XPES yielded information about the state and distribution of molybdenum and cobalt (or nickel and tungsten) ions in the structures of oxide and reduced catalysts and catalysts converted into sulphides. The model of the sulphur-elimination catalyst put forward in a number of studies [149-151], where the ions of the active component exists in the form of a monolayer and those of the promoting agent enter the tetrahedral Al_2O_3 centres, is in general confirmed by these results. At the same time, no evidence has been obtained for the presence of Mo^{3+} (W^{3+}), which are believed [149] to enter into the composition of the active centre, and no data supporting the formation of so-called "incorporated" structure have been obtained [149-151].

The influence of the nature of the additives on the structure of the $V_2O_5-MoO_3$ catalyst has been studied [152,153]. In the NaH_2PO_4 concentration range between 0 and 5% the ratio of the surface concentrations [V]/[Mo] changes by a factor of 4, while the bulk-phase ratio remains constant [152]. When the oxides of various elements were added to the $V_2O_5-MoO_3$ solid solution, a change in the degree of reduction of vanadium ($V^{4+} \rightarrow V^{5+}$) and in the [V]/[Mo] (surf.) ratio was observed. After the introduction of promoting additives into the $CoMoO_4$ α-phase, the bond energies in the cobalt and molybdenum spectra change little [154]. However, when V_2O_5 was deposited on the $CoMoO_4 + MoO_3$ surface using the layer-by-layer method, then the values of E_b for the $Co(2p_{3/2})$ level (+0.6 eV) of [Co]/[Mo] (surf.) increased with the concentration of the additive [154]. This is due to the formation of a $V_2O_5-MoO_3$ solid solution, having the same structure as $CoMoO_4$, and the increase of the charge on cobalt.

An interesting attempt at a layer-by-layer analysis of MCM catalysts (bismuth and iron molybdates with added magnesium, cobalt, and manganese) was undertaken [155]. The iron signal was not detected in the spectrum of the surface layer of the initial specimen. However, after bombardment with Ar^+ ions the surface was depleted in molybdenum and bismuth ions [under certain conditions, the intense $Bi(4f_{7/2})$ peak fully disappeared], whereupon the $Fe(2p_{3/2})$ signal appeared and its intensity increased. On the basis of these results, the following three-layer model was proposed for MCM catalysts:



It is not clear whether the possibility of the migration of the components on the surface during the bombardment with Ar^+ has been taken into account in the above study. The interaction of Bi_2MoO_6 with H_2 led to the reduction of Mo^{6+} to Mo^{4+} [156] and the UPE spectra indicated the formation of two types of donor levels above the valence band; in the last stages of the reduction process some of the bismuth was converted into Bi^{3+}.

Among deposited metal carbonyl catalysts, the $Mo(CO)_6/\gamma-Al_2O_3$ catalyst heated *in vacuo* at 400°C was investigated; molybdenum in the $0 < n < 6$ state was detected in the catalyst [157]. It has already been stated that many deposited oxides react vigorously with the Al_2O_3 surface. In addition it has been shown [158] that heat treatment of catalysts containing zinc and nickel nitrates on the $\gamma-Al_2O_3$ surface leads to an increase of the binding energy in the spectra of the metals by 1 eV relative to the oxides and to a decrease of the $Al(2p)$ binding energy by 0.7 eV. The similarity of the E_b values in the spectra of deposited cations and the corresponding aluminates led to the hypothesis that the latter are formed on the surface of the carrier. A similar conclusion was reached for CuO/Al_2O_3 [159] and WO_3/Al_2O_3. [160] It is believed [103] that the strength of the interaction of CoO with the carrier increases in the sequence $SiO_2 < \gamma-Al_2O_3 < La_2O_3$, $LaCoO_3$ being formed in the last system.

The surface composition of alumina–chromium oxide catalysts (ACC) depends on the nature of the aluminium compound chosen as the carrier [161]. The ratios of the intensities of the $Cr(2p)$ and $Al(2s)$ lines for the catalysts obtained by impregnating bayerite, boehmite, and $\gamma-Al_2O_3$ with the same amount of CrO_3 and heat-treated at 700°C are similar, while the ratio for hydrargillite is higher by a factor of 2. With certain assumptions, the ratio $I(Cr)/I[(Cr) + (Al)]$ may serve as a measure of the specific surface of Cr_2O_3 in ACC. [161] The state of the chromium ions in ACC depends on the chromium content [162]: at low concentrations Cr^{6+} ions were detected in the heat-treated specimens, and, as the chromium concentration increased, the Cr^{3+} phase appeared. The change in the splittings of the $Cr(2p_{1/2})$ and $Cr(2p_{3/2})$ lines and their shift (−1.7 eV) relative to the Cr^{6+} spectrum show that almost the entire chromium is reduced under mild conditions to Cr^{5+}. In the above study and elsewhere [112,163] attention was drawn to the possibility of the photochemical reduction of Cr^{6+} on the surface of carriers. Data [113,164] for the change in the surface composition of CrO_3/SiO_2 catalysts conflict with one another. A sharp decrease in the ratio of the $Cr(2p)$ and $Si(2p)$ signal intensities has been observed [112] as a function of the heat treatment temperature and was explained by the agglomeration of chromium into large Cr_2O_3 particles. On the other hand, the sharp increase of the Cr and Si signal intensity ratio was attributed to the formation of a dispersed $\alpha-Cr_2O_3$ phase on the SiO_2 surface [164]. According to our data, the ratio of the $Cr(2p_{3/2})$ and $Si(2s)$ signal intensities in the non-heat-treated (5% CrO_3)/SiO_2 specimen is higher by a factor of 2 than in the specimen heat-treated at 550°C. In addition, it has been shown [164] that the reduction of CrO_3/SiO_2 to cobalt *in situ* leads to a negative shift of the $Cr(2p_{3/2})$ line by 0.7 eV, which can be explained by the formation of Cr^{2+}. An AlF_3 surface complex on $\gamma-Al_2O$ has been observed [165]. This result as well as data for the interaction of HF with alumina [166] may be of interest for the study of catalysts in which the carrier is fluorinated Al_2O_3.

(b) Deposited metal and "grafted" catalysts. The principal trend in the application of the method to these systems involves the study of the interaction of metal clusters with the carrier, of the degree of reduction of metals, and of the nature of their distribution on the surface. As an example, Fig. 3 presents certain data for the Re/SiO_2 and $Re/\gamma-Al_2O_3$ catalysts [120]. The spectra of the catalysts obtained by impregnating $\gamma-Al_2O_3$ with NH_4ReO_4 and $HReO_4$ solutions differ greatly from those of Re_2O_7 or NH_4ReO_4. An appreciable broadening of the $Re(4f)$ lines and a positive shift are observed for the catalyst. To a lesser extent, this is also seen for the Re/SiO_4 specimens. The reduction of the catalysts in a stream of H_2 at 500°C leads to the appearance of a spectrum which also differs from that of the compact metal. We may note that, according to the results of chemical analysis, rhenium is almost completely reduced to the

zerovalent state. The positive shift in the Re($4f_{7/2}$) spectrum relative to the Re^0 spectrum changes as a function of the type of compound used for impregnation: $KReO_4$(0) < NH_4ReO_4 (0.3 eV) < $HReO_4$ (0.5 eV) < $Ba(ReO_4)_2$ (1.1 eV). The main effect for all the Re/SiO_2 specimens consists in a broadening of the lines. The differences between the spectra of the deposited and compact metal are apparently due to the donor–acceptor interaction between the highly dispersed rhenium particles and the carrier. The broadening of the lines may indicate an energetic inhomogeneity of the rhenium atoms on the surface.

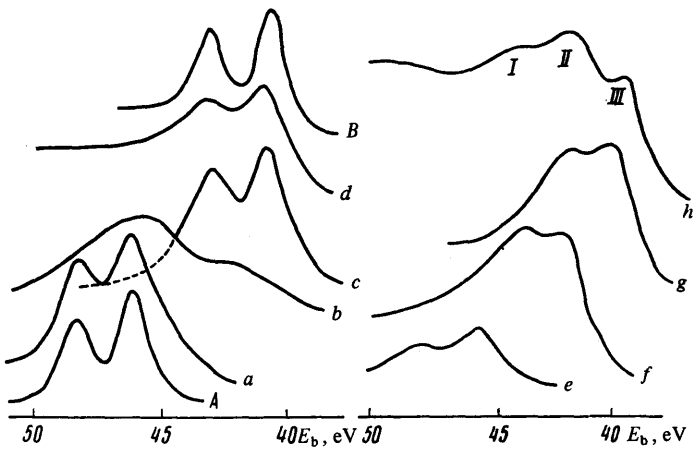


Figure 3. Re($4f$) photoelectron spectra of deposited Re/γ-Al_2O_3 and Re/SiO_2 catalysts [120]: *a*) initial Re/SiO_2; *b*) Re/SiO_2, 300°C, H_2, 10 mmHg; *d*) Re/SiO_2, 200°C, $C_6H_6 + H_2$, 30 atm; *e*) initial Re/γ-Al_2O_3; *f*) Re/γ-Al_2O_3, 500°C, H_2, 10 mmHg; *g*) Re/γ-Al_2O_3, 650°C, H_2, 10 mmHg; *h*) Re/γ-Al_2O_3, 200°C, $C_6H_6 + H_2$, 300 atm; A = NH_4ReO_4; B = Re(metal), 480°C, H_2, 10 mmHg. The I, II doublet characterises Re^{n+} (n = 3 or 4) and the II, III doublet characterises Re^0.

The differences between the spectroscopic characteristics of the deposited and bulk-phase metals have been pointed out in a number of studies: for Ir [167–169], Pt, [170–173] Pt–Ge, [173] Pt–(Mo, W, Re), [174–176] W, [178] Rh, [179] and Pd. [45] The chemical shift of the Ir($4f$) line [169] relative to Ir^0 changes as a function of the nature of the carrier: ZnO (0.3 eV) < SiO_2 (0.9 eV) < α-Al_2O_3 (1.0 eV) < TiO_2 (1.2 eV) < δ-Al_2O_3 (1.8 eV) ≤ aluminosilicate. The appearance of the shift is caused, according to the authors [169], by the equalisation of the positions of the Fermi level on the surfaces of different oxides. The broadening of the Pt($4f$) line and the appearance of an additional peak near the Fermi level has been interpreted [170] as a consequence of the interaction of Pt clusters (whose size is d = 12–20 Å) with silica gel. Similarly, a broadening of the Pd($3d$) line and a small positive shift relative to the Pd^0 spectrum have been observed for Pd/Al_2O_3. [45] In addition there is a decrease of the density of states in the vicinity of the Fermi level. Calculation with the aid of the extended Hückel method showed that the interaction of the palladium atom with the γ-Al_2O_3 surface may lead to similar changes in the spectra. According to an alternative explanation, the effects observed in the spectra of deposited metals are due to the anomalous electronic properties of the metallic clusters. The most interesting attempt to follow the changes in the spectrum in the valence region for different surface coverages by metal atoms was undertaken by Mason and coworkers [171,180] and Hamilton [181]. For low surface coverages of graphite by silver, the spectra of the valence bands show that the sp band of silver atoms is unfilled and that there is a small peak with $\Delta E\Phi = -2$ eV. Calculation by the CNDO method showed that such states are characteristic of Ag_1–Ag_4/C_{16} clusters [180]. With increase of the degree of surface coverage, the spectrum characteristic of metallic silver gradually appears.

The nature of the clusters and their interaction with carriers can in principle be inferred from XPE spectra. However, it is first necessary to solve a number of complex problems: (1) one must find a method of separating chemical relaxation shifts and shifts caused by the matrix effect. The difficulty is that the charging of the inhomogeneous surface of the specimen can also cause a broadening and distortion of the lines. More direct results can be obtained by studying the UPE and XPE spectra of the valence bands. (2) One must find a method of isolating the components responsible for the alteration of the electronic properties of the clusters and for the interaction with the support. For this purpose, it is necessary to study the clusters on inert carriers and to compare the experimental data with calculation. In view of the foregoing, studies on "grafted" catalysts, particularly on organic carriers, on which it is possible to obtain clusters with rigorously specified dimensions, appear promising. At the present time there have been few investigations, in which only metals grafted via π-allyl complexes to the silica gel surface were investigated [174–178]. In the presence of low-valence molybdenum, tungsten, and rhenium ions, the electron density of platinum diminishes [174–178]. The enhancement of the interaction of tungsten grafted to the SiO_2 surface relative to the standard specimen obtained by impregnation is indicated by the results of Shul'ga et al. [178]

It has been suggested [172] that, after the impregnation of alumina with H_2PtCl_6 and reduction, some of the platinum atoms are coordinated to chloride ions and Al_2O_3, i.e. are formally in the quadrivalent state. The state of a rhodium complex deposited on a polymer has been characterised [182]: E_b for Rh($3d$) in the catalyst was close to the value for the initial complex $RhCl_2[P(o\text{-tolyl})_3]_2$. A change in the valence state of rhodium was not observed after prolonged exposure of the specimen to air. After treating SiO_2 with hydrogen at 800°C in the presence of metals (Ni, Pt, Ta, and W) but without physical contact with them, the Si–OH groups were reduced to Si–H groups, which, judging from the XPES data, is due to transfer of traces of metals to the surface [183].

In a heterophase system the expression for the intensity ratio may be represented as follows [184]:

$$\frac{I_M}{I_C} = \frac{I_M^\infty}{I_C^\infty} \frac{f[1-e^{-c/\lambda_M(E_M)}]}{1-f[1-e^{-c/\lambda_M(E_M)}]}, \qquad (6)$$

where I_M^∞ and I_C^∞ are the signal intensities in the spectra of infinitely thick metal and carrier specimens, f is the fraction of the surface occupied by the metal, c the size of the metal crystallites, and λ_M the mean free path of electrons with a kinetic energy E_M. Thus, together with concentration, the surface coverage by the metal and the size

of its crystallites influence the intensity ratio. Evidently in the two extreme cases (where $c \ll \lambda$ and $c \gg \lambda$) with homogeneous coverage, a linear relation should be observed between I_M/I_C and the metal concentration. Indeed, a direct correlation has been noted[184,185] between the ratio $I(Pt)/I(Si)$ and the characteristics of the platinum surface, namely the volume of absorbed H_2 and the ratio of the number of Pt atoms, i.e. [Pt], to the specific surface of the carrier S_{sp}. For highly disperse systems (Pt/SiO_2 and Na/Al_2O_3), the composition determined with the aid of XPES is close to that of the bulk phase. For specimens with a lower degree of dispersion, a direct relation is observed only when $I(Pt)/I(Si)$ is plotted against $[Pt]/cS_{sp}$ (Fig. 4).

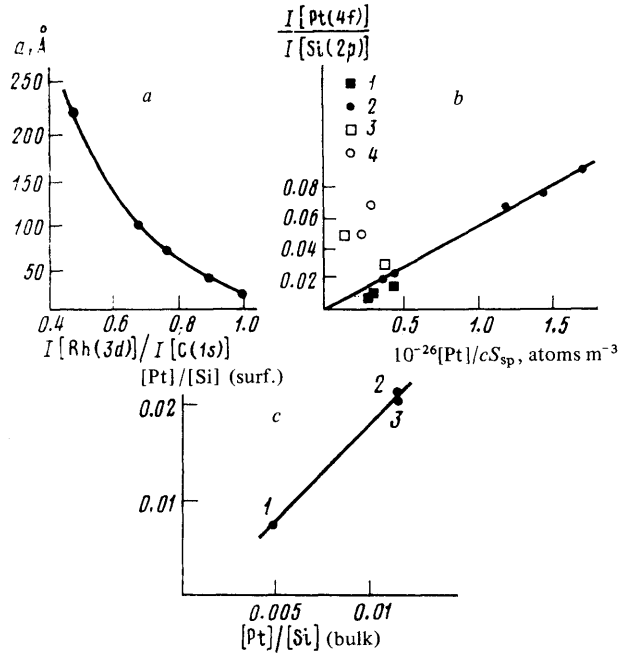


Figure 4. The influence of the particle size of the metal and of its surface concentration on the metal : carrier signal intensity ratio in the spectra of catalysts with deposited metals: *a*) dependence of the ratio $I[Rh(3d)]/I[C(1s)]$ on the particle size of Rh^0 in the catalyst [(12 wt.% Rh)/C];[186] *b*) dependence of the intensity ratio $I[Pt(4f)]/I[Si(2p)]$ on the surface concentration of platinum [see Eqn. (6)] in Pt/SiO_2 catalysts[184,185] [1) and 2) specimens prepared by ion exchange; 3) and 4) specimens prepared by impregnation]; *c*) dependence of the surface concentration of platinum {determined by analysing the $I[Pt(4f)]/I[Si(2p)]$ ratio} on the total amount of platinum in Pt/SiO_2 specimens [1) (1.2 wt.% Pt)/SiO_2, ion-exchange method; 2) (3.5 wt.% Pt)/SiO_2, ion-exchange method; 3) (3.5 wt.% Pt)/SiO_2, impregnation method].

According to the results of Shul'ga and coworkers[178], a linear relation between $I(W)/I(Si)$ and the tungsten content is characteristic both of specimens obtained by impregnation and of "grafted" catalysts. However, the increase of the slope for specimens of the latter kind indicated a higher degree of surface coverage by tungstate (higher by a factor of 20 than for the "impregnated" specimens). According to our results, the ratio [Pt]/[Si](surf.) (Fig. 4) found from the XPE spectra exceeds the average bulk-phase value. Subsequent heat treatment and reduction of the specimen led to a decrease of the ratio of the Pt and Si signal intensities. One of the causes of this is the increase in the size of the metal particles.

Similar phenomena in the spectra have been observed in other studies[120,172,173,186,187]. Thus, with increase of the size of the Rh^0 crystallites in the (12% Rh)/C catalyst from 20 to 235 Å (λ = 18 Å), the intensity ratio $I[Rh(3d)]/I[C(1s)]$ decreases by a factor of two[186] (Fig. 4). With increase in the size of the platinum crystallites from 10 to 25 Å in the (1.2% Pt)/SiO_2 ion-exchange specimens, a decrease of the Pt and Si signal intensity ratio by a factor of 1.8 was observed, and a slight decrease of the degree of dispersion of the metal (from 50 to 60 Å) in Pt/SiO_2 specimens obtained by impregnation resulted in an appreciable decrease of the intensity ratio (by a factor of 3). These data show that the change in intensities is caused not only by the change in the degree of dispersion, but also by a redistribution of the metal atoms on the surface. In consequence of the inhomogeneous distribution of the metal in the "impregnated" specimens, there is a possibility of a transition of metal atoms from pores more accessible to analysis to less accessible regions[184,185]. Clearly the ratio of the metal and carrier signal intensities may depend, other conditions being equal, on the porosity of the carrier, which has in fact been observed experimentally[188,189].

5. Zeolite Catalysts

The study of the state of elements in the surface layers of zeolites may be of considerable interest for the selection of conditions in the formation and operation of zeolite catalysts. Such information is important also because certain catalytic reactions apparently occur only in surface layers of zeolite crystals.

(a) Zeolites not containing transition metals. Fig. 5 presents the dependence of the ratio $I(Al)/I(Si)$ on the zeolite modulus obtained in a number of studies[23,190-193]. In all cases the relation is linear. However, the calculations of [Al]/[Si](surf.) carried out in these studies indicates a discrepancy between the experimental results. According to some data[23,193], within the limits of experimental accuracy and the assumptions made, the compositions of the surface and bulk-phase of A, X and Y zeolites and mordenite are similar. Systematic elimination of aluminium from the surface of zeolites of these types has been pointed out[190-192]. The ratio [Al]/[Si](surf.) increased when the zeolite structure was disrupted[197]. The lower Al and Si signal intensity ratio found by Tempere and Delafosse[190] cannot be explained by the shielding of the Al^{3+} ions by water or by other cations, because changes in these factors do not alter the intensities[196]. The discrepancies between the experimental data are probably due to the non-equivalence of the specimens used in different investigations[23,190-193]. Comparison of the Ca and Si signal intensity ratios for (NaCaA) and Na/Si(HNaY) (Fig. 5) with the degrees of exchange of the corresponding cations shows that non-transition metal ions are apparently uniformly distributed in the zeolite structure. With increase of the SiO_2/Al_2O_3 ratio, the energies of the Al lines do not change and are similar to those in

Al_2O_3, while the Si(2*p*) line shifts by 0.7 eV and the energy of the Si(2*p*) bond approaches the value observed in SiO_2.[191] These data conflict with those[123] for natural aluminosilicates where a correlation was found between the shift of the Al(2*p*) line and the average Al–O distance.

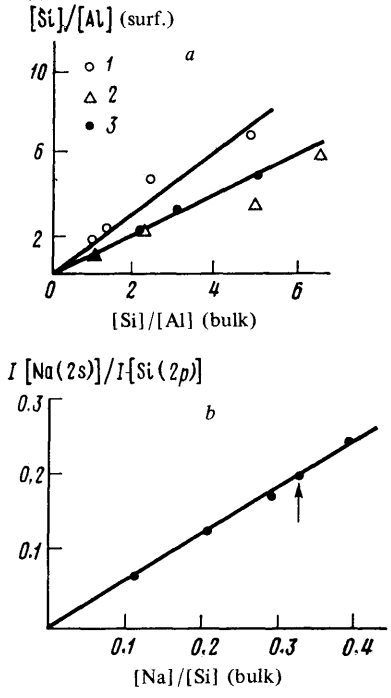


Figure 5. Composition of the surface layer of zeolites. *a*) dependence of the ratio of the numbers of silicon and aluminium atoms in the surface layers of zeolites (XPES data) on the ratio of the total numbers of these atoms in the zeolites [1) data of Temperet et al.[191]; 2) data of Finster and Lorens[193]; 3) present authors' data]; *b*) dependence of the intensity ratio $I[Na(2s)]/I[Si(2p)]$ on [Na]/[Si] in the "bulk" of partly "decationated" type Y zeolites. For the specimen marked with an arrow, [Na]/[Si](bulk) = 0.32 [Na]/[Si](surf.) = 0.39.

With increase of the degree of exchange of Na^+ for Ca^{2+} from 20 to 80%, a positive shift (0.5 eV) of the Ca(2*p*) line is observed, apparently characterising the increase of the effective charge on calcium[40]. Comparison of the positions of the Na, K, Ca, and Mg lines in the spectra of zeolites and compounds with different types of chemical bonds permits the conclusion that the cations form predominantly ionic bonds with the zeolite skeleton[23,40]. A similar conclusion was reached in other studies[194,195] for magnesium ions in MgNaX and MgNaY.

According to some data[192,196], the adsorption of pyridine on the HY zeolite at 150°C led to the reduction of surface silicon ions to the elemental state. This result is not altogether understandable from the standpoint of the thermodynamics of the reduction of silicon and apparently requires further confirmation. The adsorption of pyridine at room temperature can be used as a test for quantitative estimates of the fraction of Brønsted and Lewis acid centres[192,196]. The splitting $E[N(1s)] - E[Si(2p)]$ is 297.4 and 298.3 eV after adsorption on Lewis centres and 299.5 and 300.1 eV after adsorption on Brønsted centres[192]. A study of the adsorption of aniline on the HY zeolite was also undertaken[197].

(b) Zeolites containing transition metals. Systematic studies on individual and polycationic forms of zeolites have been made[23,40,198–205]. Since some of the results obtained have already been published in a review[200], we shall confine ourselves to an examination of certain examples.

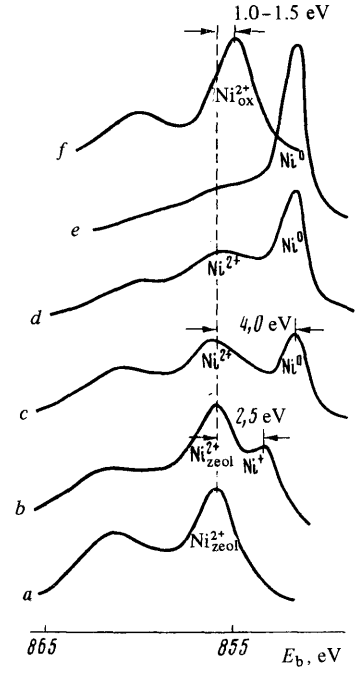


Figure 6. Variation of the valence and physical states of nickel for different methods of treatment of the NiNaY zeolite: *a*) dehydration, 400°C, air + 500°C, helium; *b*) 400°C, 10 mmHg CO; *c*) 350°C, 10 mmHg H_2; *d*) 400°C; 10 mmHg H_2; *e*) 450°C, 1 atm H_2 (the spectrum is shown in terms of a 1 : 3 scale); *f*) 450°C; H_2 + 500°C, air.

Comparison of the parameters of the spectra of Cr, Fe, Co, Ni, and Cu (the positions of the lines and of the satellite structures) in zeolites and in compounds with different types of bonds showed that the amount of ionic character of the cation–zeolite skeleton bond is close to that in fluorides or chlorides[40,203]. The capacity of cations for reduction depends on the nature of the transition metal[40,198–203], the type of structure[40,201], the degree of exchange[40,200,201], and the cationic composition[40,201–203]. As an example of the possible changes in the state of the elements in zeolites, we shall consider the spectra of Ni($2p_{3/2}$) in NiNaY, treated under different conditions (Fig. 6). Spectrum *a* is due to Ni^{2+} ions. After dehydration, the lines characterising the distribution of the ions

in regions with different crystal field symmetries are broadened somewhat. The new line in the spectrum with $\Delta E = -4$ eV, appearing after the reduction of the specimen with hydrogen, corresponds to zerovalent nickel. With increased temperature of the heat treatment in hydrogen, the degree of reduction of zerovalent nickel increases, and at high temperatures the ratio of the integral Ni and Si signal intensities increases relative to the initial value. The latter observation demonstrates the diffusion of zerovalent nickel atoms on the outer surface. On treatment in carbon monoxide, a line occupying a position intermediate between those of the Ni^{2+} and Ni^0 lines is observed. It has been attributed to the formation of the Ni^+ ion [204].

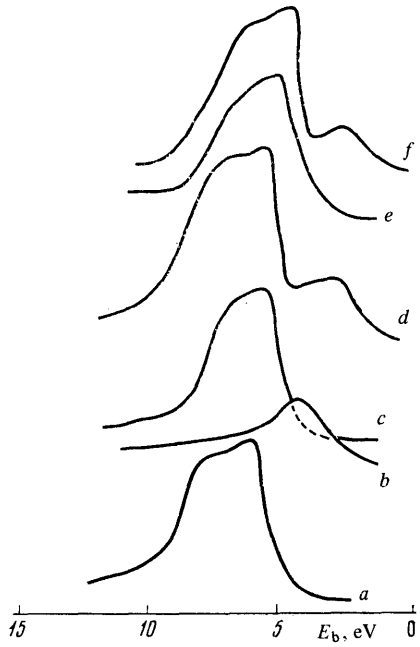


Figure 7. The interaction of metallic silver and copper in zeolites [203]; spectra: *a*) 0.14 AgNaY, 500°C, H_2; *b*) 0.26 CuNaY; 500°C, H_2; *c*) initial 0.25Ag.0.31CuNaY specimen; *d*) 0.25Ag.0.31CuNaY, 350°C, vacuum; *e*) 0.25Ag.0.31CuNaY, 500°C, H_2; *f*) result of the addition of spectra *a* and *b*.

Finally, after the oxidation of reduced Ni-zeolites, the position of the spectral line is close to that observed in the NiO spectrum [198]. This indicates the formation of the oxide phase on the outer surface. Thus XPES makes it possible to obtain information about several valence and phase states of metals in zeolites. Interesting results were obtained in the study of polycationic forms (Ag–Cu, Cu–Ni, Co–Ni, Cr–Ni) [203-205]. In all cases the capacity of cations for reduction and migration changes in relation to individual forms. This is due to the interaction of transition metals with one another. Fig. 7 illustrates the spectra of the valence bands of silver and copper in individual and polycationic forms [203]. Their comparison with one another, and also with the spectrum obtained by adding together curves *a* and *b*, shows that zerovalent silver and copper interact with one another, forming alloys on the outer surface or bimetallic clusters [202,203].

Despite the fact that quantitative analysis in zeolites containing transition metals involves a number of difficulties, one may reach certain important conclusions on the basis of the changes in signal intensities concerning the distribution of transition metals between the outer surface and the bulk of the crystals. The changes in the Cu($2p_{3/2}$), Ni($2p_{3/2}$), and Si(2*s*) lines occurring in the oxidation-reduction treatment of Ni–Cu–zeolites have been investigated [205]. After treatment with hydrogen, the increase of the Cu and Si and of the Ni and Si signal intensity ratios indicates the migration of zerovalent copper and nickel onto the outer surface, while magnetic susceptibility measurements indicate the formation of an Ni–Cu alloy [205]. Oxidative treatment of these specimens causes a decrease of the intensity ratio of the Cu and Si lines, although the absolute magnitude of the Si(2*s*) signal also diminishes by a factor of two. The decrease of the intensity of the Si(2*s*) line may be caused by the increased shielding of the surface by metals as a result of their dispersion and hence should lead to an increase of the Cu and Si signal intensity ratio. Since the opposite behaviour is observed, presumably part of the copper diffuses after oxidation to the bulk of the zeolite crystal, which has indeed been confirmed by the appearance of an EPR signal due to isolated Cu^{2+} cations [205]. As for catalysts with deposited metals, the metal distributed in the zeolite may interact with the lattice. It has been stated [206] that E_b for Pt and Pd in zerovalent palladium and platinum clusters, trapped within zeolite cavities, is greater by approximately 1.0 eV than for metallic palladium and platinum, which has been attributed to the transfer of electron density from the metal atoms to the elements of the skeleton and also by a smaller relaxation energy.

In addition, a study has been made of the reduction $Eu^{3+} \rightarrow Eu^{2+}$ in the Eu-form of the zeolite, which is accompanied by an unusually large shift of the 3*d* line of europium (–7.6 eV). [23] The photochemical reduction of nickel in nickel-containing zeolites has been observed [207]. Under the conditions adopted in the measurement of spectra [199-203], this was not observed, although such effects were noted for silver, palladium, and copper cations.

(c) Other catalysts. The surface composition of rhenium heptasulphide has been studied [208,209]: the presence of sulphur in two states (S^{2-} and S^{6+}) was noted. It was shown that the hydrogenating activity of catalysts varies as a function of the ratio of sulphate and sulphide ions. When pyrolytic graphite, with silver sputtered onto the surface of the basal planes as the catalyst, was oxidised [210], no shifts of the Ag(3*d*) lines were observed. The decrease of the intensity of the Ag(3*d*) signal was explained by the agglomeration and evaporation of (Ag). It was noted that, when WC is formed, the density of states near the Fermi level becomes close to that for platinum [211]. This explained the similarity of the catalytic properties of WC and Pt in many reactions.

6. The Surface Compositions and Catalytic Properties of Heterogeneous Catalysts

Together with direct study of the catalytic reactions by the PES method (see below), there are also other procedures for the determination of the relation between the catalytic properties of heterogeneous catalysts and the state of their surfaces.

(a) The influence of the state of the elements on the activities and selectivities of catalysts. An industrial silver catalyst for the synthesis of epoxyethane has been studied [212,213] before and after γ-irradiation. It was shown that irradiation leads to an increase of the concentration of calcium ions on the surface, which entails an increase of the activity of the catalyst. With increase of the oxide/metal ratio in Rh/C catalysts, an increase of their hydrogenating capacity was noted [214]. Comparison of XPES data obtained in the reduction of Ni-, Co-, Ni–Co, Ni–Cu-, Ni–Cr, and Cu-zeolites and the activities of the catalysts in the reactions of carbon monoxide with nitric oxide and molecular oxygen led to the conclusion that the reduction of transition metal ions to the metals entails an appreciable increase of activity [215]. The same conclusion was arrived at for the reaction of carbon monoxide with nitric oxide on NiO, Co_2O_3, and Fe_2O_3. [216] The highest activity among copper(II) oxide catalysts is shown by that containing Cu^+. After the addition of platinum, the catalytic activity of the perovskites $La_{0.7}Pb_{0.3}MnO_3$ in the oxidation of cobalt increases by a factor of 100. The increase of activity exceeds the effect expected for the homogeneous redistribution of platinum, whose activity corresponds to that of metallic platinum on Al_2O_3. XPES data show that platinum is localised in the perovskite lattice in the form of Pt^{4+}. [217]

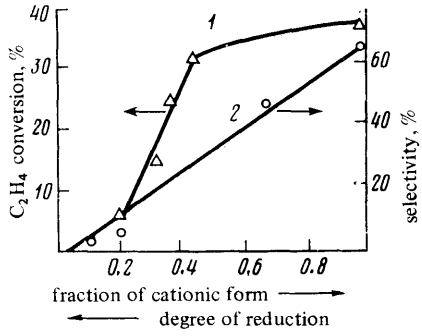


Figure 8. The influence of the state of transition elements on the activity and selectivity of zeolites in hydrocarbon conversion reactions: 1) variation of the degree of conversion of C_2H_4 on PdCaNaY [220] with the degree of reduction of palladium; 2) variation of the selectivity of NiNaY in the synthesis of s-butylbenzene with the degree of reduction of nickel [219].

Comparison of data for the catalysis of the oxidative dehydrogenation of paraffins in the presence of mixtures of nickel and tin oxides promoted by phosphorus and potassium and the results of physicochemical experiments (EPR, XPES) [218] led to the hypothesis that the lattice oxygen is involved in the reaction. The changes in the state of vanadium and of the ratio [V]/[Mo](surf.) in V_2O_5–MoO_3 catalysts promoted by Na_2HPO_4 are correlated with the changes in catalytic activity in the oxidation of furan to maleic anhydride [152]. In the case of $CoMoO_4$ modified by oxides the decisive factor determining the activity in the oxidation of propene and acrolein is the nature of the additive and not the ratio [Co]/[Mo](surf.) [155]. With increase of the fraction of Mo^{4+} bound to sulphur and oxygen in the overall amount of molybdenum in the Co–Mo–Al_2O_3 catalyst, an increase of the yield of CH_4 in the reaction involving the hydrodesulphurisation of CS_2 is observed [143].

The study of Ni- and Pd-zeolites [219,220] showed that the main factor determining the selectivity in the alkylation of benzene by ethylene to s-butylbenzene and the dimerisation of ethylene is the state of nickel and palladium respectively. In both cases cations are active in catalysis and a qualitative parallel relation between the fraction of the cationic form and the catalytic activity is observed (Fig. 8). The data examined show that in many instances a relation has been found between the state of the elements on the surface and the activity. It is also clear that, in order to obtain more far-reaching relations, additional data on the reaction mechanisms are required.

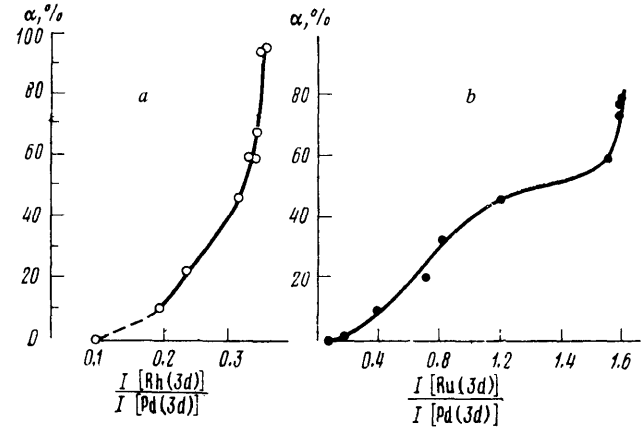


Figure 9. Correlation between the changes in the surface state of palladium alloys and their activity (α is the yield of C_6H_6) in the dehydrogenation of cyclohexane: *a*) Pd–Rh (10% Rh) [221]; *b*) Pd–Ru (10% Ru) [222].

(b) Modification of the surface of the catalysts under the influence of the reaction medium. Modification of the surface layer of catalysts in the reaction medium is characteristic of many specimens and reactions. The surface composition of binary alloys of palladium with rhodium (5 and 10%) and ruthenium (10%) changes only slightly when the catalysts are treated in H_2 and O_2. [82] At the same time the interaction of these alloys with hydrocarbons under the conditions of the dehydrogenation of cyclohexane to benzene leads to an appreciable enrichment of the surface in rhodium or ruthenium. Fig. 9 shows that there is a parallel variation of the catalytic activities of these alloys and of the surface composition [221,222]. It was shown, on the basis of these data and adsorption measurements, that the active surface is formed as a result of the segregation of the second component on the surface and the increase of the roughness of the latter [222]. A study of the initial and spent Pt–Rh catalysts for the oxidation of NH_3 showed that their deactivation is due to the segregation of rhodium on the surface

in the form of Rh_2O_3 and Rh^0, which takes place as a result of the volatilisation of oxidised platinum. The activation of the Rh/Al_2O_3 catalyst in the tricyclomerisation of ethylene was accompanied by a positive shift of the Rh(3*d*) line by 0.6–0.8 eV. This was caused by the appearance of a positive charge on rhodium as a result of its interaction with hydrocarbons. Treatment with the $C_6H_6 + H_2$ mixture leads to partial reduction of rhenium in Re/Al_2O_3 catalysts and to the appearance of catalytic activity [126] (Fig. 3). On the other hand, the reduction in ethylene of the zeolite palladium and of its reaction products deactivates the catalyst [220]. The reduction of palladium in the Pd/SiO_2 catalyst in the hydrogenation of hex-1-ene has been pointed out [224].

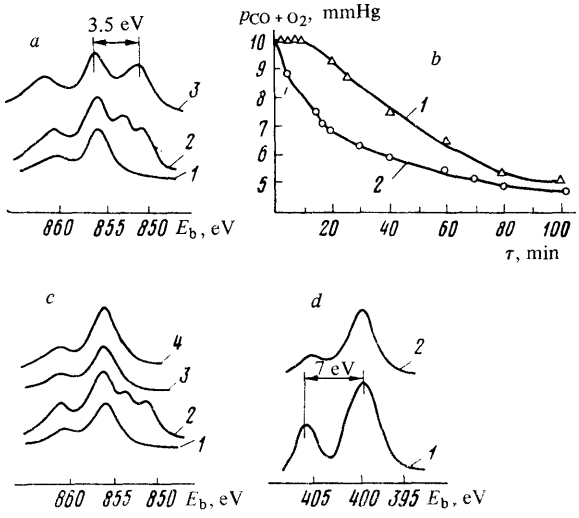


Figure 10. The influence of the state of transition elements on the catalytic activity of zeolites in the oxidation of CO by oxygen and the reduction of NO by carbon monoxide [215]: *a*) lines of Ni($2p_{3/2}$) in NiNaY [1) dehydrated specimen; 2) specimen treated with CO at 400°C; 3) specimen treated with CO + O_2 at 400°C]; *b*) kinetics of the oxidation of CO on NiNaY at 400°C [1) first experiment; 2) second and subsequent experiments]; *c*) lines of Ni($2p_{3/2}$) in CuNiNaY [1) dehydrated specimen; 2) specimen treated in CO at 400°C; 3) after subsequent treatment with NO at 400°C; 4) specimen treated in NO + CO at 400°C]; *d*) N(1*s*) lines [1) heat treatment of CuNiNaY in NO + CO at 400°C; 2) heat treatment in NO at 400°C].

Fig. 10 illustrates the changes in the XPE spectra and of the catalytic activity of NiY in the oxidation of carbon monoxide [215]. The interaction of the zeolite with the CO + O_2 mixture under the conditions of the catalysis leads to the reduction of Ni^{2+} to the metallic and possibly the univalent states. The period of the activation of the given specimen is apparently associated with this process. The concentration of Cr^{2+} in Cr/SiO_2 catalysts subjected to preliminary reduction in CO diminishes on subsequent interaction with NO at 300°C. [164] When the specimen is maintained in the NO + CO mixture, Cr^{2+} is reformed.

The activity of the complex $ReCl(NO)(Py)_2$ in the hydrogenation of pyridine or cyclohexene was four times greater than that of Re_3Cl_9. [225] According to XPES and infrared spectroscopic data, this is due to the fact that part of the rhenium in the complex retains its coordinate linkage with NO, while the surface layer of the chloride is completely reduced to zerovalent rhenium.

Thus XPES data show that changes in the surface layer under the influence of reaction medium, which may lead to both activation and deactivation of the specimens, are characteristic of catalysts of different types.

The products formed on the surface during the reactions may be investigated with the aid of XPES. The consecutive aldehyde → acid → $CO_2 + H_2O$ transformations on the selective MoO_3, MoO_2, and $CoMoO_4$ oxidation catalysts were investigated at 77–773 K. [226] The interaction of NO with CoO and NiO [227] leads to the appearance of the N(1*s*) peak, whose position indicates electron transfer from the oxide to NO. In the adsorption of nitrogen on Fe_2O_3, the Fe(3*p*) bond energy did not change, while the positive shift of the spectrum of iron in Fe_3O_4 indicated the oxidation of the surface [228]. The two forms of adsorption of NO have been observed to a lesser extent on the surfaces of nickel-containing zeolites after their interaction with NO or NO + CO at 220–550°C. [215] The higher- and lower-energy peaks characterise the formation of the nitrosyl and nitrate complexes respectively. The deactivation of zeolites at low temperatures in the reduction of NO is probably due to the formation of stable nitrate complexes [215] (Fig. 10).

Results obtained by UPE and XPE spectroscopy led to conclusions concerning the mechanisms of the decomposition of HCOOH and the adsorption of pyridine on metallophthalocyanines [229]. The adsorption of pyridine is not accompanied by a change in the charge on iron, while HCOOH dissociates heterolytically with adsorption of the formate ion on the central atom and of the proton on the bridging nitrogen atom in the porphyrin ring.

7. Results of Adsorption Studies

As mentioned above, there is an extensive literature on the application of PES to the study of adsorption [24,25,29–37]. Two international conferences have been devoted to problems associated with the interpretation of the spectra of adsorbates [32,33]. Taking this into account, we decided to give only a brief account in the present review (retaining as far as possible the complete bibliography) of the principal research trends. New results of studies on the adsorption of hydrocarbons and catalytic reactions at low pressure of reactants are described in greater detail.

(a) Adsorption on metals. The study of the interaction of simple gases with metallic surfaces is the main field of application of PES to adsorption. In these systems there is in fact a possibility of obtaining polycrystalline and single-crystal atomically pure surfaces and of deriving the maximum information with the aid of other physicochemical methods.

The interaction of CO with tungsten [230–238], molybdenum [30,232–234,239–241], platinum [232,242–250], ruthenium [248,251–255], palladium [256,257], nickel [232,233,241,249,258–262], iridium [263,264], iron [166,265], copper [232,241,266,267], titanium [268], and cobalt [269] has been studied vigorously. Several forms of adsorption of CO on polycrystalline tungsten have been observed [230,231,238]: The α-form with bonding close to that in carbonyls, which disappears in the temperature range 300–640 K, the dissociative form, and the weakly adsorbed

"virgin" state. In molecular adsorption on tungsten, and on other metals, the chemisorption linkage is formed by the 5*d* orbitals with the lone electron pair. A correlation has been observed[232] between E_b for the O(1*s*) level and the heats of adsorption on five metals, which indicated a contribution of the πd component to the chemisorption linkage. For the strongest adsorption (Ni, Pt, Pd, Ru, Fe), ΔE_b = 2 eV, and for the weakest adsorption (γ = CO/Mo) ΔE_b = −3.2 eV. According to the authors[232], there is a CO dissociation threshold at room temperature: ΔH_{ads} = 260 kJ mole^{-1}. Apart from tungsten (β-form), dissociative adsorption has been observed on molybdenum (β-form)[240], iron[265], nickel[233,261], titanium[268], and copper[266].

Polycrystalline tungsten and platinum do not catalyse the dissociation of NO at temperatures up to 100°C[30,270-272]. Ruthenium[248], iridium[273], nickel[262,274], and iron[275-277] are more active in the dissociation of NO. NO dissociates on the (1010) faces of ruthenium even at 100 K (NO exposure = 1.5 *L*). The peaks of nitride nitrogen and atomic oxygen in the spectrum of NO adsorbed on the (111) face of iridium are observed at 323–373 K; it has been suggested that oxygen blocks the active centres for the decomposition of NO.[273]

Numerous studies have been devoted to the interaction of O_2 with metal surfaces, and, together with adsorption on reconstructed surfaces, the oxidation of surface layers was investigated, from the initiation of the oxides until the formation of oxide phases. These processes may constitute the individual stages of the reactions with participation of oxygen.

The interaction of O_2 with the surfaces of polycrystalline tungsten[231,265] and the (111), (110), and (100) tungsten faces[238,274,278-280], polycrystalline molybdenum[30,240], platinum[243,248,281], palladium[256], iridium [(100)[263] and (111)[282]], ruthenium [(10$\bar{1}$0) and (001)][253,279,283], polycrystalline nickel[30,232,284-286], nickel (100)[287], polycrystalline silver[288,289], the (100) face of silver[278], polycrystalline copper[266,289-291], the (110)[292] and (100)[293] faces of copper, polycrystalline gold[289], sputtered iron[267,286,294,295], zinc[296], and tin[297], and magnesium, aluminium, chromium, manganese[238], lanthanide[299], cerium[84], titanium[84], and cobalt[269] films.

It has been stated in a report[300], and in a number of reviews[30,32,33,36,37] that the adsorption of oxygen on a number of metals (V, Mn, Fe, Co, Ni, Cu, Ag, Zn, Mo, W, Ru, Ir, Au, and Na) at room temperature leads to the appearance of the O(1*s*) peak with E_b = 530 ± 0.5 eV (in UPE spectra there is a maximum with $E_b \simeq 6$ eV). This may indicate a similarity of the structures of the adsorption complexes of oxygen, which are believed[33] to be of "the oxide-like" type. However, it is more likely that the agreement is merely formal and does not reflect the constancy of the charge on oxygen but is caused by the different contributions of the Madelung and relaxation terms to ΔE_b.

At the same time other forms of adsorbed oxygen were also observed: O(1*s*) signals with 531.4–532.0 eV (Ni, Co, Mn) and 533 eV (Pt) corresponding to them. The adsorption of O_2 on nickel at 300 K and $\theta < 1$ led to the appearance of two O(1*s*) peaks, one of which was assigned to adsorbed oxygen and the other to oxygen which penetrated underneath the surface of the crystal (531.4 eV). Three types of oxygen were observed in another study[265] in the range 77–500 K ($\theta < 1$) on nickel. Finally, the transition from adsorption to the generation of the NiO phase and the formation of the bulk-phase oxide were observed in the range $0.5 \leq \theta \leq 2.0$. The exposure and temperature required for the bulk-phase oxidation are determined by the nature and reactivity of the metal. Thus, an O_2 exposure of 2 *L* is sufficient for the formation of a ~ 10 Å cerium oxide film at room temperature[84] (Fig. 11). The first oxidised layer on titanium, magnesium, aluminium, and chromium becomes protective and prevents the formation of the bulk-phase oxide[84,293]. A kinetic study of the oxidation of iron[295] showed that the oxidation process proceeds in two stages—rapid oxidation with formation of four oxide layers, and a slow stage with formation of ten atomic oxide layers. Evidently studies in this field are extremely informative. Table 3 gives a brief compilation of the results of studies on the adsorption of other inorganic molecules: CO_2, NO_2, N_2, H_2O, and H_2.

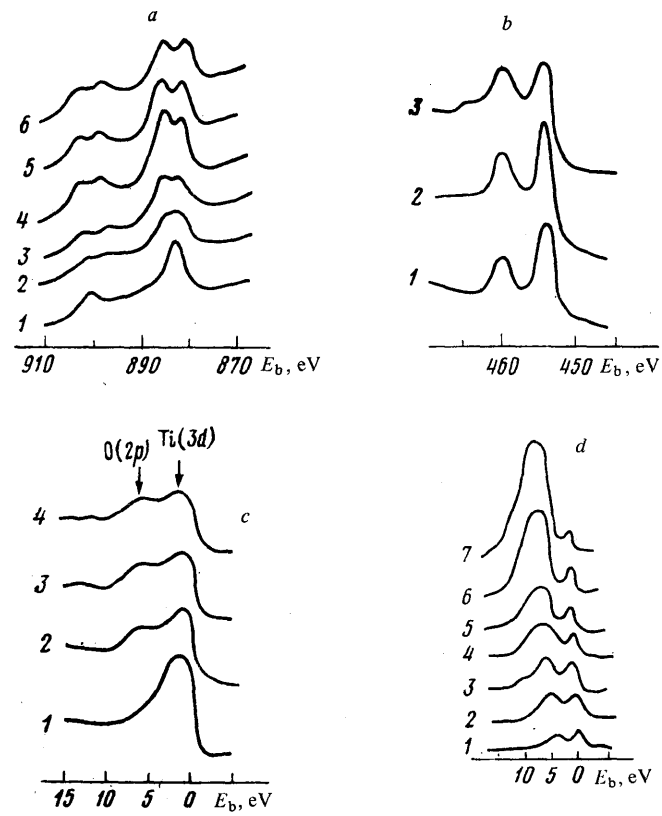


Figure 11. Adsorption of O_2 and surface oxidation of metals[84]: *a*) adsorption of O_2 on cerium, Ce(3*d*) lines [1) 0*L*; 2) 2*L*; 3) 10*L*; 4) 40*L*; 5) 100*L*; 6) 1000*L*]; *b*) adsorption of O_2 on titanium, Ti(2*p*) lines [1) 0*L*; 2) 1000*L*; 3) 3000*L*]; *c*) adsorption of O_2 on titanium, XPE spectra of the (Al K_α) valence band [1) 0*L*; 2) 300*L*; 3) 1000*L*; 4) 3000*L*]; *d*) adsorption of O_2 on titanium, UPE spectra, He(II) [1) 0*L*; 2) 1*L*; 3) 3*L*; 4) 10*L*; 5) 30*L*; 6) 100*L*; 7) 300*L*].

Until recently the number of PES studies dealing with the adsorption of hydrocarbons on metals was very limited. This was due to the experimental difficulties and the difficulties in the interpretation of the spectra. At the same time, this application of the method is of significant interest for organic catalysis. Studies which yielded extremely

interesting data about the nature of the chemical bond between a number of hydrocarbons and metal surfaces have been carried out recently.

Table 3. Results of the study of the adsorption of certain inorganic molecules on metals.

Adsorbate	Adsorbent	Principal results	References
CO_2	Mo	the reaction CO_2 (gas) → CO_{ads} + O_{ads} → C_{ads} + O_{ads} observed in the temperature range 77–298 K	240
CO_2	Au	monolayer and multilayer adsorption observed at 77 K	244
CO_2	Ni	reversible adsorption observed	262
CO_2	Pt	physical adsorption observed at 77 K	243,245
N_2	W	γ-state (weakly ads.) $\xrightarrow{300\ K}$ β-form (strongly ads.) transition observed	278
N_2	W (100)	two states of nitrogen observed	301,302
N_2	Ni	molecular adsorption found at 80 K	262,292
N_2	Fe (100)	two states of nitrogen found at 298 K	303,304
NO_2	Ni	molecular and dissociative adsorption found (77–400 K)	292,303 277
NO_2	Fe	dissociative adsorption observed at 298 K	292,303
N_2O	Ni	multilayer condensation with subsequent dissociation of N_2O observed at 80 K	
H_2O	Mo, Au	molecular and dissociative adsorption found	238,240
H_2O	Pt	molecular adsorption observed at 160 K	281
H_2O	Mg	formation of OH groups at 77 K followed by formation of MgO found	298
H_2O	Al, Cr, Mn	conditions for the formation of oxides and hydroxides investigated	298
H_2O	r.e.	the formation of oxides and hydroxides observed	299
H_2*	W	two adsorption states found on the (100) and (110) faces	302,305

*The adsorption of H_2 was also investigated on Ir(100)[268], Pd(110)[256], Ni(111)[306], Fe, Cu[266], and Ti[307].

One of the first studies dealt with the condensation and adsorption of ethylene, acetylene, and benzene on nickel [(111) face of a single crystal] and it was shown[311,308] that E_b and the intensity of the peak of the valence σ orbital depend on the type of hybridisation of carbon atoms and are consistent with LCAO-MO SCF calculations. Physical adsorption entails a relaxation shift of the σ and π orbitals relative to E_b in the gas phase. In chemisorption the energies of the π orbitals approach those of σ-orbitals, which indicates the formation of a πd-bond at right angles to the surface; there is no rehybridisation of the σ-bond. Data for C_2H_4/Ni have been used[309] to calculate the structure of the adsorption complex. It has been shown by the method of $X\alpha$-scattered waves that UPES data support the formation of a π-complex of ethylene adsorbed on two nickel atoms, the Ni–Ni bond being perpendicular to the plane of the molecule. It has been noted that UPES data do not make it possible to distinguish this structure from that of the σ-complex in which the Ni–Ni bond is parallel to the C_2H_4 plane. The latter complex may be intermediate in the catalytic process in view of the weaker C–C bond. We may note that the model proposed cannot be regarded as rigorously proved because of the assumptions made in calculations and in the separation of chemical and relaxation shifts.

In studies on the adsorption of ethylene and acetylene on copper and iron[266,310] no correlation was observed between the heats of adsorption and the shifts of the signals due to the π-levels. The importance of taking into account the interaction within the adsorption layer was pointed out in an investigation of the adsorption of ethylene on Pt (100), although it is not clear how this is reflected in the spectra[247]. Interesting results were obtained in a study of the interaction of ethylene and acetylene with the Ir(100) and α-Fe(100) surfaces by a combined method: LEED, UPES, and Auger spectroscopy[311,312]. According to the changes in the spectra, the formation of a πd-bond ("back-donation") is accompanied by perturbation of low-lying σ-orbitals, which are not directly involved in the bond. Such perturbation results in distortion (extension and twisting) of the bonds in the chemisorbed molecules, with subsequent bond dissociation and formation of fragments (Fig. 12). Depending on the reactivity of the metals and on the state of the surface (clean, carbon-coated, oxidised) the fragmentation process can occur at different temperatures. Thus, no distortion in the structure of the C_2H_2 molecule was observed on nickel and copper, on Ir(100) the acetylene molecule is stretched and twisted at 298 K[311], while on α-iron at 123 K it fragments with formation of CH_n (n = 1 or 2) radicals and possibly CCH_2.[312] The bond distortion effect in C_2H_2 diminishes on passing from the clean to the carbon-coated surface and is scarcely observed on the oxidised surface[312]. C_2H_4 behaves significantly differently: on α-iron the molecule fragments with formation of CH_2 (Fig. 12). This hypothesis is supported by data for the adsorption of H_2 on the carbon-coated surface of α-iron (Fig. 12); the spectra are close to the corresponding C_2H_4 spectra. In contrast to α-iron, on iridium and nickel at $T < 300$ K, ethylene undergoes preferential dehydrogenation with formation of acetylene[308,312] (Fig. 12). At a higher temperature (600° C) a spectral band characteristic of the σ-band of pyrolytic graphite arises in the Ni(100) spectrum, which indicates the cracking of C_2H_4.[313] The mechanism of the formation of carbon on the W(100) surface in the decomposition of butadiene at 1000 K has been investigated[301].

When halogenoalkenes interact with the Pt(100) and Pt(111) surfaces, both dissociative adsorption (vinyl fluoride and chloride), accompanied by the elimination of the halogen, and non-dissociative adsorption ($CH \equiv C-CF_3$, $CH_2=CH-CF_3$, CF_2CFCl) are observed[314,315]. The degree of dissociation of vinyl fluoride, determined from the ratio $I[F(1s)]/I[C(1/s)]$ depends on the crystal face index [80% for the (111) face and 40% for the (100) face] and is inhibited in the presence of CO on the surface. The adsorption and decomposition of methanol and formaldehyde on tungsten[316] and palladium[317] and of CH_3OCH_3, $(CH_3)CHO$ and $(CH_3)_2CO$ on palladium[317] were investigated. On tungsten, for coverages corresponding to saturation, methanol and formaldehyde form molecular complexes and at low coverages the β-CO state arises already in the early stages of adsorption[316]. At 120 K on palladium, the bond between the adsorption complex and the surface is formed via an atomic orbital of oxygen, which has a lone electron pair, while at 300 K the decomposition of the molecules begins and chemisorbed CO appears. The d-band of palladium is involved in the formation of the bond, which entails a decrease in the intensity of the spectrum on adsorption. Using the chemical shifts, an attempt was made to estimate the strength of the adsorbate–adsorbent interaction and E for the chemisorption bond within the framework of Mulliken's theory of donor–acceptor complexes[317]. Catalytic decomposition of HCOOH on copper, nickel, and gold, at 80–295 K leads to a change in the UPE spectra and a shift of the 1s level of O by 2 eV, which is associated with the formation of a formate ion[318]. With increase of temperature, the formate ion decomposes and the H_2 and CO_2 formed are desorbed into the gas phase. The activation

energies found from these data are close to those obtained in the catalytic experiment. Comparison of the catalytic activities in the sequence Au < Fe < Ag < Ni < Cu < Pt in the decomposition of HCOOH and the densities of states in the vicinity of the Fermi level in these metals led to the conclusion that there is no correlation between the above quantities [37,318].

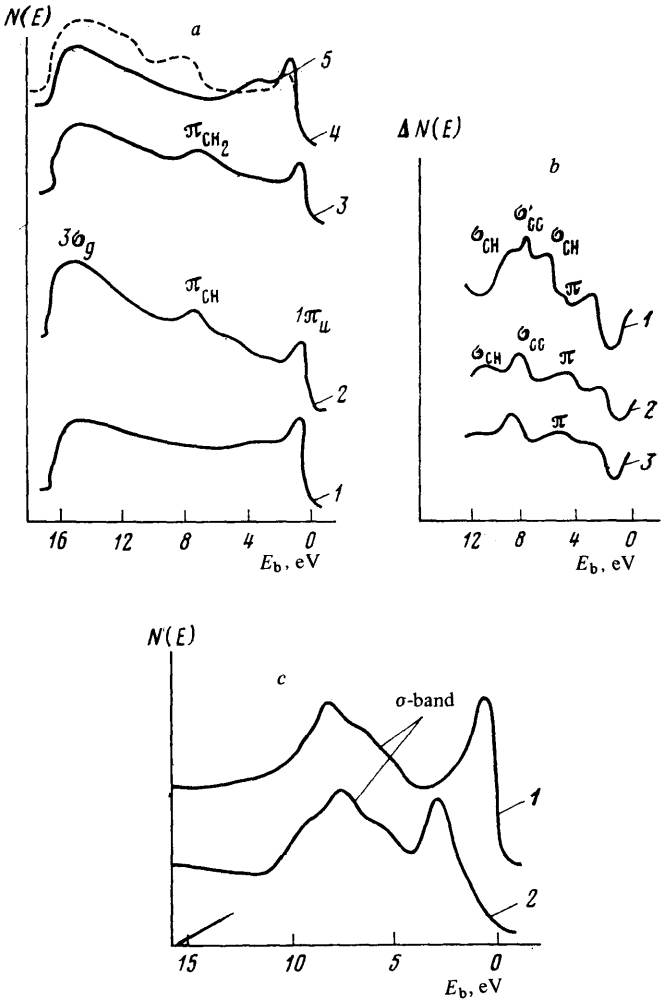


Figure 12. Adsorption of ethylene and acetylene on metals: *a*) C_2H_2, C_2H_4, and H_2 on α-Fe(100) [312], UPE spectra, He(I) [1) clean surface; 2) 123 K, C_2H_2 (6*L*); 3) 123 K, C_2H_4 (6*L*); 4) carbon-coated surface of α-Fe(100); 5) adsorption of H_2 on the carbon-coated surface of α-Fe(100)]; *b*) adsorption of C_2H_4 on nickel, differential He(I) spectra [308] [1) C_2H_4 1.2*L*, 100 K; 2) C_2H_4 1.2*L*, heating to 300 K; 3) C_2H_2 1.2*L* (100–300 K)]; *c*) high-temperature adsorption of C_2H_4 on Ni(110), He(II) UPE spectra [313] [1) C_2H_4, 780*L*, 873 K, $C_2H_4 \rightarrow 2H_2 + 2C$(graphite); 2) spectrum of pyrolytic graphite cleaved *in vacuo*] [$N(E)$ is the intensity and $\Delta N(E)$ the differential intensity].

Of the other studies which have been made, we shall mention the investigation of the layer-by-layer condensation of CB_4 [246] and the chemisorption of C_2N_2 on platinum [319]. In the latter case interaction with transfer of a *d* electron of the metal to the unoccupied $2\pi^*$ orbital of the adsorbate was postulated. There are data for the adsorption of NH_3 on W(100), [320] of iodoaniline on gold [321], and of H_2S and SO_2 on nickel [259,262].

The spectra of C_2H_6, C_6H_6, CH_3OH, C_2H_5OH, H_2CO, H_2O, and NH_3 in the gaseous state and condensed at 77 K on MoS_2 [322] confirm the hypothesis that the relaxation shifts are equivalent in different systems. In general, the same conclusion may be arrived at by examining the physical adsorption of Xe on W(111) [274] and nickel [323], for which the spectra of the inner and valence levels exhibit identical shifts relative to the gas phase (1.1–1.3 eV for nickel). However, in a study of the excited HeI line in the spectrum of the 5*p* level of Xe on the (100) face of tungsten [324] a marked broadening of the signal due to the $5p_{3/2}$ sublevel was observed and interpreted as a consequence of the splitting of the $5p_{3/2}$ xenon sublevel under the influence of the crystal field. Thus even in physical adsorption the system of adsorbate levels may undergo non-identical perturbations.

(b) Catalytic reactions on metal surfaces. The methods for the measurement of XPE and UPE spectra make it possible to investigate surface reactions under two sets of conditions: (1) with the reaction mixture passed over the catalyst and scanning of the spectra. Since the pressure of the reactants is very low ($< 10^{-7}$ mmHg), coverages sufficient for the recording of the spectra (approximately 0.05 of a monolayer) cannot always be attained; (2) reactions in the adsorption layer; in this case it is possible to achieve a higher surface concentration of one of the components. Evidently the interactions of many adsorbates with the surface, leading to a chemical alteration of the adsorbate (for example, the decomposition of NO and CH_3OH, the dehydrogenation of C_2H_4, etc.) can be regarded as reactions in the adsorption layer. However, mainly qualitative data concerning the structures of the adsorption complexes were obtained in the studies quoted above. Furthermore, there have been investigations where the reaction kinetics were studied by PES, and definite conclusions about the reaction mechanisms were reached. This applies to the investigations of reactions of molecular hydrogen with molecular oxygen [281,325,326], of carbon monoxide with molecular oxygen [253,259,264,327,328], of carbon monoxide with molecular hydrogen and nitric oxide [256,329], and of hydrogen sulphide with molecular oxygen [265].

The first attempt to investigate the reaction of H_2 with $O_{2(ads)}$/Pt directly during the scanning of the XPE spectra was apparently made in Norton's study [281]. After the adsorption of oxygen at 120 K $\{E_b[O(1s)] = 530.2$ eV$\}$, a stream of H_2 (10^{-7} mmHg) was passed through the system and the specimen was subjected to linear heating. An O(1*s*) peak with $E_b = 533$ eV (evidently $H_2O_{(ads)}$) appeared at 140 K, indicating the onset of the reaction, which terminated at 150 K. The line with $E_b = 533$ eV disappeared at 170 K and water was desorbed. The kinetics of this reaction were studied and an equation describing the reduction of $O_{2(ads)}$ was derived. In contrast to this reaction, the oxidation of adsorbed H_2 was much slower, which was explained by the poisoning of the active centres by hydrogen. According to some results [325,326] the probability of the interaction of an H_2 molecule with an $O_{2(ads)}$ molecule, leading to reaction at $\theta = 0.5$ at room temperature on

platinum, is approximately 0.7, which is ten times greater than the value found by Norton. The authors[325,326] believe that this discrepancy is caused by the inaccuracy of the measurement of pressure in Norton's study[281].

The adsorption of CO on the Ru(001) surface covered by oxygen entails a change in the O(1*s*) lines, indicating the joint adsorption of CO and O_2 and then a displacement of O_2 from the surface (15–20% of the initial coverage[257]). It is suggested that part of the CO reacts with O_2 even at low temperatures. The oxidation of CO on Ir(111) was studied directly during the recording of the spectra[328]. The results obtained with the aid of XPES show that the reaction proceeds via the Langmuir–Hinshelwood mechanism. According to data obtained with the aid of LEED, flash desorption, and UPE spectroscopy, the oxidation of carbon monoxide on Ir(111) can proceed via the Eley–Rideal mechanism[264].

The interaction of carbon monoxide with molecular hydrogen on the Ni(111) surface was studied at relatively low temperatures (< 400 K). According to LEED data, a (2 × 2) structure of the adsorbate is produced[323], although the interaction of CO with H_2 is still insignificant and does not lead to a change in the energy of the valence orbitals. At low coverages, H_2 is present in the β_1-state, passing to the β_2-state as the degree of coverage increases. The formation of reaction complexes on the surface and of the products in the gas phase was not observed under these conditions. The interaction of H_2S with O_2 adsorbed on lead is a typical instance of a surface reaction leading to a change in the state of the elements of the support[265]. The observed changes in the positions and intensities of the O(1*s*) and S(2*p*) lines constitute the basis for the hypothesis that the reaction $PbO_{surf} + H_{2gas} \rightarrow PbS_{solid} + H_2O_{gas}$ takes place.

(c) Other adsorbents. The interaction of oxygen with the basal and prismatic faces of graphite was begun by Thomas and coworkers[330,331]. In the study of catalysts having semiconducting or insulating properties certain difficulties are encountered due to the charging of the surface, the possibility of a more ready modification of the properties of the surface under the influence of radiation compared with metals, etc. One can only mention one of the first attempts to study adsorption on clean catalyst surfaces. Almy et al.[332] obtained the spectra of partly dehydrated α-Al_2O_3 (0001) and of the surface after the adsorption of H_2O, excited with the aid of He(I) lines. The specimen was subjected to preliminary cleaning in O_2 and, according to Auger spectroscopic data, its surface was free from impurities. There is an appreciable difference between the spectra of the clean surface and the surface coated by H_2O. Calculation by the method of X_α-scattered waves agreed satisfactorily with the experimental spectrum. A cluster model was chosen, according to which H_2O molecules are strongly bound to the α-Al_2O_3 surface. The number of UPE studies on powdered non-conducting specimens has been extremely limited[118,156]. Studies by the XPES method, but not under "clean surface" conditions, were examined above.

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The studies carried out hitherto demonstrate the high efficiency of the PES method in the study of catalytic and adsorption problems. The method makes it possible to obtain unique information about the structures of the surface layers of catalysts and about the nature of adsorption complexes. There is no doubt that, as the theory of the method is developed further and experimental technique is improved, the range of problems soluble by PES in this field will be extended. The wide-scale application of PES in the study of catalytic problems will assist in deepening our knowledge about the nature of the catalytic activity of solids.

REFERENCES

1. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Carlsson, I. Lindgren, and B. Lindberg, "Electron Spectroscopy" (Translated into Russian), Izd. Mir, Moscow, 1971.
2. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, H. Gelius, T. Bergmark, L. O'Werme, K. Manne, and Y. Bayer, "ESCA Applied to Free Molecules", Nort-Holland Publ., Amsterdam, 1969.
3. F. I. Vilesov, V. I. Kleimenov, and Yu. V. Chizhov, Symposium, "Uspekhi Fotoniki" (Advances in Photonics), Izd. Leningrad. Gos. Univ., Leningrad, 1969, No. 2.
4. A. D. Baker and D. Betteridge, "Photoelectron Spectroscopy" (Translated into Russian), Izd. Mir, Moscow, 1975.
5. V. I. Nefedov, "Primenenie Rentgenoelektronnoi Spektroskopii v Khimii. Stroenie Molekul i Khimicheskaya Svyaz'" (The Application of X-Ray Electron Spectroscopy in Chemistry. Molecular Structure and the Chemical Bond), Izd. VINITI, Moscow, 1973, Vol. 1.
6. V. I. Nefedov, Koordinatsionnaya Khimiya, 1, 291 (1975).
7. V. I. Nefedov, "Valentnye Elektronnye Urovni Khimicheskikh Soedinenii. Stroenie Molekul i Khimicheskaya Svyaz'" (Electronic Valence Levels of Chemical Compounds. Molecular Structure and the Chemical Bond), Izd. VINITI, Moscow, 1975, Vol. 3.
8. D. M. Hercules, Anal. Chem., 44, 106 (1972); 46, 133 (1974); 48, 294 (1976).
9. D. A. Shirley (Editor), "Electron Spectroscopy" (Translated into Russian), North-Holland Publ., Amsterdam, 1972.
10. "Proc. Internat. Conf. on ESCA 1974, Namur", J. Electron Spectroscopy, 5 (1974).
11. V. V. Nemoshkalenko and V. G. Aleshin, "Elektronnaya Spektroskopiya Kristallov" (The Electron Spectroscopy of Crystals), Izd. Naukova Dumka, Kiev, 1975.
12. D. R. Penn, J. Electron Spectr., 9, 29 (1976).
13. L. Linday and W. E. Spicer, J. Electron Spectr., 3, 409 (1974).
14. M. Klasson, A. Berndsson, J. Hedman, R. Nilsson, R. Nyholm, and C. Nordling, J. Electron. Spectr., 3, 427 (1974).
15. C. J. Powell, Surf. Sci., 44, 29 (1974).
16. W. A. Fraser, J. V. Florio, W. N. Delgass, and W. D. Robertson, Surf. Sci., 36, 661 (1973).
17. C. S. Fadley, Faraday Discuss. Chem. Soc., 60, 18 (1975).
18. S. Doniach, I. Lindau, W. E. Spicer, and H. Winick, J. Vacuum Sci. Technol., 12, 1123 (1975).
19. U. Gelius, Phys. fenn. Suppl., 9, 290 (1974).
20. P. Biloen and R. Bouwman, Ned. Tijdschr. Natuurkd., 41, 196 (1975).

21. R.M. Friedman, Silic. Ind., **39**, 247 (1974).
22. W.N. Delgass, T.R. Hughes, and C.S. Fadley, Catal. Rev., **4**, 179 (1971).
23. Kh.N. Minachev, G.V. Antoshin, and E.S. Shpiro, Problemy Kinetiki i Kataliza, **16**, 189 (1975).
24. J.J. McCarroll, Surf. Sci., **53**, 297 (1975).
25. P. Canesson and C. Defosse, J. microsc. et spectrosc. electron, **1**, 429 (1976).
26. J.C. Vedrine, J. microsc. et spectrosc. electron, **1**, 285 (1976).
27. H.D. Hagstrum, J.E. Rowe, and J.C. Tracy, Exp. Methods Catal. Res., **3**, 41 (1975).
28. J.C. Brinen, J. Electron Spectr., **5**, 377 (1974).
29. C.R. Brundle, J. Electron Spectr., **5**, 291 (1974).
30. C.R. Brundle, Surf. Sci., **99**, 48 (1975).
31. J.E. Demuth and D.E. Eastman, J. Vacuum Sci. Technol., **13**, 283 (1976).
32. Faraday Discuss. Chem. Soc., 58 (1974).
33. Faraday Discuss. Chem. Soc., 60 (1975).
34. D. Menzel, J. Vacuum Sci. Technol., **12**, 313 (1975).
35. A.D. Baker, M.A. Brisk, and D.C. Liotta, Anal. Chem., **48**, 281 (1976).
36. M.V. Gomoyunova, Zhur. Tekh. Fiz., **47**, 673 (1977).
37. R.W. Joyner, Surf. Sci., **63**, 291 (1977).
38. G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, J. Electron Spectr., **2**, 295 (1973).
39. P.H. Citrin and T.D. Thomas, J. Chem. Phys., **57**, 4446 (1972).
40. E.S. Shpiro, Candidate's Thesis, Institute of General Chemistry of the USSR Academy of Sciences, Moscow, 1975.
41. V.I. Nefedov, Ya.V. Salin, G. Leonhart, and R. Sheibe, J. Electron Spectr., **10**, 121 (1977).
42. D.A. Hucknital and R.T. McKean, Appl. Phys. Letters, **20**, 158 (1972).
43. E.H. Vakil and M.F. Ebel, Mikrochim. Acta, Suppl., 471 (1975).
44. P.M.A. Sherwood, J. Chem. Soc., Faraday Trans. II, **72**, 1791 (1976).
45. S.G. Gagarin, A.A. Krichko, E.S. Shpiro, A.B. Vol'-Epshtein, G.V. Antoshin, and Kh.M. Minachev, Teor. Eksper. Khim., **14**, 496 (1978).
46. D.A. Shirley, J. Vacuum Sci. Technol., **12**, 280 (1976).
47. O. Johnson, Chem. Scripta, **8**, 162 (1975); **8**, 166 (1975).
48. J.C. Carver, G.K. Shweitzer, and T.A. Carlson, J. Chem. Phys., **57**, 973 (1972).
49. E.-K. Viinikka and S. Larrson, J. Electron Spectr., **7**, 163 (1975).
50. M.A. Brisk and A.D. Baker, J. Electron Spectr., **7**, 197 (1975).
51. G.A. Vernon, G. Stucky, and T.A. Carlson, Inorg. Chem., **15**, 278 (1976).
52. T. Novakov, Phys. Rev., **B3**, 2993 (1971).
53. K.S. Kim and R.E. Davis, J. Electron Spectr., **1**, 251 (1973).
54. K.S. Kim, J. Electron Spectr., **3**, 217 (1974).
55. D.C. Frost, A. Ishitani, and C.A. McDowell, Mol. Phys., **24**, 861 (1972).
56. J. Matienzo, L.Y. Yin, S.O. Grim, and W.E. Swartz, Inorg. Chem., **12**, 2762 (1973).
57. Y.G. Borod'ko, S.I. Vetchinkin, S.L. Zimont, I.N. Ivleva, and Yu.M. Shul'ga, Chem. Phys. Letters, **47**, 264 (1976).
58. M.S. Ioffe and Yu.G. Borod'ko, J. Electron Spectr., **11**, 235 (1977).
59. A.J. Signorelli and G.F. Hayes, Phys. Rev., **B8**, 81 (1973).
60. T.A. Carlson and G.R. McGuire, J. Electron Spectr., **1**, 163 (1973).
61. C.D. Wagner, Anal. Chem., **44**, 1050 (1972).
62. V.I. Nefedov, N.P. Sergushin, I.M. Band, and M.B. Trzhaskovskaya, J. Electron Spectr., **2**, 383 (1973).
63. V.I. Nefedov, N.P. Sergushin, Y.V. Salyn, I.M. Band, and M.B. Trzhaskovskaya, J. Electron Spectr., **7**, 175 (1975).
64. J.H. Scofield, J. Electron Spectr., **8**, 129 (1976).
65. A. Liebsch, Phys. Rev. Letters, **32**, 1203 (1974).
66. J.W. Gadzuk, Surf. Sci., **53**, 132 (1975).
67. C.A. Evans, Anal. Chem., **47**, 818 (1975).
68. Y. Baer, Y. Bush, and P. Coln, Rev. Sci. Instrum., **46**, 466 (1975).
69. V.V. Nemoshkalenko, A.I. Senkevich, and V.G. Aleshin, Dokl. Akad. Nauk SSSR, **211**, 1089 (1973).
70. Y. Baer and G. Bush, Phys. Rev. Letters, **31**, 35 (1973).
71. J.C. Fuggle, L.M. Watson, D.J. Fabian, and P.R. Norris, Solid State Comm., **13**, 507 (1973).
72. V.V. Nemoshkalenko and V.G. Aleshin, Izv. Akad. Nauk SSSR, Ser. Fiz., **38**, 3 (1974).
73. D.A. Shirley, Phys. Rev., **B5**, 4709 (1972).
74. S.P. Kowalczyk, L. Ley, R. Pollak, and D.A. Shirley, Phys. Letters, **41A**, 455 (1972).
75. S.P. Kowalczyk, L. Ley, F.A. McFeely, and D.A. Shirley, J. Chem. Phys., **61**, 2850 (1974).
76. S. Hüfner, G.K. Wertheim, and D.N.E. Buchanan, Chem. Phys. Letters, **24**, 527 (1974).
77. S. Hufner, G.K. Wertheim, and J.H. Wernick, Phys. Rev., **B8**, 4511 (1973).
78. O.I. Klyushnikov, V.A. Trofimova, K.M. Kolobova, S.A. Nemnonov, and V.A. Trapeznikov, Symposium, "Rentgenovskaya Fotoelektronnaya Spektroskopiya" (X-Ray Photoelectron Spectroscopy), Izd. Naukova Dumka, Kiev, 1977, p. 37.
79. N.J. Shevchik and A. Goldman, J. Electron Spectr., **5**, 631 (1974).
80. R. Bouwman and P. Biloen, Surf. Sci., **41**, 348 (1974).
81. R. Holm and S. Storp, J. Electron Spectr., **8**, 139 (1976).
82. E.S. Shpiro, T.S. Ustinova, V.S. Smirnov, V.M. Gryaznov, G.V. Antoshin, and Kh.M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 763 (1978).
83. I. Lindau and W.E. Spicer, "Mezhdunarodnyi Simpozium po Rentgenovskoi Fotoelektronnoi Spektroskopii, Tezisy Dokladov" (International Symposium on X-Ray Photoelectron Spectroscopy. Abstracts of Reports), Kiev, 1975.
84. A. Platau, L.L. Johansson, A.L. Hagström, S.E. Karlsson, and S.B.M. Hagström, Surf. Sci., **63**, 153 (1977).
85. G. Ertl and K. Wandelt, Surf. Sci., **50**, 479 (1975).
86. G. Shön and S.T. Lundin, J. Electron Spectr., **1**, 105 (1973).
87. M.D. Rechtin and B.L. Averbuch, J. Phys. Chem. Solids, **36**, 893 (1975).
88. G.M. Bancroft and J. Adamsctal, Anal. Chem., **47**, 586 (1975).
89. T. Dickinson, A.F. Povey, and P.M.A. Sherwood, J. Chem. Soc., Faraday Trans. I, 298 (1975).
90. J.W. Rabalais, R.J. Colton, and A.M. Guzman, Chem. Phys. Letters, **29**, 133 (1974).

91. J.Grimblot and J.P.Bonnele, Compt.rend., **C282**, 399 (1976).
92. K.S.Kim, T.J.O'Leary, and N.Winograd, Anal. Chem., **45**, 2214 (1973).
93. K.S.Kim and N.Winograd, Chem.Phys.Letters, **19**, 209 (1973).
94. S.Evans and J.M.Thomas, J.Chem.Soc., Faraday Trans, II, 313 (1975).
95. W.G.Lang, B.D.Padalia et al., J.Electron Spectr., 5, 207 (1974).
96. G.Hollinger, Y.Jugnet, P. Pertosa, and L. Porte, Analysis, 5, 2 (1977).
97. K.Hirokawa, F.Honda, and M.Oku, J.Electron Spectr., 6, 333 (1975).
98. M.N.Colpaert, P.Clauws, L.Fiermans, and J.Vennik, Surf.Sci., 36, 513 (1973).
99. M.Oku, K.Hirokawa, and Sh.Ikedo, J.Electron Spectr., 7, 465 (1975).
100. M.Misono, Y.Nozawa, and Y.Yoneda, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A29.
101. J.P.Bonnelle, J.Grimblot, and A.D'Huysser, J. Electron Spect., 7, 151 (1975).
102. T.J.Chuang, C.R.Brundle, and D.W.Rice, Surf. Sci., 59, 413 (1976).
103. Y.Okamoto, H.Nakano, T.Imanako, and Sh.Teranishi, Bull.Chem.Soc.Japan, 48, 1163 (1973).
104. J.Grimblot, A.D'Huysser, J.P.Bonnelle, and J.P.Beaufils, J.Electron Spectr., 6, 71 (1975).
105. K.S.Kim, Chem.Phys.Letters, 26, 234 (1974).
106. G.Shön, Surf.Sci., 35, 961 (1973).
107. A.Rosencwaig and G.K.Wertheim, J.Electron Spectr., 1, 493 (1973).
108. N.C.McIntyre and M.G.Cook, Anal.Chem., 47, 2208 (1975).
109. G.Shön, Acta Chim.Scand., 27 (1973).
110. J.M.Thomas and M.J.Tricker, J.Chem.Soc., Faraday Trans., II, 329 (1975).
111. G.C.Allen and M.T.Curtis, J.Chem.Soc., Dalton Trans., 16, 1675 (1973).
112. A.Cimino, B.A.De Angelis, A.Luchetti, and G.Minelli, J.Catal., 45, 316 (1976).
113. D.M.Hercules and W.E.Swartz, Anal.Chem., 43, 1774 (1971).
114. E.L.Aptekar', M.G.Chudinov, A.M.Alekseev, and O.V.Krylov, Soobshch.po Kinetike i Katal., 1, 493 (1974).
115. A.Cimino and B.A.De Angelis, J.Catal., 36, 11 (1975).
116. J.Haber, W.Marczewski, J.Stoch, and L.Ungier, Ber.Bunsenges.Geselschaft, 79, 970 (1975).
117. K.S.Kim and N.Winograd, J.Catal., 35, 66 (1974).
118. J.Haber, J.Stoch, and L.Ungier, J.Solid State Chem., 19, 113 (1976).
119. R.J.Colton and J.W.Rabalais, Inorg.Chem., 15, 236 (1976).
120. E.S.Shpiro, V.I.Avaev, G.V.Antoshin, M.A.Ryashentseva, and Kh.M.Minachev, J.Catal. (in the Press).
121. L.Fiermans, R.Hoogewiys, and J.Vennik, Surf. Sci., 47, 1 (1975).
122. J.R.Lindsay, H.J.Rose, W.Shwartz, P.H.Watts, and K.A.Rayburn, Appl.Spectr., 27, 1 (1973).
123. D.S.Urch and M.Webber, J.microsc.et spectrosc. electron, 1, 219 (1976).
124. V.I.Nefedov, N.P.Sergushin, and Ya.V.Salin, J.Electron Spectr., 8, 81 (1976).
125. V.I.Nefedov, G.Gati, B.F.Dzhurinskii, N.P.Sergushin, and Ya.V.Salyn', Zhur.Neorg. Khim., 20, 2307 (1975) [Russ.J.Inorg.Chem., No.9 (1975)].
126. J.Haber, Z.Chem., 421 (1976).
127. Ya.Kaneko and Yu.Suginohara, Nippon Kinzoku Gakkaishi, 41, 375 (1977); Chem.Abs., 86 (1977) 197474.
128. G.K.Boreskov and P.A.Zhdan, Dokl.Akad.Nauk SSSR, **224**, 1348 (1975).
129. P.A.Zhdan, "III Mezhdunarodnyi Simpozium po Geterogennomu Katalizu, Varna, 1975" (The IIIrd International Symposium on Heterogeneous Catalysis, Varna, 1975), Preprint No.5.
130. M.Oku and K.Hirokawa, J.Electron Spectr., 10, 103 (1977).
131. I.N.Ivleva, Yu.M.Shul'ga, O.V.Krylov, V.A.Martynyuk, and Yu.G.Borod'ko, Izv.Akad. Nauk SSSR, Ser.Khim., 908 (1977).
132. T.Sugano, T.Ohta, and H.Kuroda, "Proceedings of the IInd International Conference on Solid Surfaces, Tokyo, 1974", p.779.
133. Y.Okamoto, K.Adashi, T.Imanaka, and Sh.Teranishi, Chem.Letters, 241 (1974).
134. P.K.Sharpe, J.C.Vickerman, and M.H.Stacey, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A14.
135. A.W.Miller, W.Atkinson, M.Barber, and P.Swift, J.Catal., 22, 140 (1971).
136. A.A.Slinkin, G.V.Antoshin, M.I.Loktev, E.S.Shpiro, S.B.Nikishenko, and Kh.M.Minachev, Izv.Akad.Nauk SSSR, Ser.Khim., 2225 (1978).
137. P.Ratnsamy, J.Catal., 40, 137 (1975).
138. T.A.Patterson, J.C.Carver, D.E.Leyden, and D.M.Hercules, J.Phys.Chem., 80, 1700 (1976).
139. R.M.Friedman, R.I.Declerck-Grimee, and J.J.Fripan, J.Electron Spectr., 5, 437 (1974).
140. J.Grimblot, J.P.Bonnelle, and J.P.Beaufils, J.Electron Spectr., 8, 437 (1976).
141. J.Grimblot and J.P.Bonnelle, J.Electron Spectr., 9, 449 (1976).
142. Y.Okamoto, H.Nakano, T.Shimokawa, T.Imanaka, and Sh.Teranishi, J.Catal., 50, 447 (1977).
143. G.C.Stevence and T.Edmonds, J.Catal., 44, 488 (1976).
144. G.C.Stevence and T.Edmonds, J.Catal., 37, 544 (1975).
145. P.Ratnasamy, Proc.Indian Nat.Sci.Acad., A41, 532 (1975).
146. P.Canesson, B.Delmon, G.Delvaux, P.Grange, and J.M.Zabala, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint B32.
147. P.Canesson and P.Grange, Compt.rend., **C281**, 757 (1975).
148. K.T.Ng and D.M.Hercules, J.Phys.Chem., 80, 2094 (1975).
149. F.E.Massoth, J.Catal., 30, 204 (1973).
150. J.M.J.G.Lipsch and G.C.A.Schuit, J.Catal., 15, 179 (1969).
151. G.C.A.Schuit and B.C.Gates, Amer.Inst.Chem. Engineers J., 19, 417 (1973).
152. Yu.M.Shul'ga, I.N.Ivleva, M.V.Shimanskaya, L.Ya.Margolis, and Yu.G.Borod'ko, Zhur.Fiz. Khim., 69, 2976 (1975) [Russ.J.Phys.Chem., No.11 (1975)].

153. Yu.M.Shul'ga, L.N.Karklin', M.V.Shimanskaya, L.Ya.Margolis, and Yu.G.Borod'ko, Zhur. Fiz. Khim., 51, 1234 (1977) [Russ.J.Phys.Chem., No.5 (1977)].
154. Yu.M.Shul'ga, M.Yu.Kutyrev, B.V.Rozentuller, T.M.Kachalina, and L.Ya.Margolis, Dokl.Akad. Nauk SSSR, 231, 152 (1976).
155. I.Matsuura and M.W.J.Wolfs, J.Catal., 37, 174 (1975); M.W.J.Wolfs and J.H.C.Van Hoof, "Proceedings of the Ist International Symposium on the Scientific Base of Preparation of Heterogeneous Catalysts, Brussels, 1976", Communication B3.
156. B.Grzybowska, J.Haber, W.Marezewski, and L.Ungier, J.Catal., 42, 327 (1976).
157. D.W.Whan, M.Barber, and P.Swift, Chem.Comm., 198 (1972).
158. H.Vinik and M.Ebel, Z.Phys.Chem., 99, 145 (1976).
159. A.Wolberg, J.L.Ogilvie, and J.F.Roth, J.Catal., 19, 86 (1970).
160. P.Biloen and G.T.Pott, J.Catal., 30, 169 (1973).
161. Kh.M.Minachev, Yu.S.Khodakov, G.V.Antoshin, V.V.Zasypkin, E.S.Shpiro, and G.G.Shchibrya, Izv.Akad.Nauk SSSR, Ser.Khim., 549 (1978).
162. Y.Okamoto, M.Fujii, I.Imanaka, and Sh.Teranishi, Bull.Chem.Soc.Japan, 49, 859 (1976).
163. B.A.De Angelis, J.Electron Spectr., 9, 81 (1976).
164. S.A.Best, R.G.Squires, and R.A.Walton, J.Catal., 47, 292 (1977).
165. F.P.J.M.Kerkhof, H.J.Reitsma, and J.A.Moulijn, React Kinet.Catal.Letters, 7, 15 (1977).
166. O.Pitton, C.K.Jorgensen, and H.Berthou, Chem. Phys.Letters, 40, 357 (1976).
167. J.Escard, Compt.rend., C274, 1645 (1972).
168. C.Leclere, J.P.Contour, and G.Pannetier, Ann. Chem., 3, 221 (1974).
169. J.Escard, B.Pontvianne, and J.P.Contour, J. Electron Spectr., 6, 17 (1975).
170. P.N.Ross, K.Kinoshita, and P.Stonehart, J.Catal., 32, 163 (1974).
171. M.G.Mason, L.J.Derenser, and S.-T.Lee, Phys. Rev.Letters, 39, 288 (1977).
172. J.Escard, B.Pontvianne, M.T.Chenebaux, and J.Cosyns, Bull.Soc.chim.France, 349 (1976).
173. R.Bouwman and P.Biloen, J.Catal., 48, 209 (1977).
174. Yu.I.Ermakov, M.S.Ioffe, Yu.A.Ryndin, and B.N.Kuznetsov, Kinetika i Kataliz, 16, 807 (1975).
175. M.S.Ioffe, B.N.Kuznetsov, Yu.A.Ryndin, and Yu.I.Ermakov, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A5.
176. M.S.Ioffe, Yu.M.Shul'ga, Yu.A.Ryndin, B.N.Kuznetsov, A.N.Startsev, Yu.G.Borod'ko, and Yu.I.Ermakov, React.Kinet.Catal.Letters, 4, 229 (1976).
177. Y.Iwasawa and S.Ogasawara, "IV Soviet-Japan Catal.Seminar, 1977", Preprint 13.
178. Yu.M.Shul'ga, A.N.Startsev, Yu.I.Ermakov, B.N.Kuznetsov, and Yu.G.Borod'ko, React.Kinet. Catal.Letters, 6, 377 (1977).
179. J.C.Brinen, Acc.Chem.Res., 2, 86 (1976).
180. M.G.Mason and R.C.Baetzold, J.Chem.Phys., 64, 271 (1977).
181. J.F.Hamilton, J.Vacuum Sci.Technol., 13, 319 (1976).
182. T.Imanaka, K.Kaneda, Sh.Teranishi, and M.Terasawa, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A41.
183. A.W.Meerbeek, A.Jelli, and J.J.Fripiat, J.Catal., 46, 320 (1977).
184. P.J.Angevine, W.N.Delgass, and J.C.Vartuli, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint B1.
185. [This reference is missing from the original Russian text. Instead, the authors of Ref. 186 are listed twice. (Ed. of Translation)].
186. J.C.Brinen, L.Schmitt, W.R.Doghman, P.A.Achorn, L.A.Siegel, and W.N.Delgass, J. Catal., 40, 295 (1975).
187. N.S.McIntyre, N.H.Sagert, R.M.L.Pouteu, and W.G.Proctor, Canad.J.Chem., 51, 1670 (1973).
188. J.S.Brinen and J.L.Schmitt, J.Catal., 45, 277 (1976).
189. D.Briggs, J.Electron Spectr., 9, 487 (1976).
190. J.F.Tempere and D.Delafosse, Chem.Phys. Letters, 33, 95 (1975).
191. J.F.Tempere, D.Delafosse, and J.P.Contour, Adv.Symposium Ser., 40, 76 (1977).
192. C.Defosse, B.Delmon, and P.Canesson, Adv. Symposium Ser., 40, 86 (1977).
193. J.Finster and P.Lorens, Chem.Phys.Letters, 50, 223 (1977).
194. H.Vinek, H.Noller, and M.Ebel, Z.Phys., 103, 325 (1976).
195. H.Vinek, H.Noller, M.Ebel, and K.Schwars, J. Chem.Soc., Faraday Trans.I, 734 (1977).
196. C.Defosse, P.Canesson, and B.Delmon, J.Phys. Chem., 80, 1028 (1976).
197. C.Defosse and P.Canesson, React.Kinet.Catal. Letters, 3, 161 (1975).
198. Kh.M.Minachev, G.V.Antoshin, E.S.Shpiro, and Ya.I.Isakov, Izv.Akad.Nauk SSSR, Ser.Khim., 2131 (1973).
199. Kh.M.Minachev, G.V.Antoshin, E.S.Shpiro, and T.A.Novruzov, Izv.Akad.Nauk SSSR, Ser.Khim., 2134 (1973).
200. Kh.M.Minachev, G.V.Antoshin, and E.S.Shpiro, Izv.Akad.Nauk SSSR, Ser.Khim., 1015 (1974).
201. Kh.M.Minachev, A.V.Antoshin, and E.S.Shpiro, Metallofizika, 55 (1975).
202. Kh.M.Minachev, G.V.Antoshin, Yu.A.Yusifov, and E.S.Shpiro, Symposium, "Rentgenovskaya Fotoelektronnaya Spektroskopiya" (X-Ray Photoelectron Spectroscopy), Izd.Naukova Dumka, Kiev, 1977, p.99.
203. Kh.M.Minachev, G.V.Antoshin, E.S.Shpiro, and Yu.A.Yusifov, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint B2.
204. Kh.M.Minachev, G.V.Antoshin, Yu.A.Yusifov, and E.S.Shpiro, React.Kinet.Catal.Letters, 4, 137 (1976).
205. A.A.Slinkin, G.V.Antoshin, M.I.Loktev, E.S.Shpiro, E.A.Fedorovskaya, A.M.Rubinshtein, Yu.A.Yusifov, and Kh.M.Minachev, Kinetika i Kataliz, 19, 754 (1978).
206. J.C.Vedrine, M.Dufaux, C.Naccache, and B.Imelik, J.Chem.Soc., Faraday Trans.I, 440 (1978).
207. C.Defosse, R.M.Friedman, and J.Fripiat, Bull. Soc.chim.France, 1513 (1975).
208. M.A.Ryashentseva and V.I.Nefedov, Izv.Akad. Nauk SSSR, Ser.Khim., 1642 (1973).
209. V.I.Nefedov, N.P.Sergushin, and M.A.Ryashentseva, Dokl.Akad.Nauk SSSR, 213, 600 (1973).

210. R.J.M.Griffiths and E.L.Evans, J.Catal., **36**, 413 (1975).
211. L.H.Bennet, J.R.Cuthill, A.J.McAlister, N.E.Erickson, and R.E.Watson, Science, **184**, 563 (1974).
212. J.J.Carberry and G.C.Kuczynski, Nature Phys. Sci., 235 (1972).
213. J.J.Carberry, G.C.Kuczynski, and E.Martinez, J.Catal., **26**, 247 (1972).
214. J.S.Brinen and A.Melera, J.Phys.Chem., 76, 2525 (1972).
215. Kh.M.Minachev, G.V.Antoshin, Yu.A.Yusifov, and E.S.Shpiro, Adv.Symposium Ser., 40, 559 (1977).
216. K.Sakurai, Y.Okamoto, T.Imanaka, and Sh.Teranishi, Bull.Chem.Soc.Japan, 49, 1732 (1976).
217. D.W.Johnson, P.K.Gallaher, G.K.Wertheim, and E.M.Vogel, J.Catal., 48, 87 (1977).
218. E.J.Marak, A.J.Moffat, and M.A.Woldrop, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A28.
219. Kh.M.Minachev, Ya.I.Isakov, G.V.Antoshin, V.P.Kalinin, and E.S.Shpiro, Izv.Akad.Nauk SSSR, Ser.Khim., 2537 (1973).
220. A.L.Lapidus, V.V.Mal'tsev, E.S.Shpiro, G.V.Antoshin, V.I.Garanin, and Kh.M.Minachev, Izv.Akad.Nauk SSSR, Ser.Khim., 2454 (1977).
221. T.S.Ustinova, E.S.Shpiro, V.S.Smirnov, V.M.Gryaznov, G.V.Antoshin, and Kh.M.Minachev, Izv.Akad.Nauk SSSR, Ser.Khim., 441 (1976).
222. T.S.Ustinova, V.S.Smirnov, V.M.Gryaznov, G.V.Antoshin, E.S.Shpiro, F.A.Onvodi, V.I.Shimulis, and Kh.M.Minachev, Soobshch.po Kinetike i Katal. (in the Press).
223. J.P.Contour, G.Mouvier, M.Hoogewys, and C.Leclere, J.Catal., 48, 217 (1977).
224. B.N.Kuznetsov, V.L.Kuznetsov, M.Mak-Llairi, M.S.Ioffe, and Yu.I.Ermakov, "III Sovetsko-Yaponskii Seminar po Katalizu, Alma-Ata, 1975" (The IIIrd Soviet-Japanese Seminar on Catalysis, Alma-Ata, 1975), Preprint 21.
225. M.A.Ryashentseva, Kh.M.Minachev, E.P.Belanova, E.S.Shpiro, and N.A.Ovchinnikova, Izv.Akad. Nauk SSSR, Ser.Khim., 2647 (1976).
226. J.Haber, W.Marchewski, J.Stoch, and L.Ungier, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint B22.
227. W.Dianis and J.F.Lester, Surf.Sci., 43, 602 (1974).
228. J.P.Contour and G.Mouvier, J.Catal., 40, 342 (1975).
229. T.Kawai, M.Soma, Y.Matsumoto, J.Onishi, and K.Tamaru, Chem.Phys.Letters, 37, 378 (1976).
230. T.E.Madey, J.T.Yates, and N.E.Erickson, Chem. Phys.Letters, 19, 487 (1973).
231. J.T.Yates, T.E.Madey, and N.E.Erickson, Surf. Sci., 43, 257 (1974).
232. R.W.Joyner and M.W.Roberts, Chem.Phys.Letters, 29, 447 (1974).
233. J.M.Baker and D.E.Eastman, J.Vacuum Sci. Technol., 28, 516 (1974).
234. S.J.Atkinson, C.R.Brundle, and M.W.Roberts, Chem.Phys.Letters, 24, 175 (1974).
235. A.M.Bradshaw, D.Menzel, and M.Steinkelberg, Chem.Phys.Letters, 10, 223 (1973).
236. J.W.Linnett, D.L.Perry, and W.F.Egelhoff, Chem. Phys.Letters, 36, 331 (1975).
237. B.Feuerbacher, Surf.Sci., 47, 115 (1975).
238. J.T.Yates, A.E.Madey, N.S.Erickson, and S.D.Worley, Chem.Phys.Letters, 39, 113 (1976).
239. S.J.Atkinson, C.R.Brundle, and M.W.Roberts, Chem.Phys.Letters, 2, 105 (1973).
240. S.J.Atkinson, C.R.Brundle, and M.W.Roberts, Faraday Discuss.Chem.Soc., 58, 63 (1974).
241. C.R.Brundle, J.Electron Spectr., 7, 484 (1975).
242. T.A.Clarke, K.Mason, and M.Tescari, Proc.Roy. Soc., A331, 321 (1972).
243. P.R.Norton, Surf.Sci., 44, 624 (1974).
244. P.R.Norton, Surf.Sci., 47, 98 (1975).
245. P.R.Norton and P.J.Richards, Surf.Sci., 49, 567 (1975).
246. P.Biloen and A.A.Holscher, Faraday Discuss. Chem.Soc., 58, 107 (1974).
247. T.A.Clarke, I.D.Gay, and R.Mason, Chem.Phys. Letters, 27, 172 (1974).
248. H.P.Bonzel and T.E.Fisher, Surf.Sci., 51, 213 (1975).
249. P.R.Norton and R.L.Tapping, Chem.Phys.Letters, 38, 207 (1976).
250. W.E.Spicer, D.M.Collins, and J.B.Lee, Surf. Sci., 55, 389 (1976).
251. J.C.Fuggle, T.E.Madey, M.Steinkelberg, and D.Menzel, Chem.Phys.Letters, 33, 233 (1975).
252. J.C.Fuggle, T.E.Madey, M.Steinkelberg, and D.Menzel, Phys.Letters, A51, 163 (1975).
253. J.C.Fuggle, T.E.Madey, M.Steinkelberg, and D.Menzel, Surf.Sci., 52, 521 (1975).
254. J.C.Fuggle, M.Steinkelberg, and D.Menzel, Chem. Phys., 11, 307 (1975).
255. J.C.Fuggle, E.Umcach, P.Feulner, and D.Menzel, Surf.Sci., 64, 69 (1977).
256. H.Conrad, G.Ertl, and E.E.Latta, Faraday Discuss Chem.Soc., 58, 116 (1974).
257. J.Küppers, H.Conrad, G.Ertl, and E.F.Latta, "Proceedings of the IInd International Conference on Solid Surfaces, Tokyo, 1974", p.255.
258. T.Gustafsson, E.W.Plummer, D.E.Eastman, and J.L.Frecouf, Solid State Comm., 17, 391 (1975).
259. P.J.Page, D.L.Trimm, and P.W.Williams, J. Chem.Soc., Faraday Trans.I, 1769 (1974).
260. P.R.Norton, R.L.Tapping, and J.W.Goodall, Chem.Phys.Letters, 41, 246 (1976).
261. R.W.Joyner and M.W.Roberts, J.Chem.Soc., Faraday Trans.I, 1819 (1974).
262. C.R.Brundle and A.F.Carley, Faraday Discuss. Chem.Soc., 60, 51 (1975).
263. T.R.Rhodin and G.Broden, Surf.Sci., 60, 466 (1976).
264. J.Küppers and A.Plagge, J.Vacuum Sci.Technol., 13, 259 (1976).
265. K.Kishi and M.W.Roberts, J.Chem.Soc., Faraday Trans.I, 1715 (1975).
266. K.Y.Yu, W.E.Spicer, I.Lindau, P.Pianetta, and S.F.Lin, Surf.Sci., 57, 157 (1976).
267. H.Conrad, G.Ertl, J.Küppers, and E.E.Latta, Solid State Comm., 17, 613 (1975).
268. D.E.Eastman, Solid State Comm., 10, 933 (1972).
269. R.B.Moes and M.W.Roberts, J.Catal., 49, 216 (1977).
270. T.E.Madey, J.T.Yates, and N.E.Erickson, Surf. Sci., 43, 526 (1974).
271. H.P.Bonzel and G.Pirug, Surf.Sci., 62, 45 (1977).
272. G.Pirug and H.P.Bonzel, J.Catal., 50, 64 (1977).
273. P.A.Zhdan, G.K.Boreskov, W.F.Egelhoff, and W.N.Weinberg, J.Catal., 45, 281 (1976).

274. J.T.Yates and N.E.Erickson, Surf.Sci., **44**, 489 (1974).
275. K.Kishi and I.Ikeda, Bull. Chem.Soc.Japan, **47**, 2531 (1974).
276. G.K.Boreskov and P.A.Zhdan, Dokl.Akad.Nauk SSSR, **225**, 112 (1975).
277. F.Honda and K.Hirokawa, J.Electron Spectr., 8, 199 (1976).
278. A.M.Bradshaw, D.Menzel, and M.Steinkelberg, Faraday Discuss. Chem.Soc., 58, 47 (1974).
279. J.C.Fuggle and D.Menzel, Surf.Sci., 53, 21 (1975).
280. A.Barric and A.M.Bradshaw, Phys.Letters, 55A, 306 (1975).
281. P.R.Norton, J.Catal., 36, 211 (1975).
282. P.A.Zhdan, G.K.Boreskov, A.I.Boronin, W.F.Egelhoff, and W.H.Weinberg, Surf.Sci., 61, 25 (1976).
283. J.C.Fuggle and D.Menzel, Chem.Phys.Letters, 33, 37 (1975).
284. K.S.Kim and N.Winograd, Surf.Sci., 43, 625 (1974).
285. C.R.Brundle and A.F.Carley, Chem.Phys.Letters, 31, 432 (1975).
286. A.Nishijima, Y.Nikei, M.Kudo, and H.Kamada, "Proceedings of the IInd International Conference on Solid Surfaces, Tokyo, 1974", p.93.
287. N.G.Krishnan, W.N.Delgass, and W.D.Robertson, Surf.Sci., 57, 1 (1976).
288. E.L.Evans, J.M.Thomas, M.Baker, and R.J.M.Griffiths, Surf.Sci., 38, 245 (1973).
289. S.Evans, E.L.Evans, D.E.Parry, M.J.Tricker, M.J.Walters, and J.M.Thomas, Faraday Discuss. Chem.Soc., 58, 97 (1974).
290. S.Evans, J.Chem.Soc., Faraday Trans.II, 1044 (1974).
291. S.Evans, D.E.Parry, and J.M.Thomas, Faraday Discuss.Chem.Soc., 60, 71 (1975).
292. G.G.Tibbets, J.M.Burkstrand, and J.C.Tracy, Phys.Rev., B15, 3652 (1977).
293. M.J.Braithwaite, R.W.Joyner, and M.W.Roberts, Faraday Discuss. Chem.Soc., 60, 89 (1975).
294. K.Kosaku and I.Shigero, Bull. Chem.Soc.Japan, 46, 341 (1973).
295. J.K.Gimzewski, B.D.Padalia, S.Affrossman, L.M.Watson, and D.J.Fabian, Surf.Sci., 62, 386 (1977).
296. D.Briggs, Faraday Discuss. Chem.Soc., 60, 81 (1975).
297. R.A.Powell and W.E.Spicer, Surf.Sci., 55, 681 (1976).
298. J.C.Fuggle, L.M.Watson, D.J.Fabian, and S.Affrossman, Surf.Sci., 49, 61 (1975).
299. B.D.Padalia, J.K.Gimzevski, S.Affrossman, W.C.Lang, J.M.Watson, and D.J.Fabian, Surf. Sci., 61, 468 (1976).
300. R.W.Joyner and M.W.Roberts, Chem.Phys.Letters, 28, 246 (1974).
301. W.F.Egelhoff, J.W.Linnett, and D.L.Perry, Faraday Discuss. Chem.Soc., 58, 35 (1974).
302. B.Feuerbacher, Surf.Sci., 47, 115 (1975).
303. C.R.Brundle, J.Vacuum Sci.Technol., 13, 301 (1976).
304. F.Bozso, G.Ertl, M.Grunze, and M.Weiss, J. Catal., 49, 18 (1977).
305. B.Feuerbacher, Phys.Rev., B8, 4890 (1972).
306. P.E.Gregory, P.Chye, H.Sunami, and W.E.Spicer, J.Appl.Phys., 46, 3525 (1975).
307. K.A.Kress and G.J.Lapeyre, Phys.Rev.Letters, 28, 1639 (1972).
308. J.E.Demuth and D.E.Eastman, Phys.Rev., B13, 1523 (1976).
309. N.Rösch and T.N.Rhodin, Faraday Discuss. Chem. Soc., 58, 29 (1974).
310. K.Y.Yu, W.E.Spicer, I.Lindau, P.Pianetta, and S.L.Lin, J.Vacuum Sci.Technol., 13, 277 (1976).
311. G.Broden, T.R.Rhodin, and W.Copehart, Surf. Sci., 61, 143 (1976).
312. C.Brucker and T.R.Rhodin, J.Catal., 47, 214 (1977).
313. P.J.Page and P.W.Williams, Faraday Discuss. Chem.Soc., 58, 80 (1974).
314. T.A.Clarke, I.B.Gay, and R.Mason, Chem. Comm., 331 (1974).
315. T.A.Clarke, I.D.Gay, B.Law, and R.Mason, Faraday Discuss. Chem.Soc., 60, 119 (1975).
316. W.F.Egelhoff, J.W.Linnett, and D.L.Perry, Faraday Discuss. Chem.Soc., 60, 127 (1975).
317. H.Lüth, G.W.Rubloff, and W.D.Grobman, Surf. Sci., 63, 325 (1977).
318. R.W.Joyner and M.W.Roberts, Proc.Roy.Soc., A350, 107 (1976).
319. H.Conrad, J.Küppers, and F.Nitschke, Chem. Phys.Letters, 46, 571 (1977).
320. K.Schoenhammer, Solid State Comm., 22, 51 (1977).
321. L.Balsenc, H.Berthou, and C.K.Jorgensen, Chimia, 29, 64 (1975).
322. K.Y.Yu, J.C.McMcnamin, and W.E.Spicer, J. Vacuum Sci.Technol., 12, 286 (1975).
323. R.J.Tapping and P.R.Norton, Chem.Phys.Letters, 41, 252 (1976).
324. R.J.Waclawski and J.K.Herbst, Phys.Rev.Letters, 35, 1594 (1975).
325. D.M.Collins, J.B.Lee, and W.E.Spicer, Phys. Rev.Letters, 35, 592 (1975).
326. D.M.Collins, J.B.Lee, and W.E.Spicer, J. Vacuum Sci.Technol., 13, 266 (1976).
327. T.V.Vorburger, D.R.Sandstrom, and B.J.Waclawski, Surf.Sci., 60, 211 (1976).
328. P.A.Zhdan, G.K.Boreskov, W.F.Egelhoff, and W.H.Weinberg, Surf.Sci., 61, 377 (1976).
329. H.Conrad, G.Ertl, J.Küppers, and E.E.Latta, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A33.
330. J.M.Thomas, E.L.Evans, M.Barber, and P.Swift, Trans.Faraday Soc., 67, 1875 (1971).
331. M.Barber, E.L.Evans, and J.M.Thomas, Chem. Phys.Letters, 18, 423 (1973).
332. D.B.Almy, D.C.Foyt, and J.M.White, J.Electron Spectr., 11, 129 (1977).

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