Translated from *Uspekhi Khimii*, **55**, 427-449 (1986) U.D.C. 541.128

Application of Electron Paramagnetic Resonance and Ultraviolet Spectroscopy to the Study of Coordination-unsaturated Transition Metal Ions on the Surfaces of Catalysts

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The methodological characteristics of the application of the EPR and ultraviolet spectroscopic methods to the study of heterogeneous catalysts and reactions on their surfaces are briefly described. The concept of the coordination-unsaturated ions and the causes hindering their identification on catalyst surfaces by spectroscopic methods are discussed. Studies where the coordination and valence states of the surface coordination-unsaturated transition metal ions and their properties have been investigated with the aid of EPR and diffuse scattered light ultraviolet spectroscopy are examined. Data concerning the formation of surface complexes by the coordination-unsaturated ions with adsorbed molecules are analysed.
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INTRODUCTION

The electron paramagnetic resonance (EPR) and ultraviolet and visible spectroscopic methods have come to be widely used in chemistry because of the large amount of information which they can yield. They have been widely employed also in heterogeneous catalysis for the investigation of the structures and properties of catalysts, adsorption, and reaction mechanisms. The majority of heterogeneous catalysts are known to contain transition metal ions and such catalysts will be in fact be considered in this review.

The ideas of the chemistry of coordination compounds and of the ligand and crystal field theories, according to which the central ion of the complex or the transition metal ion of the catalyst are in an electric field generated by the ligands in their immediate vicinity, proved applicable to the description of the structures of the surfaces of heterogeneous catalysts, the properties of the transition metal ions in their composition, and the nature of the surface compounds. Within the framework of these theories, it is possible to describe fairly adequately the dependence of the optical and EPR spectra of the transition metal ions in the catalysts on the symmetry of the first coordination sphere and on the nature of the chemical bonds between the ion and the ligand. This leads to the possibility of determining from spectroscopic data the electronic and geometrical structures of the active centres of the catalysts containing transition metal ions and the changes undergone by them following the adsorption of various molecules.

The so-called coordination-unsaturated (CU) ions are considered in the majority of investigations as the active centres of the catalysts containing transition metal ions. The concept of the existence of CU ions follows naturally from the development of our knowledge of the structures of the lattices of solids and conditions in their activation necessary for the appearance of catalytic activity. In fact, heterogeneous catalysts become active as a rule after treatment at fairly high temperatures, i.e. under conditions where the surface hydroxy-groups and adsorbed water molecules are at least partly removed. It might have been supposed that vacant sites appear as a result of these processes in the coordination spheres of the surface cations. This concept is so natural that it led to a wide-scale employment of the concept of CU ions in heterogeneous catalysis.[1-4] However, the study of the electronic structures of these ions and of their coordination and valence states (the term valence state is used in this review rather than "oxidation state" because it is more common in the literature devoted to heterogeous catalysts) has become possible only in the last two decades as a result of the application for this purpose of spectroscopic methods, in the first place the EPR and ultraviolet spectroscopic methods. Fairly reliable methodological procedures have now been developed for the detection of surface CU ions and for the investigation of their electronic and geometrical structures. Many detailed investigations of their properties have been made. This review is devoted to a systematic account and a survey of studies on these lines.

The first investigations of heterogeneous catalysts containing transition metal ions by the EPR and optical spectroscopic methods date back to 1950's. The application of these methods showed that, with their aid, it is possible to obtain sufficiently reliable information about the coordination, valence, and phase states of the transition metal ions in the bulk of the catalysts. On the other hand, the study of surface ions has encountered appreciable difficulties due mainly to the following two factors. Firstly, the number of surface ions is frequently much smaller than the total number of ions in the catalyst. It is therefore almost impossible to study them by the above spectroscopic methods owing to the background of the ions in the bulk of the catalysts. Secondly, since the coordination sphere of the surface CU ions is greatly distorted as a result of the removal of one or several ligands, the spectra are more difficult to interpret than those of ions in a more symmetrical environment. Even when a distinct spectrum is obtained the question whether a surface or a bulk phase ion is responsible for its appearance is likewise not always trivial. The simplest and most reliable experimental criterion for the assignment of ions to surface CU ions is their accessibility at low

temperatures to adsorbable molecules which behave as typical ligands, for example water, carbon monoxide, ammonia, etc. When these molecules are adsorbed, they enter the first coordination sphere of the CU ions, altering their coordination environment, which is reflected by a change in the parameters of the optical and EPR spectra. However, in this case the assignment of an ion to surface ions is not always evident, because such changes may be induced by other processes, for example, by the hydrolysis of the layer of catalyst near the surface, or by a change in the oxidation state of the ion due to the outer-sphere electron transfer to a molecule adsorbed at a fairly long distance from the given ion. As a rule, only a combined study of the properties of the catalyst surface therefore makes it possible to solve the problem of the assignment of a particular spectrum to surface CU ions.

The interaction of adsorbed molecules on CU ions with formation of surface complexes can proceed without change in the valence state of the CU ions and also with a change in this state. Complexes of the first type are formed as a rule when molecules which are typical ligands in homogeneous complexes and have no oxidation-reduction properties under the adsorption conditions are adsorbed. The complexes of the second type, involving a change in the oxidation state of the CU ions, are particularly characteristic of oxidant molecules (O_2, N_2O, SO_2, etc.). Electron transfer from the ion to the adsorbed molecule with formation of radical-anions, stabilised in the coordination sphere of the CU ions, takes place fairly frequently in this case. The structure and properties of such radical species have been studied vigorously by EPR,[5–9] because they play a significant role in many catalytic processes. Examination of studies of the radical-anions requires a special review and here we shall therefore consider them only to demonstrate the ability of the CU ions to form such charge-transfer complexes and attention will be concentrated on complexes of CU ions of the first type.

Deposited catalysts, i.e. catalysts prepared by depositing in one way or another transition metal compounds onto a support, in which the concentration of the CU ions is relatively high, are most convenient for investigation. However, in this case too the deposited ions can form either a solid solution in the carrier lattice or they can give rise to microcrystals of the deposited substance, i.e. they may exist in the bulk of the solid and not on the surface. During the last decade, zeolite catalysts into which transition metal ions have been introduced by ion exchange have come to be widely used. The study of such catalytic systems, as well as deposited catalysts, can yield rich information about the properties of the CU ions. The EPR and ultraviolet spectroscopic studies of CU ions in zeolites have been reviewed.[10,11]

II. METHODOLOGICAL CHARACTERISTICS OF THE APPLICATION OF THE EPR AND ULTRAVIOLET SPECTROSCOPIC METHODS FOR THE STUDY OF HETEROGENEOUS CATALYSTS

The application of the ultraviolet spectroscopic method to the investigation of solid catalysts has a number of characteristic features which distinguish it from its application to liquids. This is due to the fact that, for catalysts which are usually finely dispersed systems, light is appreciably scattered and reflected which hinders and in many cases virtually precludes the observation of their transmission spectra. In order to diminish light scattering, one can place the disperse solid in a medium, for example, liquid paraffin, with the same refractive index, and then measure the absorption spectra. However, it is much more convenient to deduce the absorption spectrum from the information carried by the light scattered by the specimen. For this purpose, it is necessary to measure the diffuse reflectance spectra. The method of measurement of such spectra is relatively simple and has therefore come to be widely used nowadays.[12–17]

The reflectance spectrum of the specimen is usually obtained from measurements of the relative diffuse reflectance coefficient R_{diff} as a function of the wavelength. The quantity R_{diff} is defined as the ratio of the intensities of the light subjected to diffuse reflectance by the specimen and a standard. Strongly reflecting white powders, for example MgO, SiO_2, $MgSO_4$, Al_2O_3, and NaCl are used as standards. Kubelka and Munk and, independently of them, Gurevich, Girin, and Stepanov proposed an equation for the dependence of R_{diff} on the concentration of the absorbing centres in the specimen c and on their extinction coefficient ε:

$$(1-R_{diff})^2/2R_{diff} = S\varepsilon c,$$

where S characterises the properties of the medium and is independent of the light wavelength.[12–15] Since the quantity S is usually unknown, it is impossible to determine εc exactly. However, the position of the absorption maximum (the maximum value of ε) can be determined from measurements of R_{diff}, i.e. it is possible to obtain the same information about the energy of the optical transitions as in the measurements of absorption spectra.

The application of the EPR method to the study of catalysts does not entail any special methodological difficulties, because it is suitable for the study of substances in any state of aggregation. The spectra are usually measured in quartz bulbs, which makes it possible to subject the specimen to different types of treatment, including a high-temperature treatment, and to carry out adsorption and other operations in the absence of air or in a controlled atmosphere. The interpretation of the EPR spectra is sometimes difficult because polycrystalline or amorphous specimens have more complex spectra than single crystals and their elucidation requires special procedures.[18–20] The theoretical principles of the EPR method have been sufficiently fully described in various monographs, for example Refs.19–22.

III. IONS OF METALS IN THE FIRST TRANSITION SERIES

We shall describe the available data in order of increasing atomic number of the transition element forming part of the catalyst. This method of exposition constitutes in our view the most rational way of giving a systematic account of the literature data.

1. Titanium Ions

The EPR and optical spectroscopic studies on surface titanium CU ions published hitherto refer mainly to Ti^{3+} with the electronic configuration $(A)\ (3d)^1$, where (A) is a completed electron shell. Titanium dioxide in two modifications (anatase and rutile) and deposited catalysts have been studied.

At the beginning of the 1960's it was shown that the adsorption of oxygen at room temperature on partly reduced anatase specimens leads to the appearance of a signal due to adsorbed oxygen radical-anions in the EPR spectrum.[23,24] The observation of this phenomenon led to a whole series of studies by different investigators[25–30] of the coordination

and valence states of the titanium ions on the surface of partly reduced TiO_2 and of their role in the formation of radical-anions. In a detailed investigation of specimens of partly reduced anatase, Kazanskii and co-workers observed in the EPR spectra, measured at the temperature of liquid nitrogen, a broad absorption line, whose form depended on the degree of reduction of the specimens.[25] In the spectra of specimens subjected to a vacuum heat treatment in the range 300–500 °C, the form of this line is determined by the anisotropy of the g-factor ($g_\perp = 1.97$ and $g_\parallel = 1.90$). On the basis of the values of the g-factors for the line and its disappearance when oxygen is adsorbed, the authors concluded that the line is due to surface tetrahedrally coordinated Ti^{3+} ions.

A broad line has been frequently observed in the EPR spectra of partly reduced anatase at the temperature of liquid nitrogen also in other investigations.[26–28] The authors likewise attributed this to surface Ti^{3+} ions. However, some workers[26,27] believe that the Ti^{3+} ions responsible for its appearance exist in a tetragonal ligand field, i.e. are surrounded by five or four lattice oxygen ions forming a square pyramid or a square respectively. These coordinations arise from the initial octahedral environment of titanium ions when one or two lattice oxygen ions are removed in the reduction process. A specific type of coordination of the surface Ti^{3+} ions of anatase was not discussed by Cornaz et al.,[28] but they noted that there are three sites in the coordination sphere of titanium ions.

Partly reduced specimens of another modification of TiO_2 (rutile) have also been investigated by EPR.[29,30]. A signal with $g_\perp = 1.959$ and $g_\parallel = 1.946$ appeared in the spectra of specimens subjected to a vacuum heat treatment at 500 °C (measurements at 77, 4.2, and 1.6 K). Analysis of the g-factors and spin–lattice relaxation times at the temperature of liquid helium and also the disappearance of the signal following the adsorption of oxygen showed that the signal is due to surface CU Ti^{3+} ions tetragonally coordinated. Such coordination arises as a result of the abstraction of one or two oxygen ions located at a distance of 1.988 Å from the titanium ion (the remaining four oxygen ions are at a distance of 1.944 Å). The authors suggest that the width of the signal at 4.2 K is determined by the spin–lattice relaxation time and not by the dipole–dipole interaction and on this basis they concluded that the distance between the Ti^{3+} ions should be not less than 6 Å.

In later studies[31–33] it was concluded from the analysis of the EPR signal parameters that the CU Ti^{3+} ions on the rutile surface are most probably formed when one oxygen ion is removed from the first coordination sphere of the initially octahedrally coordinated titanium ions. Fluorinated rutile specimens have also been studied[31–33] and it has been shown that CU Ti^{3+} ions involved in a square-pyramidal coordination, in the coordination spheres of which the oxygen ions have been partly replaced by fluoride ions, are present on the surface of such specimens. In these studies the EPR signal was assigned to surface CU ions not only from the analysis of the magnetic resonance parameters but also on the basis of the study of the formation of complexes by the CU ions with water and ammonia molecules. When the molecules of these substances were adsorbed at room temperature, they entered the first coordination sphere of the CU Ti^{3+} ions, altering their coordination to octahedral, which changed the corresponding EPR parameters. After the vacuum heat treatment at 400 °C of specimens with adsorbed water molecules, the initial form of the spectrum due to the Ti^{3+} ions and its intensity were restored, and the changes in the signal in repeated adsorption–desorption cycles were found to be fully reversible.

The conditions in the formation of the CU Ti^{3+} ions on the surface of deposited titanium silicate catalysts and their properties were investigated for the first time by Shvets and Kazanskii,[34] who showed that the reduction and subsequent vacuum heat treatment at 500 °C lead to the formation of CU Ti^{3+} ions. In the presence of a high titanium content in the specimens (≥2 wt.%) the ions exist mainly in square-pyramidal coordination, while in the presence of low titanium content (~0.2 wt.%) they exist in tetrahedral coordination. Both these and other ions serve as centres for the adsorption of the molecules of typical ligands, for example, water.

The surface Ti^{3+} ions of silica gel have been obtained[35] by the reaction of $Ti(CH_2C_6H_5)_4$ with hydroxy-groups. It has been shown by EPR that this involves the formation of $(-O-)_2TiR$ and $(-O-)TiR_2$ complexes, in which titanium ions can apparently be regarded as coordination unsaturated. The adsorption of H_2 and C_2H_4 entails the formation of complexes with a Ti–H bond.

The method of optical spectroscopy in diffusely scattered light has been used[36] to study the coordination state of surface quadrivalent titanium ions deposited on the surface of silica gel by the reaction of $TiCl_4$ with OH groups. Analysis of the position of the absorption band enabled the author to attribute it to octahedrally coordinated Ti^{4+} ions formed as a result of the interaction of the initial CU tetrahedrally coordinated Ti^{4+} ions with water molecules.

2. Vanadium Ions

Hitherto the most detailed studies have been made of the Cu V^{4+} ions [electronic configuration $(A)\ (3d)^1$]. V_2O_5 has been studied widely by EPR. However, it was not possible to observe effects associated with the formation of surface CU ions. Only recently it has been shown[37] that tetrahedrally coordinated V^{4+} ions, whose EPR spectrum is not observed at room temperature, are formed on the surface of V_2O_5 subjected to a vacuum heat treatment at temperatures up to 200 °C. At the same time V_2O_5 contains also V^{4+} ions in square-pyramidal coordination, although it is not clear whether they are present in the bulk phase or on the surface of the catalyst. It has been concluded that the tetrahedrally coordinated ions serve as centres for the adsorption of formic acid molecules. Following adsorption, the tetrahedral coordination of the V^{4+} ions changes to square-pyramidal and their spectrum is observed at room temperature.

The CU ions on the surface of different deposited catalysts have been studied in greater detail. It has been shown[38] that the surface of vanadium silicate catalysts reduced *in vacuo* at 500 °C contains tetrahedrally coordinated V^{4+} ions. The authors arrived at this conclusion by comparing the EPR spectra of the reduced catalysts measured at 20 K and of VCl_4 in which the V^{4+} ion is tetrahedrally coordinated to chloride ions. The EPR spectrum of the tetrahedrally coordinated V^{4+} ions, measured at room temperature, is greatly broadened and can hardly be observed. It has been shown[38] from the change in the spectrum after the adsorption of water at room temperature that these ions serve as centres for the adsorption of water molecules. After adsorption, the EPR spectrum of the tetrahedrally coordinated V^{4+} ions disappears and is replaced by the vanadyl ion spectrum. This spectrum can be observed both at low and room temperatures. After the adsorption of water molecules, the V^{4+} ions are in square-pyramidal or distorted octahedral coordination where one

of the bonds is shortened, which in fact results in the formation of the vanadyl bond.

Detailed EPR studies[39-42] of the properties of tetrahedrally coordinated CU V^{4+} ions on the surface of V/SiO_2 catalysts showed that they adsorb not only H_2O but also NH_3, CH_3OH, C_2H_5OH, SO_2, N_2O, and CO. Even complexes with the molecules of N_2,[39] olefins (for example, propene[43]), and aromatic compounds (for example o-xylene, toluene, and benzene[44,45]) have been observed. The parameters of the EPR spectra of the complexes with hydrocarbons are close to those of the vanadyl complexes.

It has been shown[9,46,47] that the adsorption of O_2 on the reduced V/SiO_2 catalysts in the temperature range 77–300 K leads to the appearance of two new EPR signals with $g_1 = g_1 = 2.023$, $g_2 = 2.011$, $g_3 = 2.004$, and $g_1 = 2.026$ ($g_\parallel < g_1$), which are due to the adsorbed O_2^- and O^- radical-anions. The O_2^- radical-anions are formed as a result of electron transfer from the CU V^{4+} ions to adsorbed water molecules. The O^- radical-anions are formed on dissociation of O_2^-. A hyperfine structure due to one vanadium nucleus is observed in the EPR spectra, which indicates the stabilisation of the radical-anions in the first coordination sphere of the CU vanadium ions. A calculation has been carried out[48] for a model of the adsorption complex formed under these conditions, while in other investigations the reactivity of complexes with charge transfer from the CU ion to oxygen was studied in detail by EPR.[49-52]

Tetrahedrally coordinated V^{4+} ions are formed on the surface of V/SiO_2 catalysts not only on thermal reduction but also on photoreduction at 77 K in an atmosphere of H_2.[53,54] Two absorption bands, at 13 100 and 19 500 cm^{-1}, correspond to these ions in the diffuse electronic spectra, which indicates an appreciable distortion of their tetrahedral coordination. It is of interest that the photoreduction in an atmosphere of CO leads to the formation of CU V^{3+} and not V^{4+} ions. These ions cannot be detected by EPR at 77 K and above, but they have been reliably identified from the optical spectra (absorption bands at 11 800, 17 000, and 23 000 cm^{-1}). The H_2O, NH_3, CO, and C_2H_4 molecules can enter the first coordination sphere of the V^{3+} ions with formation of surface complexes.

The coordination states of the ions in the V/Al_2O_3 and V/SiO_2 catalysts are different. The characteristic vanadyl ion signal has been observed in the EPR spectra of aluminovanadium specimens.[38] The adsorption of water molecules does not alter its form. It was concluded that the ions are present in a layer of γ-Al_2O_3 near the surface and have square pyramidal coordination. Other workers[39,55,57] arrived at an analogous conclusion. However, one should note that, since the EPR parameters of the V^{4+} ions in "vanadyl" coordination are determined mainly by the presence of a shortened metal–oxygen bond, it is difficult to reach a conclusion from the data obtained whether such square pyramidal ions, even if they are located on the surface, can serve as centres for the adsorption of polar molecules. Some increase in the intensity of the signal due to vanadyl ions has been observed after the adsorption of water and certain other substances. This can be explained by the fact that, before adsorption, CU V^{4+} ions were present on the surface in a non-vanadyl type of coordination. The results of a study[57] where bands corresponding to vanadyl ions and tetrahedrally coordinated V^{4+} ions were found in the EPR spectra of deposited aluminovanadium and vanadium–magnesium catalysts are of interest.

The coordination state of quadrivalent vanadium ions deposited on the surfaces of cabosil, γ-Al_2O_3, gibbsite, and boehmite [modifications of Al_2O_3] has also been investigated by allowing the surface OH groups to react with VCl_4.[58] When it is adsorbed on cabosil heated to 700 °C, VCl_4 reacts with only one OH group, forming tetrahedrally coordinated V^{4+} ions. V^{4+} ions which are both tetrahedrally coordinated and having the vanadyl coordination are formed on rehydrated cabosil. The ions on the γ-Al_2O_3 surface always have the vanadyl coordination, while on boehmite the authors observed a complex spectrum with three g-factors, apparently indicating the formation of ions involved in a strongly distorted octahedral coordination.

CU V^{4+} ions have been observed and investigated on the surface of vanadium–zirconium catalysts.[59] A distinctive feature of these systems is that both CU ions and surface complexes with adsorbed water, methanol, and ammonium molecules have EPR spectra characteristic of the vanadyl coordination. The formation of complexes is manifested by a change in the magnetic resonance parameters, in the first place in $A_\perp$. Thus the CU V^{4+} ions of the vanadium–zirconium catalysts are apparently involved in a square-pyramidal coordination.

Data concerning the existence of surface CU V^{3+} ions on vanadium–phosphorus catalysts deposited on silica gel have been published.[60] These ions form surface complexes with water molecules. The subsequent adsorption of oxygen at room temperature leads to their oxidation to V^{4+}, which is manifested by a sharp increase of the EPR signal intensity.

The V^{5+} ions, having the electronic configuration $(A)(3d)^0$, are non-paramagnetic and cannot be detected by EPR. The optical reflection and luminescence spectroscopic methods have therefore been used to detect the CU ions and to investigate their properties.[61-63] It has been shown that the CU V^{5+} ions on the surfaces of vanadium silicate catalysts have distorted tetrahedral coordination (one of the vanadium–oxygen bonds is appreciably shortened and constitutes the vanadyl bond) and are capable of adsorbing various molecules (H_2O, NH_3, alcohols, etc.). Tetrahedrally coordinated CU V^{5+} ions have been detected by reflection spectroscopy also on the surfaces of vanadium silicate catalysts prepared by molecular layer-by-layer deposition.[64-66] It has been suggested[67] that the presence of tetrahedrally coordinated CU vanadium ions on the surface of silica gel is responsible for the selectivity of the oxidation of propene to acrolein.

3. Chromium Ions

The extensive application of chromium-containing catalysts in various industrial processes (polymerisation of ethylene, dehydrocyclisation, dehydrogenation etc.) led to the publication of a large number of studies on such catalysts by EPR and optical spectroscopic methods. Although the coordination state of the chromium ions on the catalyst surface has been discussed in many communications, much less attention has been devoted to the direct investigation of the formation and properties of CU ions. We shall examine them in order of decreasing oxidation state of the chromium ions.

The Cr^{6+} ions have no unpaired electrons and therefore do not give rise to an EPR signal. However, they have an intense absorption band in the near ultraviolet due to a ligand-to-cation charge-transfer transition. When Cr^{6+} ions are deposited on silica gel and aluminosilicate, dichromate ions are formed,[68] while their deposition on γ-Al_2O_3 leads to chromate ions.[68,69] It has been shown[70-72] that chromate ions are present together with dichromate ions on the surface of silica gel.

When deposited chromium catalysts are heated in air or *in vacuo*, Cr^{5+} ions are formed, which were first observed by EPR.[73-76] The amount of Cr^{5+} ions in catalysts subjected to a high-temperature treatment *in vacuo* or in oxygen is

usually several per cent relative to the total deposited chromium.[73,75–79] The remaining chromium ions exist mainly in the hexavalent state. There is also several per cent of ions in the tervalent state.

The EPR spectrum of the Cr^{5+} ions in aluminochromium catalysts consists of an almost isotropic line with a width of approximately 40–50 G and $g = 1.96$. When the spectrum is measured in the 8 mm range, the line becomes anisotropic.[76] On the basis of the broadening of the line after the adsorption of oxygen, it has been concluded[77] that it is due to surface ions. It has been shown[38] that the Cr^{5+} ions in the aluminochromium catalysts subjected to a vacuum heat treatment at 500 °C are stabilised in the form of chromyl ions $(Cr{=}O)^{3+}$ in truncated square pyramidal coordination.

The reflection spectra of the aluminochromium catalyst activated at 300 °C consist of three bands with absorption maxima at 14 000, 18 200, and 22 700 cm^{-1}.[80,81] These spectra are close to those of various complexes containing the chromyl ion $(Cr{=}O)^{3+}$. In view of this finding and also from the comparison of the experimental g-factors of the EPR signal ($g_\perp = 1.97$ and $g_\parallel = 1.95$), measured in the 8 mm range, with the values calculated theoretically the authors concluded that the Cr^{5+} ions on the surface of the aluminochromium catalysts are stabilised in square-pyramidal coordination. The optical and EPR spectra of the catalysts activated at 300° and 500 °C are different. It was concluded that the Cr^{5+} ions can exist on the surfaces of the aluminochromium catalyst in two coordinations—tetrahedral and square-pyramidal. The number of centres of each type depends on the temperature of the heat treatment of the specimens.

EPR studies on chromium(V) ions in catalysts on other carriers have shown that the absorption line form for these ions depends on the nature of the carrier, indicating different types of coordination of the Cr^{5+} ions on the surfaces of different carriers. A theoretical calculation led Aleksandrov et al.[82] to conclude that the ions in a deposited chromium silicate catalyst are stabilised on the surface of silica gel in oxygen tetrahedra. The tetrahedra are distorted, leading to anisotropy of the g-factor of the EPR signal. By measuring the EPR spectra in the range from room temperature to 20 K, it was possible to confirm this conclusion and also to show that only less than 1% of the Cr^{5+} ions have square-pyramidal coordination.[38] Measurements of the integral intensities of the spectra have shown that both at room temperature and at the temperature of liquid nitrogen only a proportion of the ions are manifested. The explanation is that the catalyst surfaces contain tetrahedrally coordinated Cr^{5+} ions distorted in different ways. The distortions of the tetrahedra lead to differences in the spin–lattice relaxation times of the Cr^{5+} ions, which entails in its turn a different dependence of the width of the signals on the temperature of measurement of the EPR spectra. As a result, some of the Cr^{5+} ions give rise to absorption lines in the measurement at room temperature and even at the temperature of liquid nitrogen which are so broad that they cannot be observed by EPR. Thus measurements of the concentration of chromium ions in chromium silicate catalysts from the intensities of the EPR spectra must be carried out at least at the temperature of liquid hydrogen.

Measurements of the optical spectra of deposited chromium silicate catalysts have also confirmed that the Cr^{5+} ions are stabilised on the surface in oxygen tetrahedra. These investigations were first made by Pecherskaya and Kazanskii.[80,81] They observed that the optical spectra of the catalyst and the compound $Sr_5(CrO_4)_3OH$, in which the Cr^{5+} ions are tetrahedrally coordinated, are identical. Later these conclusions were confirmed in other investigations.[71,72]

Studies on chromium oxide catalysts where aluminosilicates are used as carriers have shown that Cr^{5+} ions in both tetrahedral and square-pyramidal coordination are formed on the surface, i.e. ions characteristic of chromium silicate and aluminochromium catalysts.[83,84]

We shall now consider the results of EPR and optical spectroscopic studies of the interaction of adsorbed molecules with surface Cr^{5+} ions. Detailed EPR investigations of the character of the interaction of water and ammonia molecules with tetrahedrally coordinated CU Cr^{5+} ions on the SiO_2 surface have been carried out.[38] Analysis of the EPR spectra at 20 K has shown that the adsorption of H_2O and NH_3 at room temperature leads to the formation of Cr^{5+} ions in square pyramidal coordination. For specimens activated at 500 °C, the ratio of the $(CrO_4)^{3-}$ (tetrahedron) and $(Cr{=}O)^{3+}$ (square pyramid) signal intensities was 100; after the adsorption of H_2O and NH_3 for 1 h at room temperature, the $(CrO_4)^{3-}$ signal intensities were negligibly small, while the $(Cr{=}O)^{3+}$ signal intensities were 4 and 140 respectively. Thus the adsorption of H_2O molecules at room temperature leads to the disappearance of most of the Cr^{5+} ions. The phenomenon is caused by the disproportionation of the Cr^{5+} ions to Cr^{6+} and Cr^{4+} ions when water is adsorbed.

The adsorption of water also leads to a fourfold increase of the concentration (compared with the initial value) of Cr^{5+} ions having square-pyramidal coordination. After NH_3 adsorption the concentration of the Cr^{5+} ions exceeds the initial value, which is apparently associated with the partial reduction of the Cr^{5+} [Cr^{6+}?] ions by ammonia. Thus the tetrahedrally coordinated Cr^{5+} ions on the SiO_2 surface serve as centres for the adsorption of polar molecules, i.e. they are CU ions. The adsorbed molecules enter the first coordination sphere of the CU ions and form surface complexes.

Changes in the coordination state of Cr^{5+} ions on the γ-Al_2O_3 surface, occurring on adsorption of various molecules, are much more difficult to observe. However, in this case too it has been possible to establish[38] that the adsorption of H_2O molecules decreases the anisotropy of the absorption line due to ions with a square-pyramidal coordination. Measurement of the intensities of these spectra in the range from room temperature to 20 K showed that Curie's law holds in both cases. It was therefore concluded that both before and after the adsorption of H_2O, the Cr^{5+} ions forms a chromyl bond with one of the oxygen ions in the catalyst lattice.

The formation of complexes by the adsorbed molecules of water, ammonia, alcohols, and aldehydes with the CU Cr^{5+} ions has also been observed in other studies.[85–87] The EPR spectra of the complexes are characteristic of Cr^{5+} ions with a shortened chromyl bond. Thus in all cases the chromium ions in such complexes have a distorted octahedral or square-pyramidal coordination.

The reduction of the deposited chromium oxide catalysts in H_2 or CO leads to the disappearance of the absorption lines from the optical spectra and of the EPR signals characteristic of the Cr^{6+} [sic] and Cr^{5+} ions. The EPR spectrum of the reduced deposited aluminochromium catalysts consists of a superposition of a very broad asymmetric line in the range 1500–1800 G (δ-phase) and a symmetrical line with $g \cong 2$ (β-phase).[76] The δ-phase consists of magnetically isolated Cr^{3+} ions in an axial electric field (apparently in the field of a distorted octahedron). The broad symmetrical line is due to the Cr^{3+} ions forming a magnetically concentrated system. The Cr^{3+} ions of the β-phase apparently form clusters in which there is a fairly intense exchange and dipole–dipole interaction between the ions. However, the structure of the β-phase differs from that of Cr_2O_3 and is

closer to the chromium oxide gel, which is paramagnetic at room temperature.

When oxygen is admitted at room temperature, the intensity of the EPR line due to the δ-phase diminishes and the EPR signal characteristic of the Cr^{5+} ions appears.[76,88,89] The intensity of the δ-phase signal does not change under these conditions, which shows that some of the Cr^{3+} ions of the β-phase are present on the catalyst surface.

The properties of surface CU ions in reduced aluminochromium catalysts have been studied in greater detail in other investigations.[90–92] It follows from the analysis of the optical spectra of the reduced specimens containing adsorbed water that all the Cr^{3+} ions are involved in octahedral coordination. The desorption of water at 500 °C alters both the optical and EPR spectra. The width of the β-phase line in the EPR spectra increases from 750 to 1070 G. After the adsorption of water at room temperature, the line width diminished and returned to the initial level. The adsorption of methanol at room temperature likewise entails an analogous effect. In contrast to this, the adsorption of ammonia does not induce narrowing of the β-phase absorption line. The broadening of the line on desorption of water was accounted for by the diminution of the indirect exchange interaction via the O_2 ions as a consequence of the formation of CU Cr^{3+} ions in a coordination sphere of which one or several oxygen atoms are missing. On adsorption, polar molecules enter the coordination spheres of all the ions and, when the adsorbed molecule contains oxygen atoms, the exchange interaction intensifies and the EPR line becomes narrower.

Measurements of the optical spectra of the aluminochromium catalysts agree well with EPR data.[91,92] After the desorption of water, maxima at 10500, 28800, and 31200 cm^{-1}, corresponding to Cr^{3+} ions with square-pyramidal coordination, appear together with the signals of octahedrally coordinated Cr^{3+} ions. The adsorption of ammonia and methanol shifts the absorption maxima of the CU Cr^{3+} ions with square-pyramidal coordination to the short-wavelength region. These effects are caused by the formation of surface complexes with a distorted octahedral coordination. It is of interest to note that the CU Cr^{3+} ions with square-pyramidal coordination form complexes with ethylene and benzene on the surface of aluminochromium catalysts at room temperature.[92]

It has been observed[88] that, after the reduction with hydrogen and subsequent vacuum heat treatment of the deposited aluminochromium catalysts containing 2 wt.% of chromium, the β-phase band virtually disappears from the EPR spectra, reappearing after the adsorption of water at room temperature. The authors assume that the disappearance of the line is associated with the reduction of the Cr^{3+} ions to Cr^{2+} and its appearance after the adsorption of water is due to the oxidation of the Cr^{2+} ions to Cr^{3+}. Although there is no doubt about the formation of Cr^{2+} ions in the reduced aluminochromium catalysts,[93–95] nevertheless the increase of the intensity of the EPR band due to the β-phase of the Cr^{3+} ions, observed also in the adsorption of methanol,[90–92] is undoubtedly caused, in our view, by its narrowing and the increase of the amplitude as a consequence of the formation of surface complexes, as stated in the discussion just completed, and not by the oxidation of the Cr^{2+} ions by water molecules, which hardly occurs at room temperature.

The complexes of Cr^{3+} ions, deposited on the carrier surface by different methods, as well as the CU ions formed on their decomposition, have been investigated by EPR and optical spectroscopy in several studies. It was shown that the vacuum heat treatment of the complexes $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$, and several others at 500 °C leads to the formation of CU Cr^{3+} ions, characterised by a structureless absorption in a broad region of the optical spectrum.[96,97] Such CU ions are centres for the adsorption of polar molecules. In the adsorption of water molecules, their coordination returns to the initial octahedral coordination. The study of the adsorption of ethylene on CU Cr^{3+} ions, stabilised on the silica gel surface, has shown that these ions serve as polymerisation centres.[96,97]

Chromium(III) complexes grafted or deposited on the surface have been investigated by optical spectroscopic and EPR methods.[98–100] The high-temperature dehydration of the specimens caused the same broadening of the EPR line as for the aluminochromium catalyst.[90–92] It is caused by the formation of CU ions.[100]

The reduction of deposited chromium silicate catalysts in an atmosphere of CO or H_2 leads to the formation mainly of Cr^{2+} ions, in contrast to the aluminochromium systems.[40,93,95,101] The chromium silicate catalyst reduced in CO at 500 °C assumes a blue colour. Its optical spectrum consists of one band with an absorption maximum at 13000 cm^{-1}. Absorption bands have not been observed in the EPR spectrum of such a specimen either at room temperature or at the temperature of liquid nitrogen. The adsorption of polar molecules (water or ammonia) at room temperature does not entail the appearance of absorption lines in the EPR spectra, but it does induce a change in the optical spectrum: after the adsorption of water, the absorption maximum undergoes a hypsochromic shift and is observed as 15500 cm^{-1}, while after the adsorption of ammonia it occurs at 16400 cm^{-1}. The presence of a single absorption maximum in the optical spectra of reduced chromium silicate specimens both before and after the adsorption of polar molecules and the hypsochromic shift of this maximum after adsorption indicate the tetrahedral coordination of the Cr^{2+} ions in the reduced chromium silicate specimen.[40,95] After adsorption at room temperature, the water and ammonia molecules enter the first coordination sphere of the tetrahedrally coordinated CU Cr^{2+} ions without altering their oxidation state and their coordination is built up to the octahedral coordination. It has also been shown that the concentration of Cr^{2+} ions depends on the nature of the reductant and the amount of deposited Cr^{6+} ions.

The CU Cr^{2+} ions on the SiO_2 surface are also capable of forming complexes with CO molecules without change in the oxidational state.[101–103] Depending on the pressure and temperature, the adsorption of CO can lead to complexes containing both two molecules and one molecule. The interaction of CU ions with oxygen induces their rapid oxidation, which makes it possible to employ reduced chromium silicate systems for the elimination of traces of oxygen from various gases.[93] Chromium silicate catalysts for the polymerisation of ethylene also contain CU Cr^{2+} ions, which are believed to be the active centres for this reaction.[93,101,104] However, doubts have been cast on this conclusion[96,97] and it has been shown that the active catalyst contains CU Cr^{3+} ions. It has been recently established that both these valence states of chromium ions are active in the polymerisation of ethylene.[105]

CU Cr^{2+} ions on the SiO_2 surface can be obtained not only by thermal reduction at high temperatures but also by photochemical reduction in CO at 20 °C.[106] These ions have a tetrahedral coordination and are characterised by the absorption band at 11800 cm^{-1}. Photochemical reduction leads to the formation of CU ions which are more uniform as regards coordination than those obtained by thermal reduction. A very interesting property of CU Cr^{2+} ions obtained by photochemical reduction has been noted, namely their ability to undergo a rearrangement of their coordination environment at temperatures above 150 °C, which alters

their optical spectrum and properties. The reduction of the Cr/SiO_2 catalyst in CO at the temperature of liquid nitrogen leads to the formation of CU Cr^{4+} ions and not Cr^{2+} ions. Absorption bands due to the *d–d* transitions at 9400 and 17 000 cm^{-1} correspond to these ions. Apparently the existence of Cr^{4+} ions on the catalyst surfaces was demonstrated fairly reliably for the first time by Pershin et al.[106] It has also been shown that the CU Cr^{4+} ions form the complexes $Cr^{6+}.NO^{2-}$ with NO molecules, transferring two electrons to the adsorbed molecule, which leads to the appearance of an EPR signal with $g_{\parallel} = 2.046$, $g_{\perp} = 1.99$, $A_{\parallel}^{N} = 0$ G, and $A_{\perp}^{N} = 10$ G.

The formation of CU Cr^{2+} ions on the surfaces of reduced aluminochromium catalysts has been observed by EPR from the interaction with the adsorbed NO molecules.[107] The adsorption of NO at room temperature led to the formation of the surface complexes $Cr^{+}.NO^{+}$ in a low-spin state as a result of electron transfer from the adsorbed molecules to the CU Cr^{2+} ions.

The formation of CU ions in the vacuum heat treatment of mononuclear and dinuclear complexes of Cr^{2+} ions deposited by ion exchange or grafted on to SiO_2, γ-Al_2O_3, and MgO has been investigated.[96,108] The vacuum heat treatment of such complexes on SiO_2 leads to the formation of tetrahedrally coordinated Cr^{2+} ions, while on MgO and γ-Al_2O_3 a considerable proportion of the ions are oxidised to Cr^{3+}.

In conclusion of this Section, one should note that, in connection with the extensive application of chromium-containing systems as catalysts, the formation and properties of the CU chromium ions in a wide variety of oxidation states has been studied in greatest detail compared with other transition metal ions.

4. Manganese Ions

In the EPR study of manganese oxides, both pure and deposited on MgO,[109–112] it was not possible to separate the spectra of the bulk-phase and surface ions, although an increase of the width of the lines due to the Mn^{2+} ions with increase of the specific surface of MgO, caused by the formation of surface ions, has been noted, for example, by Cordishchi et al.[110] Yamamura et al.[111] assumed that they were able to observe surface octahedrally coordinated Mn^{2+} ions in MgO, but later[112] this conclusion was subjected to a fairly convincing criticism.

The Mn^{2+} ions deposited on silica gel surface have been investigated[113,114] by EPR. At a manganese concentration up to several per cent, a broad line due to a magnetically concentrated phase or clusters of Mn^{2+} ions was observed. At low concentrations it was possible to observe a spectrum which was attributed to individual Mn^{2+} ions. The change of their symmetry and coordination compared with a solution has been noted,[114] but in the above studies the formation of CU manganese ions was not investigated under conditions of high-temperature hydration, although their existence on the SiO_2 surface can be demonstrated with the aid of the interaction of manganese silicate specimens with oxygen: the presence of such ions permits the use of these systems as sorbents for trace amounts of oxygen in olefins.[115] Yamamura et al.[111] showed only that, in the high-temperature dehydration of octahedral complexes of Mn^{2+} ions deposited on silica gel, their EPR signal disappears, apparently owing to the great band width for the highly distorted surface complexes.

5. Iron Ions

The conditions in the formation and properties of CU Fe^{2+} ions on SiO_2 have been investigated[116] by diffuse reflectance optical spectroscopy. The formation of CU ions of two types was established: tetracoordinated at activation temperatures *in vacuo* up to 700 °C and bicoordinated at 1000 °C. The former adsorb H_2O, NO, and O_2 at room temperature, while the latter also adsorb CO, C_2H_4, and N_2 molecules. It has been noted that the complexes with CO, O_2, and N_2 are unstable and are readily decomposed after the adsorption of water. The catalytic reactivity of such CU Fe^{2+} ions on SiO_2 in the reactions involving the decomposition of NO and its reduction by CO has been studied.[117]

The formation of surface compounds of Fe^{3+} ions in the Fe_2O_3–SiO_2 and Fe_2O_3–SiO_2–Al_2O_3 catalysts in the high-temperature heat treatment in air have been investigated by EPR and diffuse reflection spectroscopy.[118] It has been observed that water molecules and hydroxy-groups enter the coordination sphere of the surface Fe^{3+} ions.

6. Cobalt Ions

The study of deposited cobalt silicate catalysts by the joint application of the EPR and optical spectroscopic methods has shown that the vacuum heat treatment at 700 °C leads to the formation of surface CU Co^{2+} ions in a tetrahedral coordination and that tetrahedra compressed along the trigonal axis are produced.[119] The optical spectra change after the adsorption of H_2O and NH_3 molecules at 20 °C, which indicates the formation of complexes with a square-pyramidal or highly distorted octahedral coordination.

The optical spectra of specimens obtained by impregnating silica gel with aqueous $CoCl_2$ and $Co(NO_3)_2$ solutions and by ion exchange have been compared.[99] It was found that the properties of the surface complexes depend both on the methods of their deposition on the surface and on the nature of the cobalt compound. Thus, whereas the octahedral coordination of the Co^{2+} ion on the catalyst surface, obtained by impregnation with a $Co(NO_3)_2$ solution, does not change after drying at room temperature, nevertheless under the same conditions the octahedral coordination of the Co^{2+} ions obtained from $CoCl_2$ changes to the tetrahedral coordination. The introduction of Co^{2+} ions by ion exchange immediately leads to tetrahedrally coordinated ions. After specimens prepared by impregnation had been heat treated in air at 500 °C, cobalt ions with a tetrahedral coordination are also formed.

Much attention has been devoted to the investigation of the state of the cobalt ions deposited on Al_2O_3 and MgO.[120–122] Changes have been observed in the optical spectra of tetrahedrally coordinated Co^{3+} ions on the Al_2O_3 surface after the adsorption of propene.[120] On the MgO surface, some of the Co^{2+} ions are in square-pyramidal coordination, which changes to distorted octahedral coordination on adsorption of NH_3.[122]

The surface CU Co^{2+} ions have been detected by optical spectroscopy also in mixed Co–Mo–Al_2O_3 catalysts.[123] The changes in the spectra after the adsorption of CO, H_2O, thiophen, and pyridine indicate the localisation of the main bulk of the ions in the oxygen tetrahedra. A small proportion of the Co^{2+} ions are present on the surface in a trigonal coordination. Analysis of the optical spectra showed that the presence of the MoO_3 phases is essential for the formation of such CU trigonally coordinated ions.

7. Nickel Ions

In one of the first studies of nickel ions in catalysts by optical spectroscopy,[124] it was shown that the spectrum of dispersed NiO, obtained *in vacuo*, resembles the spectrum of the complex $Ni(H_2O)_6^{2+}$. The absorption of O_2 leads to the same changes in the spectra of the specimens as the introduction of Li^+ ions. On this basis, it has been suggested that the effect of O_2 is associated with the conversion of some of the Ni^{2+} ions into Ni^{3+}. The adsorption of H_2 and CO leads to the partial reduction of the oxide and the formation of Ni^+ ions. Klier[124] was unable to establish whether the Ni^+ and Ni^{3+} ions formed on adsorption are present on the surface layer of NiO or in its layer next to the surface.

Much attention has been devoted in the literature to nickel silicate catalysts. In one of the first studies of these catalysts it was shown[125] that the initial distorted octahedral coordination of the ions in specimens prepared by impregnation with aqueous $NiCl_2$ solutions persists on heating in air up to 500 °C. It was noted that the adsorption of ammonia influences the optical spectra of such specimens albeit fairly weakly. The coordination of the Ni^{2+} ions remains octahedral after adsorption. Conditions for the formation of CU Ni^{2+} ions on the SiO_2 surface were found in subsequent investigations.[126] It was shown that the ions are most likely to have distorted tetrahedral coordination and serve as centres for the adsorption of polar molecules.

Measurements of optical reflectance spectra somewhat later[127] led to the conclusion that the Ni^{2+} ions on the SiO_2 surface after evacuation at 1000 °C have a coordination number of two and their coordination sphere can therefore include up to four adsorbed molecules. The formation of surface complexes with CO, C_2H_4, NO, and NO_2 molecules have been observed. One should note that the possibility of such low coordination of surface ions (with a coordination number of two) requires, in our view, more rigorous evidence, although the existence of CU Ni^{2+} ions and their complexes on the SiO_2 surface is not in fact open to doubt.

Using the EPR method, the interaction of surface Ni^{2+} ions with anthracene and diphenylpicrylhydrazine to form charge-transfer complexes has been investigated by EPR.[128–130] It has been suggested that anthracene is adsorbed on Ni^{2+} ions with tetrahedral coordination.

Together with the traditional method for the preparation of deposited catalysts by impregnation with inorganic nickel salts, the catalysts have been prepared by the interaction of bis-π-allylnickel with SiO_2.[131] It has been established that, when the specimens are heated in O_2 above 300 °C, the organic ligand is fully oxidised and CU Ni^{2+} ions in a state with a low symmetry are formed. The exact coordination state could not be established.

The formation of CU nickel ions on MgO has also been investigated by EPR and optical spectroscopy,[132,133] It has been observed that the intensity of the EPR signal due to the Ni^{2+} ions involved in an octahedral coordination increases after the adsorption of H_2O, NH_3, and HBr molecules at 20 °C. This was caused by the presence on the surface of CU Ni^{2+} ions involved in a square-pyramidal or tetrahedral coordination, which were undetectable by the EPR method before the adsorption. Analysis of the optical spectra led the authors to give preference to the square-pyramidal coordination.[133]

On reduction of the Ni/SiO_2 catalyst by ultraviolet light in H_2 at 77 K, the formation of CU Ni^+ ions with distorted tetrahedral coordination, containing an H_2 molecule in the coordination sphere, was observed.[134] Their EPR spectrum is characterised by the g-factors: $g_1 = 2.015$, $g_2 = 2.30$, and $g_3 = 2.64$. After vacuum heat treatment at 520 K, the coordination environment of these ions changes, as shown by the change in the g-factor. The CU Ni^+ ions form complexes with the adsorbed O_2, H_2O, NH_3, and CO molecules, complexes with one, two, and three CO molecules being present in the last case. At a low temperature, even N_2 molecules can enter the coordination spheres of the CU Ni^+ ions.

The nickel ions deposited on the silica gel surface can be reduced to the metallic state. Examination of studies on such catalysts is outside the framework of the present review. Nevertheless we would wish to note an interesting study[135] in which the poisoning of a nickel silicate catalyst in the course of the hydrogenation of butene was investigated by ultraviolet spectroscopy and it was shown that this entails the formation of surface complexes of nickel with hydrogen sulphide and the hydrocarbon. These complexes can be extracted from the catalyst and the spectra of the solution and the surface complex are analogous.

8. Copper Ions

The EPR study of Cu^{2+} ions deposited on SiO_2 by impregnation with an aqueous $Cu(NO_3)_2$ solution showed that CU Cu^{2+} ions in different coordination environments, particularly in distorted tetrahedral coordination, are formed on vacuum heat treatment at 500 °C.[136] Some of the CU Cu^{2+} ions cannot be detected at all by EPR at 77 K apparently owing to the short spin–spin lattice relaxation time. The H_2O, NH_3, C_5H_5N, C_2H_5OH, and SO_2 molecules adsorbed at 20 °C enter the coordination spheres of the CU Cu^{2+} ions and form surface complexes having distorted octahedral coordination. Reactions involving substitution in the coordination spheres of the surface complexes of one set of adsorbed molecules by another have been observed.

The adsorption properties of the CU Cu^{2+} ions on the SiO_2 surface after the introduction of copper ions by ion exchange in the form of the $Cu(NH_3)_4^{2+}$ and $Cu(H_2O)_6^{2+}$ ccmplexes have been investigated.[137,138] It was shown that the initial copper complexes lose the coordinated ligand molecules on vacuum heat treatment and form CU Cu^{2+} ions. In the case of specimens prepared by exchange with $Cu(NH_3)_4^{2+}$, tetrahedrally coordinated ions are formed, as in the study of Bogdanov et al.[136] The coordination of the ions in catalysts prepared by exchange with $Cu(H_2O)_6^{2+}$ could not be determined owing to the poor resolution of the EPR spectrum. The adsorption of NH_3 and C_5H_5N molecules leads to the formation of tetragonally distorted octahedral complexes of the CU ions. In the adsorption of H_2O two different EPR spectra were observed, which indicates the existence of two types of complexes with different coordination sphere symmetries.

The formation of exchange-linked ion pairs, which possess the properties of CU ions, i.e. are able to stabilise the different molecules in their coordination spheres, has been observed[139] for deposited copper silicate specimens heated *in vacuo* at 650–950 °C. After the adsorption of polar and non-polar molecules, the ion pairs decomposed and the signals due to the isolated Cu^{2+} involved in different types of coordination were observed in the EPR spectra. Thus octahedral complexes were formed after the adsorption of NH_3 and H_2O and complexes involved in coordination corresponding to a truncated octahedron or a tetrahedron compressed along the threefold axis (the EPR spectra have $g_\perp > g_\parallel$) were noted after the adsorption of C_2H_4 and CO. The copper ions forming part of the composition of the ion pairs are also capable of forming covalently bound complexes with O_2 molecules.

Much attention has been devoted in the literature to aluminocopper catalysts.[140–143] Although it has now been fairly reliably established that the bulk-phase copper ions

in such catalysts have both octahedral and tetrahedral coordination,[144] the coordination state of the surface Cu^{2+} ions has not been determined quite so reliably. On the basis of the analysis of EPR spectra, it has been suggested[145] that the Cu^{2+} ions on the surfaces of oxidised specimens are involved mainly in square-pyramidal coordination. On reduction, some of the Cu^{2+} ions are converted into Cu^0 atoms, which form diamagnetic clusters.

In an EPR study of the state of copper in copper-magnesium oxide catalysts,[146] four types of signals were observed, one of which was due to the Cu^{2+} ions in an axial field ($g_\parallel = 2.34$, $g_\perp = 2.058$, $A \cong 150$ G, $B = 28$ G) and was attributed to surface copper complexes with CO_2 molecules. This finding indicates the formation of CU Cu^{2+} ions, but their coordination state could not be determined. The appearance of the characteristic EPR spectra after the adsorption of molecules revealed the presence of CU Cu^{2+} ions also on the CuO surface.[147,148] It has been shown that the adsorption of various amines at room temperature entails the appearance of broad signals ($\Delta H \cong 700$–900 G), which has been attributed to surface copper complexes. Following the adsorption of NH_3, a fairly narrow signal arose with g-factors of 2.211, 2.122, and 2.071. The Cu^{2+}–NH_3 complexes responsible for this signal are stable up to 130 °C. The coordination state of the Cu^{2+} ions before the adsorption was not investigated.

IV. THE IONS OF METALS IN THE SECOND AND THIRD TRANSITION PERIODS

1. Molybdenum Ions

There have been very many fewer studies by EPR and optical spectroscopy of the CU ions of metals in the second and third transition Periods than for the metal ions of the first transition Period. Only molybdenum ions have been studied in fair detail.

In oxidised molybdenum silicate specimens molybdenum exists in a hexavalent state and forms tetrahedral and octahedral complexes according to reflectance spectroscopic data.[149–153] An analogous conclusion was also reached from measurements of luminescence spectra.[62] The surface acidity of the carrier influences significantly the position of the charge transfer band for the Mo^{6+} ions, which is due to the formation of polymeric species incorporating both tetrahedral and octahedral molybdenum ions.[149] It has been suggested that these species are the anions of molybdosilicic heteropolyacid.[154,155]

The reduction of molybdenum silicate catalysts leads to the appearance of an intense EPR signal due to the Mo^{5+} ions with the $A(4d^1)$ electronic configuration.[154–158] Analysis of the spectrum showed that these ions have molybdenyl coordination ($g_\perp = 1.940$; $g_\parallel = 1.882$; $B = 44$ G, $A = 98$ G).[154, 156,157] Furthermore, a considerable proportion of the CU ions on the surface have apparently distorted tetrahedral coordination.[156] At room temperature these ions were not detected in the EPR spectra and at 77 K their signal was superimposed on that due to the molybdenyl ions. On adsorption of H_2O, NH_3, CO, and other molecules, surface complexes of the CU ions are produced. The EPR spectra indicate their distorted (compressed) octahedral structure. The EPR spectrum of the CU Mo^{5+} ions involved in a low coordination could be observed in a "pure" form on the Mo/SiO_2 surface on reduction of the catalyst by exposure to light in an atmosphere of H_2 and not thermally.[159] The EPR parameters are as follows: $g_1 = 1.811$, $g_2 = 1.929$, $g_3 = 1.952$, $A_1 = 82$ G, $A_2 = A_3 = 29$ G. The photochemical reduction of the same catalysts in a CO atmosphere leads to the formation of the CU Mo^{4+} ions.[160,161] After the adsorption of NO at 77 K an EPR signal is generated ($g_\parallel = 2.075$, $g_\perp = 1.996$, and $A_\perp^N = 15$ G); it is due to the $Mo^{6+}.NO^{2-}$ complexes, formed as a result of the transfer of two electrons from the CU Mo^{4+} ion to the orbitals of the NO molecule. The unusually strong reductive properties of the CU Mo^{4+} ions, caused by the anomalous coordination, have been observed. For example, the interaction of Mo^{4+} with CO_2 at 100 °C entails their oxidation to Mo^{6+} and the liberation of CO molecules to the gas phase. After the reduction of molybdenum silicate catalysts with trimethylaluminium in suspension in toluene, an EPR signal with $g = 1.989$ and seven hyperfine lines having a splitting of 4.9 G, attributed to a surface complex of Mo^+ with two toluene molecules, was observed.[162]

The CU Mo^{5+} ions formed on the SiO_2 surface on reduction also serve as centres for the adsorption of O_2 and N_2O molecules. The adsorption results in the formation of the O_2^- and O^- radical-anions respectively in the coordination spheres of the CU ions.[9,156,163] The O_2^- and particularly O^- radical-ions are highly reactive and can participate in various reactions.[9,50,52,156] Thus O_2 and N_2O molecules are activated in the coordination spheres of the CU Mo^{5+} ions, which makes it possible to regard them as active centres for catalytic oxidation reactions.

Oxidised aluminomolybdenum catalysts contain both Mo^{6+} [164, 165] and Mo^{5+} [166] ions. At low concentrations the Mo^{6+} ions have tetrahedral coordination, but, with increase of the molybdenum content, octahedrally coordinated ions are also formed.[164] The reduction of the aluminomolybdenum catalysts leads to the formation of appreciable amounts of Mo^{5+} ions. According to the majority of investigators,[165,167–170] the EPR spectrum indicates their square-pyramidal or compressed octahedral coordination. Some workers[171,172] assume, however, that the Mo^{5+} ions have a distorted tetrahedral coordination. Nevertheless in the majority of studies it has not been possible to observe clear-cut effects indicating the possibility of the stabilisation of polar molecules in the coordination sphere of the Mo^{5+} ions on the Al_2O_3 surface and hence to confirm the formation of CU ions. It is noteworthy that the formation of CU molybdenum ions on the surfaces of aluminomolybdenum catalysts has been demonstrated reliably by EPR on the basis of the stabilisation of the O_2^- radical-anions in their coordination sphere.[6,173]

Surface Mo^{5+} ions have been detected by EPR in molybdenum–magnesium systems[173–175] from the broadening of the lines after the adsorption of molecular oxygen at low temperatures. The question of their coordination state has not been ultimately elucidated. Both distorted octahedral and tetrahedral coordinations have been suggested,[173,174] while other workers[175] believe that the ions exist only in distorted octahedral coordination. It has been observed[175] that the adsorption of CO, C_3H_6, N_2O, H_2O, and NH_3 molecules increases the anisotropy of the EPR signals by altering $g_\perp$ ($g_\parallel$ is almost constant), which indicates, according to the investigators, a lengthening of the $Mo^{5+} = O$ bond owing to the interaction of the adsorbed molecules with oxygen.

Surface Mo^{5+} ions with square-pyramidal coordination as well as the bulk-phase ions have also been detected in the EPR study of bismuth–molybdenum and zinc–molybdenum catalysts.[176–178] A decrease of the intensity of their EPR signal following the adsorption of water and its increase after the adsorption of propane have been observed.[177] It has been suggested that these changes are caused by the decrease and increase respectively of the spin–lattice relaxation time of the ions as a consequence of the increased degree of symmetry of their environment in the case of H_2O and its decrease in the case of C_3H_8.

CU Mo^{6+} and Mo^{5+} ions formed on the surface of carriers in the decomposition of grafted organic or carbonyl complexes of molybdenum have also been studied by EPR and ultraviolet spectroscopy[179,180] and it has been shown that, on the SiO_2 and Al_2O_3 surfaces, these ions have distorted tetrahedral coordination and the nature of the active centres in catalysts of this type has been discussed.

2. Rhodium Ions

It has been shown by EPR that evaluation in the temperature range 200–500 °C of Rh/SiO_2 specimens containing Rh^{3+} ions in the initial state leads to the formation of CU Rh^{2+} ions with the $A(4d)^9$ electronic configuration and distorted tetrahedral coordination ($g_1 = 2.68$, $g_2 = 2.22$, $g_3 = 2.00$) as well as octahedrally coordinated Rh^{2+} ions ($g_\parallel = 2.00$, $g_\perp = 2.43$).[181] The fraction of the CU ions increase with increase of the evacuation temperatures and in the specimens heated at 500 °C there are virtually no octahedrally coordinated Rh^{2+} ions. The adsorption of H_2O, NH_3, CH_3OH, and C_2H_4 molecules entails the expansion of the coordination sphere of the CU ions and the formation of octahedral complexes of Rh^{2+} ions ($g_\perp = 2.43$, $g_\parallel = 2.00$).

Tetrahedrally coordinated Rh^{2+} ions, formed as a result of the disproportionation of the Rh^{3+} ions *in vacuo* at 500–700 °C, have been observed on the γ-Al_2O_3 surface.[182] CO and O_2 molecules can enter their coordination sphere on adsorption, forming paramagnetic surface complexes. The EPR spectra of Rh/Al_2O_3 specimens reduced in H_2 also show a signal due to the surface complexes of O_2 ($g_\parallel = 2.043$, $g_\perp = 2.004$) and CO ($g_\parallel = 2.038$, $g_\perp = 2.003$) with a CU Rh^0 atom.[182]

3. Palladium Ions

The application of the EPR method to the study of deposited Pd/Al_2O_3 [183] and Pd/MgO [184] catalysts made it possible to detect CU Pd^+ and Pd^{3+} ions on the surface with the $A(4d)^9$ and $A(4d)^7$ configurations respectively. The CU Pd^+ ions are formed on high-temperature activation (reduction, evacuation, partial oxidation, and re-evacuation) of Pd/Al_2O_3. Their concentration is several per cent relative to the total palladium content in the specimen. These ions behave as centres for the adsorption of H_2O, NH_3, CO, and O_2 molecules. The EPR spectra of the complexes with CO molecules labelled with the ^{13}C isotope show that the complexes contain different numbers of molecules. The adsorption of O_2 leads to the formation of the O_2^- radical-anions stabilised in the coordination spheres of the CU palladium ions. The CU Pd^{3+} ions are formed on the Pd/MgO surface under severe oxidation conditions (800 °C). At room temperature *in vacuo* or in an atmosphere of O_2 they disproportionate together with the Pd^+ ions, present simultaneously in the catalyst, to form Pd^{2+} ions: the CU Pd^{3+} ions are readily reduced in H_2 and CO.

4. Tungsten Ions

The reduction of deposited W/SiO_2 catalysts does not lead to the appearance of any signals in the EPR spectra measured at 77 and 300 K.[185] However, after the adsorption of CO or NH_3 on the reduced specimens, intense EPR signals are generated. Their parameters (CO: $g_\perp = 1.901$ and $g_\parallel = 1.784$, NH_3: $g = 1.800$ and $g = 1.674$) indicate the formation of surface distorted octahedral complexes of the W^{5+} ions. Consequently, before adsorption, CU W^{5+} ions, undetectable by EPR at 77–300 K owing to their short spin–lattice relaxation time, are present on the surfaces of these catalysts. The adsorption of O_2 stabilises the O_2^- radical-anions in the coordination spheres of the CU ions.[179,185]

5. Platinum Ions

The EPR method has been used to identify the paramagnetic centres in deposited Pl/Al_2O_3 and Pt/SiO_2 catalysts.[186] It has been shown that heat treatment of the Pt/Al_2O_3 specimens in O_2 at 623 K induces the appearance of an intense EPR signal with $g_\perp = 2.222$ and $g_\parallel = 2.046$, which has been attributed to the Pt^{3+} ions with the electronic configuration $A(5d)^7$. The adsorption of O_2 entails a decrease of the intensity of this signal and the appearance of signals due to oxygen radicals. It has been concluded that the Pt^{3+} ions are present on the catalyst surface, but their coordination state has not been established. In contrast to Pt/Al_2O_3, the formation of paramagnetic platinum ions could not be observed on the Pt/SiO_2 catalyst. When Pt/Al_2O_3 and $Pt–Ir/Al_2O_3$ catalysts containing chlorine were heated, the formation of paramagnetic CU Pt^+ ions, stabilised in the form of the surface $[PtCl_2]^-$ complex, was observed.[187] It has been suggested that the Pt^+ ion in this complex is an active centre for the dehydrocyclisation of paraffinic hydrocarbons.

V. CONCLUSION

The data presented show that electron paramagnetic resonance and optical spectroscopy of diffusely scattered light permit a reliable identification of the formation of CU transition metal ions on the surfaces of catalysts and an investigation of their properties.

It is possible to demonstrate, fairly reliably, tetrahedral coordination of the CU transition metal ions, distorted in different ways, on the silica gel surface. When alumina was used as the carrier, the formation of CU ions in square-pyramidal and tetrahedral coordinations was observed. Thus the coordination state is determined to a large extent by the nature of the carrier. The methods of deposition of the transition elements, their concentration, and the conditions in their activation also play an important role.[60,65,66,127,136,139,153,188,189] The literature data show that the coordination state of the surface ions influences significantly the selectivity and rate of catalytic reactions.[153,158,188–190] The stabilisation of transition metal ions on the catalyst surfaces in an oxidation state atypical for the bulk phase (Cr^{5+}, Cr^{2+}, Mo^{5+}, Rh^{2+}, W^{5+}, etc.) is also associated with their unusual coordination.

The CU transition metal ions are able to interact with various adsorbed molecules to form surface complexes, which in the case of molecules behaving as typical ligands in solutions, have as a rule a distorted octahedral coordination. There is a possibility of the formation of complexes having a more involved structure, for example, those with olefinic hydrocarbons, SO_2, O_2, and N_2O. It is noteworthy that the stabilisation of polar molecules in the coordination spheres of CU ions in many cases does not apparently reduce solely to the filling of the vacant sites by adsorbed molecules. The coordination environment of the ions also undergoes a rearrangement under these conditions.

The formation of complexes between the adsorbed molecule and the CU ions can lead to an increase of its reactivity. Thus the adsorption of O_2 molecules entails in many cases the formation of O_2^- radical-anions stabilised in the coordination sphere of the CU ion. Their reactivity is much higher than that of O_2 molecules. On raising the temperature, the

molecules adsorbed in the coordination spheres of the surface CU ions can be both desorbed and can undergo chemical changes as a result of their interaction with the CU ions, as has been demonstrated, for example, in the case of H_2O molecules in the coordination spheres of the Cr^{3+} ions[95] or N_2O molecules in the coordination sphere of the V^{4+} ions.[39,46] There is also a possibility of the substitution of one set of molecules adsorbed in the coordination sphere by another, for example, in the case of the surface copper complexes on SiO_2 when ammonia and methanol are adsorbed.[136]

The adsorption of carbon monoxide molecules frequently leads to the formation of surface paramagnetic complexes of the carbonyl type. A weak bond between the CO molecule and the ion, which is ruptured even on evacuation at room temperature, is characteristic of these complexes. On the other hand, the changes in the optical and EPR spectra occurring in such complex formation indicate that, although this type of weak adsorption of CO corresponds to physical adsorption as regards bonding energy, it nevertheless entails significant changes in the electronic state of the adsorption centre—the CU transition metal ion. Consequently it occurs with participation of the electrons of the adsorption centre and constitutes chemical adsorption.

The anomalous, compared with the bulk phase, coordination of the surface CU transition metal ions also leads to a difference in the oxidation-reduction properties [compared with the bulk-phase]. Thus the interaction of the CU Cr^{2+} ions in tetrahedral coordination on the SiO_2 surface with oxygen leads to their oxidation to the quinquevalent and hexavalent states even at room temperature, whereas the octahedrally coordinated Cr^{2+} ions are oxidised under these conditions to the tervalent state.[95]

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