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Physical Methods for the Investigation of Catalysis *in situ*

O.V.Krylov and A.D.Berman

The principal problems and certain examples of the application of physical methods for investigations in the course of catalysis are examined. The methods for the investigation of the role of phase transformations in heterogeneous catalysis and the application of infrared spectroscopy to the study of surface compounds are considered in greatest detail.
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I. INTRODUCTION

The state of both the active catalyst surface and of the structure of its bulk phase differs under the conditions of catalysis from the corresponding state before and after catalysis. The chemical and phase compositions of the catalyst can change during catalysis. The study of the structure of the surface layer and of the bulk-phase and surface phase transformations of the catalyst is essential for the understanding of the nature of selectivity in complex catalytic processes and for the elucidation of the causes of the non-stationary phenomena in heterogeneous catalysis. Hence the necessity for the application of physical (spectroscopic, structural, etc.) methods to direct investigations during the course of the catalytic reaction is evident.

It is possible to distinguish two main problems for the solution of which one employs physical methods in investigations *in situ*, i.e. directly under the conditions of the catalytic process.

1. The elucidation of the structure of the active centre and of the phase composition of the catalyst and also of the changes undergone by them during catalysis.

2. The elucidation of the structure of the surface compounds formed by the reactants and of their role in the catalytic reaction.

X-Ray diffraction analysis, Mössbauer spectroscopy, EPR and other methods are used for the solution of the first problem, while the second problem is solved most successfully by infrared spectroscopy.

In terms of the specific features of their application, the physical methods can be divided into stationary and non-stationary. In the former measurements are performed at a constant temperature and constant reactant concentrations under conditions where there are no changes whatever in the measured quantities as a function of time. In this case the decisive factor is the sensitivity of the method and (a less fundamental factor) the duration of the measurement. For this reason, a method such as, for example, Mössbauer spectroscopy, which requires a long time for the measurement of the spectrum is employed mainly under stationary conditions. The stationary methods make it possible to characterise the chemical or phase composition of the catalyst and the state of its surface in the course of the catalytic reaction. In principle, it is possible to identify also the surface compounds formed under stationary conditions.

By studying the dependence of the rate of the catalytic reaction on the concentrations of the surface compounds measured by physical methods under stationary conditions, it is possible to formulate certain hypotheses about the process mechanism. However, the stationary methods do not permit direct measurements of the rates of the processes occurring on the surface or in the bulk phase of the catalyst, without which it is frequently difficult to assess also their role in heterogeneous catalysis (for example, the involvement of the surface compounds in the reaction). The test of hypotheses about the mechanisms of catalytic processes frequently requires measurements or comparison of the rates of individual stages.

Non-stationary methods are used to solve problems of this kind†. In this case measurements are made of the rate of the catalytic reaction and of the concentrations of various structures in the bulk phase and on the surface of the catalyst under the non-steady-state conditions arising when several parameters are altered: reactant concentrations, temperature, etc. Together with sensitivity, the speed of the response of the apparatus is important in non-stationary measurements. The shorter the time constant of the apparatus the faster the stages susceptible to measurement and the greater the amount of information which can be derived, in principle, about the mechanism of heterogeneous catalysis. We shall consider certain examples of the application of physical methods in the course of catalysis.

This review covers studies where physical methods have been used to investigate the phase transformations of the catalyst and also the surface compounds formed directly under the conditions of the catalysis. The methods most widely used for such purposes are considered: X-ray diffraction analysis, Mössbauer spectroscopy, electron paramagnetic resonance, and infrared spectroscopy. The examples are selected in order to demonstrate specific features and the scope of the application of the physical methods *in situ* and also to reflect the most interesting, in our view, results obtained recently by these methods. More detailed information about the application of physical methods in catalysis can be found in other reviews, references to which are given in the text below.

II. THE STUDY OF PHASE TRANSFORMATIONS IN HETEROGENEOUS SYSTEMS

1. X-Ray Diffraction Analysis

Studies of the changes in the phase composition of the catalyst under the conditions of catalysis present considerable difficulties. The standard high-temperature X-ray cameras are relatively unsuitable for this purpose. With

†The non-stationary methods are also referred to as response or transient methods.

such cameras, it is not always possible to heat the gas phase whose composition is to be monitored. Furthermore, the volume of the cameras is usually too great and precludes the rapid determination of the change in the composition of the gaseous medium as the phase composition of the catalyst is altered.

A differential flow reactor with a small volume (1 cm^3) has been developed for the study of the changes in the structure of catalysts during the reaction.[1] The X-ray reactor-camera can be charged with 0.5 g of the catalyst. The reactor has a beryllium window which is transparent to X-rays; at the outlet of the reactor-camera a gas chromatograph is mounted for the measurement of the composition of the reaction products. By recording the changes in the intensities of the individual lines in the X-ray spectrum of the catalyst in the reaction medium, it is possible to measure directly the kinetic parameters of the phase transformation under the conditions of the catalysis.

The study of complex catalysts of selective oxidation have shown that their phase composition, determined on rapid cooling to room temperature, differs from that under the conditions of the catalytic process.[1,2] This result, obtained for nickel molybdates, emphasises the need to investigate the phase composition of the catalyst in the course of the reaction.

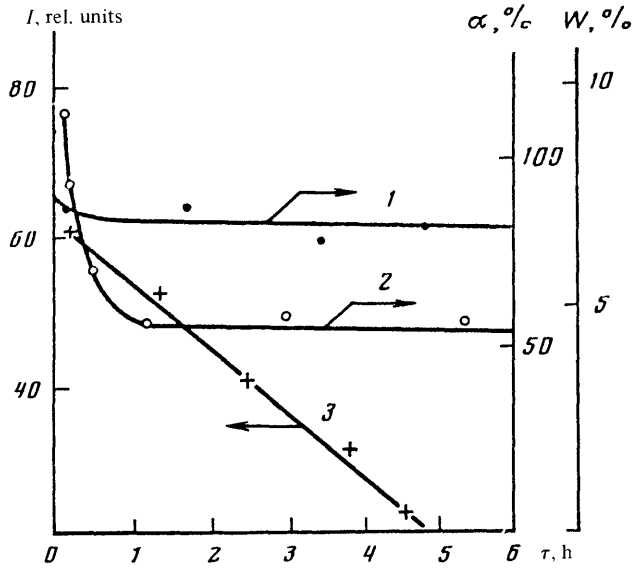


Figure 1. Variation of the degree of conversion α of propene (curve *1*), of the yield of CO_2 *W* (curve *2*), and of the intensity *I* of the principal line due to iron(III) molybdate (curve *3*) for the complex Co–Mo–Bi–Fe–O catalyst in the oxidation of propene to acrolein (according to the data of Shiryaev et al.[3]).

The method developed has been used[3] to investigate the phase transformations and rearrangements of the crystal structures of complex oxide catalysts ($Co_6Mo_{12}Bi_{1.0}$, $Fe_{1.5}O_x$, $Mg_6Mo_{12}Bi_{0.75}Fe_{0.35}K_{0.25}O_x$, $Co_6Mo_{12}Bi_{0.75}P_{0.25}O_x$, and $Mo_{12}Bi_{1.0}Fe_{1.5}O_x$) for the oxidation of propene to acrolein. Experiment showed that the iron(III) molybdate present in the complex multicomponent catalysts is reduced during the oxidation of propene at 623 K in a reaction mixture whose composition is stoichiometric for the mild oxidation of propene to acrolein ($C_3H_6:O_2:He = 1:1:8$). It is of interest that no reduction was observed in the experiments with pure $Fe_2(MoO_4)_3$ and mechanical mixtures of $Fe_2(MoO_4)_3$ and $Bi_2(MoO_4)_3$. Fig. 1 illustrates the variation of the contents of different phases in the complex catalyst under the conditions of the catalysis. The content of $Bi_2(MoO_4)_3$ hardly changes. The increase of the intensities of the lines due to cobalt molybdate β-$CoMoO_4$, which is isostructural with β-$FeMoO_4$, accompanied by the simultaneous decrease of the intensities of the $Fe_2(MoO_4)_3$ line indicates the reduction of ferric ions to the bivalent state. The virtually identical parameters of the unit cells of cobalt and iron molybdates lead to the superposition of their lines on the diffractometer traces. Fig. 1 shows that the time taken for the catalytic activity to reach a stationary level is 1–2 h under these conditions. After this, the catalytic activity does not change although the amount of iron molybdate continues to vary. The active centres on the catalyst surface are apparently formed before the rearrangement of the bulk-phase structure of the catalyst is completed.

The phase composition of the deposited V_2O_5–SiO_2 catalusts has been investigated in the oxidation of tetrahydrofuran (THF).[4] It was shown that the reduction with hydrogen or THF at 200 °C leads to the formation of the V_4O_9 phase. After exposure to a mixture of THF and oxygen at 200 °C for 16 h, V_4O_9 was also detected together with a small amount of the initial V_2O_5 phase.

A phase transition in the orthorhombic molybdenum oxide MoO_3 has been observed[5] when a mixture of methanol and helium was passed through the specimen. It was shown that this entails the formation of bronzes having the composition H_xMoO_3; dimethyl ether is formed from ethanol. The oxidation of methanol was observed in the CH_3OH–O_2–He mixture, but the content of the MoO_3 phase did not change.

2. Mössbauer Spectroscopy

It is possible to distinguish two ways in which Mössbauer spectroscopy can be applied in heterogeneous catalysis: (1) absorption spectroscopy based on the fact that the radiation emitted by a standard radioactive source is absorbed by the "Mössbauer" isotope in the specimen; (2) emission spectroscopy based on the fact that a radioactive isotope, which is in fact used as the source of radiation, is added to the specimen. In this case the radiation is emitted from the specimen itself and is then absorbed by a standard adsorbent containing the "Mössbauer" isotope. We shall examine certain examples of the application of Mössbauer spectroscopy *in situ*.

(a) Absorption spectroscopy. Mössbauer spectra were obtained for the first time in the course of a catalytic reaction in a study[6] of the oxidation of propene to acrolein in the presence of complex Co–Mo–Fe catalysts (the composition of the catalysts was indicated above in the description of X-ray diffraction analysis). The Mössbauer spectra were recorded *in situ* in a specially designed small cell (60 ml) which served at the same time as a flow-circulation reactor.[7] The design of the cells for the measurement of Mössbauer spectra *in situ* has also been described.[8,9] Fig. 2, illustrating typical spectra of the Co–Mo–Bi–Fe–O catalysts,[7] shows that under the conditions of the catalysis the singlet line characteristic of the crystalline garnet-like $Fe_2(MoO_4)_3$ is transformed into a four-line spectrum arising from two structurally non-equivalent positions of the iron atoms, Fe(1) and Fe(2), of iron(II) molybdate β-$FeMoO_4$ having the

scheelite structure. However, tervalent iron is also retained in the system, probably in a highly dispersed state, which is not detectable by X-ray methods.

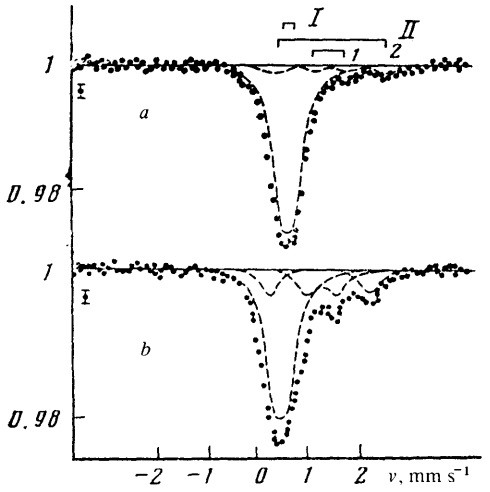


Figure 2. The Mössbauer spectra of the Co–Mo–Bi–Fe–O catalyst obtained at 623 K in a stream of O_2 (*a*) and in the $C_3H_6 + O_2$ mixture (*b*): I) $Fe_2(MoO_4)_3$ signal; II) β-$FeMoO_4$ signal [1) Fe(1) position; 2) Fe(2) position].

Fig.3 presents the temperature variation of the isomer shift (i.s.) in the Mössbauer spectrum of iron(III) molybdate and of the overall rate of oxidation of propene w in the presence of the same catalyst.[7] The continuous line represents the theoretical dependence of the isomer shift on temperature in terms of the classical Debye approximation. The arrows denote the boundary temperatures between the selective and extensive oxidation of propene, which are 680 ± 20 K: the mild oxidation of C_3H_6 to acrolein predominates at the lower temperature, while extensive oxidation predominates at the higher temperature. Fig.3 also indicates the values of the relative concentrations r of bivalent iron determined from the ratio of the area under the Fe^{2+} spectrum to the overall area of the spectrum.

Fig.3 shows that, in measurements in air (curve *1*), the temperature dependence of the isomer shift is described satisfactorily by the theoretical curve. This can be said also of the experiments *in situ* at 300–520 K. However, at $T \geq 520$ K the isomer shift exhibits a striking anomaly, deviating from theoretical values and reaching a constant value of 0.52 ± 0.02 mm s^{-1} in the region of selective catalysis. In the temperature range 520–680 K the variation of the isomer shift along the dashed curve in Fig.3 is reversible. At 680 K (the onset of extensive oxidation) significant changes take place in the catalyst. The fraction of β-$FeMoO_4$ increases abruptly (r rises from 10 to 35%). The temperature variation of the isomer shift is then described by another straight line whose slope differs sharply from the theoretical value. The latter dependence persists in the temperature range 300–750 K both in experiments *in situ* (under the conditions of the catalysis) and in air. The irreversible changes occurring at $T \geq 680$ K in iron(III) molybdate are confirmed also by X-ray data, indicating a change in its structure.

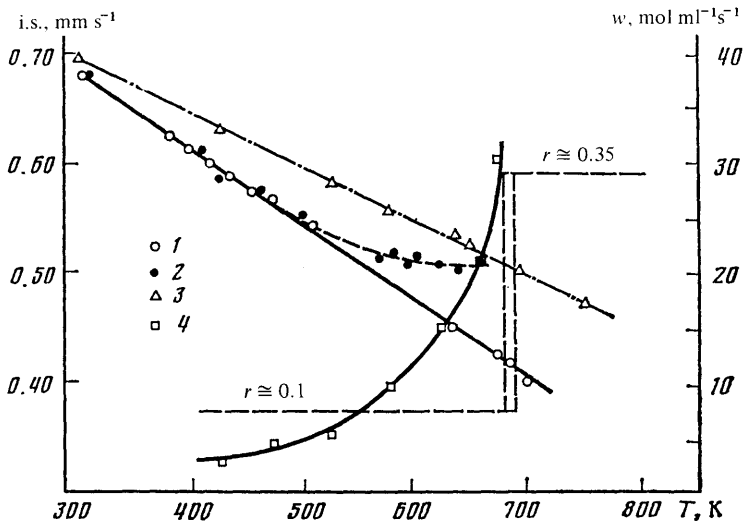


Figure 3. Temperature variation of the isomer shifts in the spectra of iron(III) molybdate obtained under static conditions in air (1), *in situ* in the selective oxidation region (2), and *in situ* after experiments at 680 K (3) and the temperature variation of the overall rate of oxidation of propene w (4) on the CoMo–Bi–Fe–O catalyst. The dashed band denotes the boundary temperatures between the mild and extensive oxidation processes; r = fraction of β-$FeMoO_4$ below and above the boundary temperatures (according to the data of Maksimov et al.[7]).

The results obtained[7] can be accounted for as follows. At the boundary of the iron molybdate crystal anionic vacancies are formed in the course of selective oxidation owing to the removal of oxygen from the O_L lattice in accordance with the following scheme:

$$Fe_2Mo_3O_{12} \rightleftarrows [Fe_2Mo_3O_{12-x}\square_x]^*_x + xO_L ,$$

where $\square$ is an anionic vacancy. Thermally activated ionisation of the vacancies leads to the appearance of an excess negative charge, which influences the electronic state of the iron ions in the molybdate. In these experiments a change in the spectrum of the entire iron molybdate crystal is observed, indicating a rapid (over a period of 10^{-7}–10^{-8} s) shift of electron density in the excited $[Fe_2Mo_3O_{12-x}\square_x]^*$ crystal. The iron passes from the $3d^5$ state in the initial crystal to the $3d^{5+\Delta}$ state. The latter is intermediate between the state of iron in the oxidised and reduced iron(III) and iron(II) molybdates respectively.[7] At the iron molybdate–cobalt molybdate interface $Fe_2(MoO_4)_3$ is reduced to $FeMoO_4$, the structural correspondence of β-$FeMoO_4$ and β-$CoMoO_4$ promoting the formation of the nuclei of the β-$FeMoO_4$ phase. A concentration of vacancies $\square_x$ in excess of the equilibrium value is generated at the interface between the iron(II) and iron(III) molybdates in the course of the catalysis. The vacancies, diffusing towards the surface, can serve as centres for the dissociative adsorption of oxygen from the gas phase with formation of O_L. Oxygen is apparently absorbed on the β-$FeMoO_4$ phase. The non-equilibrium polarised $[Fe_2Mo_3O_{12-x}\square_x]^*$ structure constitutes an "arterial highway" supplying the necessary amount of O_L to the active centres for the oxidation of propene to acrolein, which are located, according to the model proposed.[10,11] at the interfaces. In the region of extensive oxidation irreversible changes take place in the $Fe_2(MoO_4)_3$ phases. There is a sharp increase in the amount of β-$FeMoO_4$, which cannot be fully reoxidised. C_3H_6 is oxidised mainly by surface, possibly molecular, oxygen and not O_L, with formation of CO and CO_2.

The phase transformations in the reduction and reoxidation of the Fe–Mo–O catalyst with the ratio Mo/Fe = 2.4 have been investigated.[12] The reduction of the catalyst with methanol at T < 553 K results in the formation of α-$FeMoO_4$. If the specimen is then reoxidised at 600 K, a metastable phase appears, in which Fe^{3+} in a high spin state is located in a distorted octahedron.

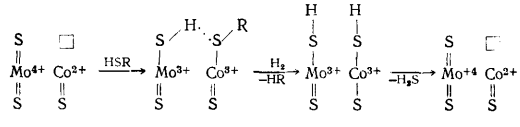
The variation of the composition of the Fe/Al_2O_3 catalyst for the Fischer–Tropsch synthesis has been studied.[13] The measurements were made in a steel cell with a beryllium window.[8] The apparatus made possible the mass-spectrometric analysis of the reaction products. It was shown that the rate of reaction in the reduced catalyst reaches a maximum during the first hour of the experiment and then falls. The Mössbauer method has been used to test the hypothesis that the activation of the catalyst is associated with the formation of carbides. Experiment showed that a mixture of the carbides $Fe_{2.5}C$ and $Fe_{2.2}C$ is formed in the presence of CO and H_2.

(b) Emission spectroscpy. Emission Mössbauer spectroscopy is frequently used to study cobalt-containing catalysts. Such catalysts do not contain an isotope which would permit the employment of the absorption spectroscopy. However, by adding the ^{57}Co isotope, it is possible to use it subsequently as a source of radiation in Mössbauer experiments. Information about the cobalt atoms is obtained by studying the signal of the ^{57}Fe isotope formed on decomposition of ^{57}Co. The observed valence and spin states of ^{57}Fe can, however, differ from the states of the initial ^{57}Co isotope. One of the causes of this difference is that the Co and Fe atoms have different chemical and electronic properties. Furthermore, the decomposition itself can induce unstable but fairly long-lived (10^{-7} s) changes in the environment of the Mössbauer nuclei.[9] A general consideration of the "after-effect" has been described.[14] In conducting materials it can be neglected but the "after-effect" is important in the case of insulators. For example, the Fe^{2+} and Fe^{3+} signals are observed[15] in the emission spectra of CoO, although only Co^{2+} had been detected before decomposition.

However, the "after-effect" is unable to induce a significant displacement of the nuclei, for example, to cause the removal of ^{57}Fe from the lattice sites previously occupied by ^{57}Co. The environment of the ^{57}Fe atom is almost identical with that of the ^{57}Co atom before decomposition, which makes it possible to employ the emission spectroscopy for the investigation of the catalyst structure. It has been established by this method that cobalt chromite $CoCr_2O_4$ has a direct spinel structure in which the Co^{2+} ions occupy tetrahedral vacancies in the anionic sub-lattice, while the Cr^{3+} ions occupy octahedral vacancies.[16]

In certain cases cobalt-containing phases can be identified by comparing the spectra of the catalysts with those of model compounds. As an example, we shall consider the study of Co–Mo sulphide catalysts for hydrodesulphurisation. It has been shown[9] that in the course of catalysis the Co–Mo–S phase is formed both in the catalysts deposited on the Al_2O_3 and in the non-deposited catalysts and has the MoS_2 structure. This conclusion is based on the analysis of the spectra of the catalyst obtained *in situ* and on the study of the spectra of a whole series of model compounds (Co/Al_2O_3, $CoMoS_4$, Co_9S_8, Co_3S_4).

A series of $Co–Mo/Al_2O_3$ catalysts with different Co/Mo ratios at a constant molybdenum content have been investigated.[17] The study of the Mössbauer spectra showed that cobalt can enter into three different phases: into the Al_2O_3, Co_9S_8, and Co–Mo–S lattices. A linear correlation has been obtained between the catalytic activity and the amount of cobalt in the Co–Mo–S phase. According to Topse and co-workers,[9,17] the mechanism of the hydrodesulphurisation is as follows:



Mössbauer spectroscopy is also used in the study of bimetallic catalysts.[18] In cases where one or both metals are active in the Mössbauer effect, it is possible to obtain information about the interactions of the metals with one another or with the carrier. Mössbauer spectroscopy is useful for the elucidation of the positions of the iron ions in the skeletons of zeolite catalysts and their migrations on dehydration of the zeolite. Information about these and other applications of Mössbauer spectroscopy in catalysis can be found in other reviews.[19,20]

3. The Method of Electron Paramagnetic Resonance

The EPR method is widely used in catalytic studies because of its sensitivity and the large amount of information which it yields. For example, the method makes it possible to investigate the interaction of oxygen radical-ions with hydrocarbons or the interaction of transition metal ions with the components of oxidation reactions.[21–23]

The difficulties in the employment of the method for the study of catalytic reactions *in situ* at a fairly high pressure, particularly for oxidation reactions, are associated with the broadening of the signal due to the surface ions and radicals after the physical adsorption of O_2, H_2O, and other molecules on the catalyst surface owing to dipole–dipole interaction. Surface ions or radicals have therefore hardly ever been observed by EPR under the conditions of stationary catalysis.

The EPR method can be used successfully in the study of exchange processes between the surface and bulk of the oxide. Thus it has been shown[24] that the appearance of active centres for the isomerisation of olefins on the MoO_3 catalyst is associated with the formation of anionic vacancies on the MoO_3 surface and the deactivation of the catalyst is associated with the diffusion of the vacancies into the bulk phase. The diffusion of the vacancies was followed from the EPR signal of the Mo^{5+} ion stabilised in the vicinity of the vacancy.

The EPR method has been used[25] to investigate the phase transformations in $BaTiO_3$, which undergoes a transition from the tetragonal to the cubic phase at 120 °C. This transition could be observed by using impurity Mn^{2+} or Fe^{3+} ions as labels. Owing to local structural distortions in the tetragonal ferroelectric phase, the EPR spectral lines due to Mn^{2+} are broadened, the signal intensity increasing almost by an order of magnitude after the removal of the distortions (on transition to the cubic paraelectric phase). The adsorption of various gases influences the phase transition temperature T_C. Only the cubic phase is catalytically active in relation to the oxidation of CO. At low temperatures (130–170 °C) the adsorption and catalytic properties of $BaTiO_3$ are fully determined by the impurity manganese ions. Following the adsorption of CO, the intensity of the EPR signal of the impurity Mn^{2+} ion increases and the amount of Mn^{2+} ions which have appeared is equivalent to the number of CO molecules removed in conformity with the equation:

$$CO + Mn^{4+} + O^{2-}_{surf} \rightarrow CO_2 + Mn^{2+}.$$

On the other hand, Mn^{2+} ions disappear when O_2 is adsorbed:

$$2Mn^{2+} + O_2 \rightarrow 2Mn^{4+} + 2O^{2-}_{surf}.$$

A specific feature of the model proposed[25] is that the active centres are present not only on the surface but also in the bulk of barium titanate. The catalytic oxidation of CO takes place via an oxidation-reduction mechanism at a certain constant stationary concentration of Mn^{2+} in $BaTiO_3$, which is determined by the depth of diffusion of the electrons from the Mn^{2+} ions near the surface to the surface. The influence of the phase transition on the catalytic properties of $BaTiO_3$ is associated with the fact that electron transfer from the surface to the bulk phase is possible only in the paraelectric phase.

Another example of phase transformations in the course of the catalysis has been observed in the study of the oxidation of SO_2 to SO_3 in the presence of vanadium catalysts.[26] The change of the state of the vanadium ions on passing from the melt to the solid state has been followed by EPR. The deactivation of the catalysts and the long relaxation times of the rate of reaction are associated with this process. Studies of the application of EPR *in situ* have also been described in another review.[27]

4. Video-LEED—A New Method for the Investigation of Surface Phase Transformations

The methods examined above make it possible to investigate the changes in the bulk-phase structure of the catalyst. A new Video-LEED method (direct observations of the structure from the diffraction of slow electrons) has been developed recently[28,29] and has been used successfully to investigate the rearrangement of the (100) phase of platinum during the adsorption of CO and in the course of the oxidation of CO by oxygen. The method makes it possible to record simulcaneously the intensities of the signals from several two-dimensional structures. At coverages $\theta_{CO} < 0.5$, the (5×20) structure is stable, while at higher coverages the (1×1) structure is stable. The phase transition proceeds via a mechanism involving the formation and growth of nuclei. The transformations of these structures, which take place as the degree of surface coverage is altered, lead to auto-oscillations in the rate of oxidation of CO. A possible relation between the two-dimensional phase transformations and the non-stationary phenomena in heterogeneous catalysis has been indicated.[30] This relation was demonstrated experimentally for the first time by Thiel et al.[28]

We may note that the direct observation of the structure of the surface phase by the Video-LEED method under the conditions of the catalysis is possible only at fairly low pressures ($\sim 10^{-3}$ Pa), where the electrons probing the surface are not scattered by the gas. This applies also to other electronic methods for the study of the properties of the surface (X-ray and photoelectron spectroscopy, Auger spectroscopy, and energy loss spectroscopy with slow electrons), whose application to the study of adsorption and catalysis is still in the initial stage but is developing rapidly.

III. APPLICATION OF INFRARED SPECTROSCOPY IN KINETIC STUDIES

In order to understand the mechanism of catalysis, it is extremely important to have information about the structure and properties of the surface compounds. It is also important that such data should be obtained directly in the course of the catalysis. Such a possibility is provided, in principle, by infrared spectroscopy. The method yields most information in cases where it is possible to determine quantitatively the concentration of the surface compounds to measure the rate of their formation and consumption, and to compare it with the rate of the catalytic reaction.

In this section we shall consider mainly studies in which infrared spectroscopy was used in kinetic investigations. We shall deal with problems associated with the limitations as regards sensitivity and deviations from the Bouguer–Lambert–Beer law. Other reviews[31–34] have been devoted to other aspects of the application of infrared spectroscopy in catalysis.

In the study of the kinetics of heterogeneous processes, it is essential that the cells used as reactors should make it possible to obtain spectra under the conditions of the catalytic process and should permit a reliable determination of its rate. The present cell designs enable us to carry out catalytic reactions in cells at high temperatures[35] and pressures.[36,37] The flow cells operate under the conditions of a differential reactor for low degrees of conversion. A design for a gradient-free reactor with circulation of the reaction mixture has also been proposed. Since discs containing 20–100 mg of the catalyst are normally used in

infrared spectroscopy, the sensitivity of the detectors usually used for the gas phase may prove inadequate for the detection of the reaction products. In this case an additional amount of the catalyst can be included in the circulation system.[38]

The question of the sensitivity of the method is important. The extinction coefficients in the absorption bands of different functional groups or bonds in a molecule vary within the limits of 2–3 orders of magnitude. Approximate estimates have shown that, under most favourable conditions, concentrations of adsorbed substances of the order of 10^{12}–10^{13} molecules cm^{-2} can be measured with the aid of conventional spectrometers (without Fourier transformation). In general, one may say that the method is applicable to catalysts with a high specific surface (10–100 $m^2\ g^{-1}$) when conventional spectrometers are employed. Fourier spectrometers, whose sensitivity is higher by two orders of magnitude, make it possible to investigate surface compounds also on industrial catalysts.

1. The Bouguer–Lambert–Beer Law

Quantitative measurements by the infrared spectroscopic methods are based on the Bouguer–Lambert–Beer law, from which it follows that the optical density D is proportional to the concentration of the surface compound:

$$D=\varepsilon c l, \qquad (1)$$

where l is the thickness of the disc (cm), c the concentration of the surface compound expressed in terms of the number of molecules per unit volume of the specimen, and ε the extinction coefficient (molecules^{-1} cm^2). The extinction coefficient data for surface compounds are extremely limited; some can be found in Refs. 39–41.

We shall only note that the Bouguer–Lambert–Beer law does not always hold. For example, it is known that interactions between adsorbed molecules can lead to deviations from this law.[42] We shall consider certain experimental data concerning the validity of Eqn. (1) for surface compounds.

Intermolecular interactions are not apparently manifested for low coverages of zeolite catalysts. Thus it has been shown[43] that the Bouguer–Lambert–Beer law holds satisfactorily for formate and acetate complexes formed on interaction of formaldehyde, acetic acid, and acetaldehyde, with NaX zeolite (the concentration of the complexes did not exceed one molecule per cavity). Linear relations have been obtained[39] between the intensity of the absorption band at 1630 cm^{-1} (of the C=C bond) and the concentration of butenes absorbed by NaY zeolite up to the concentrations corresponding to three molecules per large zeolite cavity. However, at high coverages the optical density is almost independent of the amount of butenes absorbed by the zeolite. The Bouguer–Lambert–Beer law holds also for formate complexes on γ-Al_2O_3 [40] at coverages of the order of 10^{13} molecules cm^{-2}, in the adsorption of CO on platinum deposited on aerosil,[44] and in the adsorption of CO on a number of oxides and zeolites.[45]

At the same time, it has been shown[46] that, for the methoxide ions (absorption band at 2830 cm^{-1}) on zinc oxide, the Bouguer–Lambert–Beer law holds only at low optical densities ($D < 0.25$). The interactions in the surface layer can also be manifested by a shift of the corresponding absorption bands as the surface coverage is altered. It has been shown[47,48] that the character of the interaction in the layer following the adsorption of CO on deposited platinum catalysts and in the oxidation of CO on the same catalyst is different. The authors[47,48] attribute this to the formation of "islands" of molecules adsorbed on the catalyst surface in the oxidation of CO. Inspection of literature data has shown that in most cases it is possible to distinguish a linear section on the relation between the optical density and the concentration of certain compounds. However, when quantitative measurements are made, the validity of the Bouguer–Lambert–Beer law must be tested.

We shall now examine certain experimental data obtained in the study of the formation of surface compounds during catalysis.

2. Stationary Measurements

Surface compounds have been detected by infrared spectroscopy in a whole series of studies under the conditions of stationary catalysis (see, for example, Bell[37]). However, it is difficult to reach a conclusion about the role of a particular surface compound in catalysis on the basis of stationary measurements, because dead end forms are possible.[37] Under stationary conditions, one can attempt, in principle, to establish correlations between the rate of reaction and the concentration of surface compounds at different reactant concentrations in the gas phase and at different temperatures. Such data might be employed to test kinetic equations. However, hitherto there have been few examples of studies of this kind. In an investigation of the Fischer–Tropsch synthesis on Ru/Al_2O_3, Rh/SiO_2, Pt/SiO_2, and Pt/TiO_2 deposited catalysts, no correlations whatever were found between the activity of the catalyst and the concentrations of the surface compounds detected.[49] We may note a study[50] in which it was shown that the rate of hydrogenation of ethylene on the Pt/Al_2O_3 catalyst is proportional to the product of the degrees of surface coverage by ethylene (θ_e) and hydrogen (θ_H). It was also found that θ_H and θ_e are functions of the ratio of the partial pressures p_{H_2}/p_e. In the synthesis of methanol from CO_2 and H_2 in the presence of catalysts containing CuO, ZnO, and Al_2O_3 a clear-cut dependence of the rate on the concentration of the surface formate complexes has been obtained.[51]

One may conclude that the study of the infrared spectra of the surface compounds under stationary conditions is undoubtedly useful. However, in the general case it does not permit a solution of the problem of their role in the catalytic reaction.

3. Non-stationary Measurements

Reliable conclusions about the involvement of surface compounds in a catalytic reaction can be reached when data are available for the rates of formation and consumption of these compounds relative to the rate of the catalytic reaction. An effective approach to the problem of identifying the real reaction intermediates involves the study of their dynamic behaviour under the reaction conditions.[52] In this case the experiment consists of the measurement of the concentration of the chemisorbed species under conditions involving sharp changes in the composition of the reactants (for example, when one of them is replaced by its isotopic analogue) and changes in the reaction temperature or the pressure of one of the reactants.

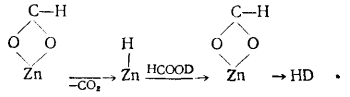
As stated above, a rapid response of the apparatus is important for non-stationary measurements. In the widely used infrared spectrometers without Fourier transform the usual rate of scanning employed to obtain a qualitative

spectrum does not exceed 100 cm^{-1} min^{-1} and the time taken to measure the spectrum in the frequency range 600–4000 cm^{-1} is therefore 30–40 min. When the instrument is tuned to the maximum in a fixed absorption band, it is possible to record processes lasting ~1 s. The rate at which Fourier spectrometers respond can be altered within wide limits—from fractions of a second to several hours depending on the number of scans, which is determined by the required sensitivity of the apparatus. Reports concerning the development of an instrument specially designed for the study of rapid processes have appeared recently; the time taken to traverse half the scale is 0.02 s.[53] A modern apparatus for the study of non-stationary processes by infrared spectroscopy, consisting of an infrared spectrometer, a mass spectrometer and a computer, has been described.[53]

The infrared spectroscopic method is used under non-stationary conditions for the following purposes: (1) for the qualitative test of hypotheses concerning the process mechanisms; (2) for the determination of the kinetic parameters of individual stages occurring with the participation of surface compounds; (3) for a detailed investigation of the kinetics of heterogeneous reactions and for the construction of non-stationary kinetic models.

The decomposition of formic acid on alumina and on silica has been investigated.[52,54,55] It is known that the decomposition of formic acid on various metals and oxides leads to the formation of formate ions and it was assumed that formic acid decomposes via these compounds. However, it was shown with the aid of infrared spectroscopy that the rate of decomposition of formate ions on Al_2O_3 is lower by approximately two orders of magnitude than the rate of decomposition of formic acid at the same temperatures and for the same coverages.[52] Experiments were also performed on isotope exchange. After the attainment of the steady state, the formic acid having the composition DCOOD (used as the initial reactant) in the gas phase was rapidly replaced by HCOOH and the variation of the concentrations of the chemisorbed species was followed from the absorption bands at 2915 cm^{-1} ($HCOO^-$) and 2220 cm^{-1} ($DCOO^-$). If the formate ions are intermediates in the decomposition reaction of formic acid, then the $DCOO^-$ ions should be replaced by $HCOO^-$ at a rate equal to that of the catalytic reaction. However, this was not observed experimentally and it was therefore concluded that the decomposition of formic acid does not proceed via formate ions.

In the study of the decomposition of formic acid on zinc oxide at 448–493 K [54] surface formate ions were also detected. Experiments showed that the rate of decomposition is independent of the formic acid pressure and that the ratio of products CO_2/H_2 is unity when formic acid is present in the gas phase. On the other hand, when formic acid is removed (frozen out) from the system, the evolution of hydrogen ceases, while the evolution of carbon dioxide proceeds at the previous rate. HD was evolved in the decomposition of HCOOD on zinc formate. It was concluded that the formate ions on the surface of zinc oxide are intermediate species and the following mechanism was proposed for the decomposition of formic acid on ZnO:[55]



Non-stationary measurements have been used[36] to test the hypotheses of the adsorption or impact mechanisms of the oxidation of CO on the Pt/SiO_2 deposited catalysts. The surface concentration of CO was deduced from the absorption band at 2074–2080 cm^{-1} (linear form). Fig.4 presents results obtained in experiments where a stream of oxygen was passed through the reactor after the preliminary adsorption of carbon monoxide. The curves describing the time variation of the degree of surface coverage θ_{CO} show an induction period, which depends on the flow rate. These data suggest that the reaction proceeds via an adsorption mechanism and the presence of the induction period is attributed to the liberation of sites for the dissociative adsorption of oxygen in the course of the desorption of carbon monoxide. The induction period shortens when the temperature is raised as a consequence of the desorption of CO. With increased flow rate, the induction period is also reduced, because the concentration of CO in the gas phase is diminished and the readsorption of carbon monoxide is retarded. Fig.5 presents the results obtained when a stream of CO is passed through the system after the preliminary adsorption of oxygen. Evidently, there is no induction period. The authors[36] explained these results by the establishment of a preadsorption state in the interaction of CO with the platinum surface. Carbon monoxide in this state can react with the adsorbed oxygen (modified impact mechanism) or can pass to a chemisorbed state. Afterwards there is also a possibility of reaction with the adsorbed oxygen (the adsorption mechanism).

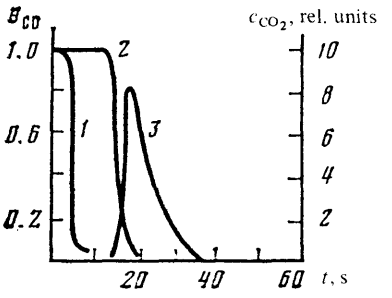


Figure 4. Interaction of oxygen with preadsorbed carbon monoxide on the Pt/SiO_2 catalyst at 160 °C: 1) and 2) variation of the degrees of surface coverage by CO at flow rates of 133 and 9.5 cm^3 min^{-1}; 3) variation of the concentration of CO_2 in the gas phase (according to Dwyer and Bennet's data[36]).

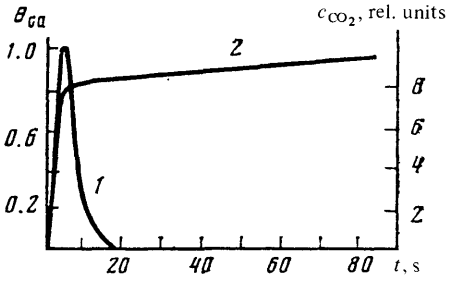


Figure 5. The interaction of carbon monoxide with preadsorbed oxygen on Pt/SiO_2 catalyst at 160 °C: 1) variation of the CO_2 concentration in the gas phase; 2) variation of the surface coverage by carbon monoxide (according to Dwyer and Bennet's data[36]).

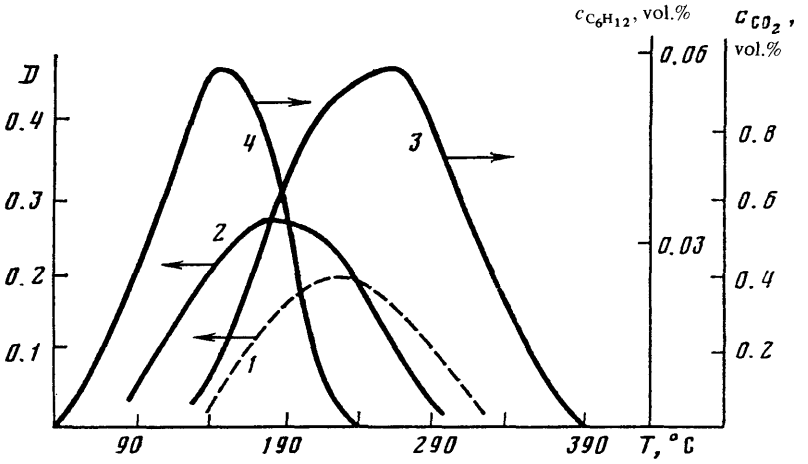


Figure 6. The oxidation of cyclohexane on NaX zeolite during programmed heating:[56] 1) and 2) variation of the optical densities in the absorption bands at 1620 and 1710 cm^{-1} respectively; 3) and 4) variation of the CO_2 and C_6H_{12} concentrations in the gas phase.

Interesting information can be obtained by combining the infrared spectroscopic and thermal desorption methods. As an example, we shall consider a study[56] of the oxidation of cyclohexane on NaX zeolite. In the course of the extensive oxidation of cyclohexane, carbonyl, formate, and acetate complexes were detected (bands at 1710, 1620, and 1580 cm^{-1} respectively). Fig.6 illustrates the variation of the optical densities of the absorption bands of the surface compounds and the CO_2 concentration in the gas phase during programmed heated.[56] Evidently, the carbonyl and carboxylic complexes are formed and decompose at temperatures where CO_2 is evolved into the gas phase. These data agree with the hypothesis that the reaction proceeds via the complexes indicated.

The response method combined with infrared spectroscopy makes it possible in many instances to elucidate the mechanism of the reactions of the surface compounds. In particular, an attempt may be made to find the answer to the question whether the surface compounds are formed via a parallel or a consecutive mechanism. For this purpose, the concentrations of the starting materials in the gas phase are reduced sharply (almost to zero) under the conditions of the catalytic reaction. If the concentrations of some surface compounds then increase, while those of others decrease, we have evidence in support of the consecutive mechanism. On the other hand, if the concentrations of the surface compounds do not vary with time, one may use this as an argument in support of the parallel mechanism. It has been shown by this procedure[57] that carbonyl and carboxylate complexes are formed on NaX zeolite from adsorbed cyclohexane via a parallel mechanism. Similarly, it has been possible to demonstrate[58] that the oxidation of propene on the Bi_2O_3.MgO and Bi_2O_3.MoO_3.MgO model oxide catalysts leads to the formation of surface compounds (allyl, polyene, and carboxylate) also via a parallel mechanism.

The question whether the surface compounds detected by infrared spectroscopy are formed on the same or different centres is important for the construction of a kinetic model. If one of these compounds can be obtained on the surface in preliminary experiments, it is then possible to compare the rates of formation of the second compound on the initial catalyst specimen and on the specimen containing the first surface compound. Such data have led to the conclusion that the carbonyl and carboxylate complexes are formed on different centres in the oxidation of cyclohexane on NaX zeolite (Fig.7).[57]

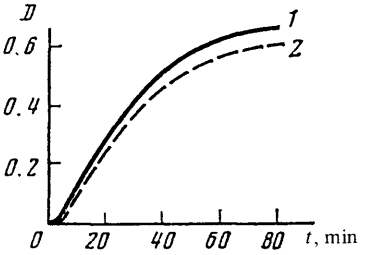


Figure 7. Time variation of the optical density in the 1710 cm^{-1} absorption band at 368 K: 1) stream of cyclohexane directed to a conditioned NaX zeolite specimen; 2) stream of cyclohexane directed to the NaX zeolite after the preliminary formation of carboxylate complexes on the latter.[57]

In a whole series of studies the infrared spectroscopic method has been used to determine the rate constants and activation energies for individual stages of heterogeneous reactions. The effective activation energy has been found[59] for the overall process involving the hydrogenation and desorption of surface compounds formed in the hydrocracking of n-hexene on nickel and platinum. The activation energies for the oxidation of the carboxylate complexes formed in the oxidation of propene on Cr_2O_3 and NiO have been determined.[60] The results proved close to the activation energies for the oxidation of propene obtained in a gradient-free reactor. On this basis, it was concluded that the carboxylates are intermediates in the oxidation of propene on Cr_2O_3 and NiO and that the rate-limiting stage is the oxidation of the carboxylate. We may note that, generally speaking, comparison of the activation energies is insufficient to reach this type of conclusion.

The effective activation energies for the oxidation of the surface forms of CO adsorbed on CoO–MgO solid solutions and MgO have been obtained.[51,62]

The kinetics of the reactions of a series of surface compounds, namely π-allyl (1510 cm^{-1}), a polyene (1605 cm^{-1}), a carboxylate (1580 and 1430 cm^{-1}), and a propene degradation product (1340 cm^{-1}), formed in the oxidation of propene on the Bi_2O_3.MgO and Bi_2O_3.MoO_3.MgO model oxide catalysts, have been investigated[58] by infrared spectroscopy in the temperature range 200–400 °C. The introduction of molybdenum ions into the Bi_2O_3.MgO catalyst sharply reduces the activation energies for the formation and decomposition of the π-allyl complex.

Despite the comparatively large number of studies in which infrared spectroscopy was used directly in the course of catalysis, there have been almost no investigations in which the kinetics were studied in detail and a kinetic model constructed on the basis of the study of the surface compounds. One of the few examples of this kind involves the investigation of the oxidation of cyclohexane on NaX zeolite.[63,64] The authors of the review[63] studied the kinetics of the oxidation of the oxygen-containing complexes formed in the oxidation of cyclohexane under isothermal conditions and during programmed heating; the results are presented in Table 1. They made it possible to compare the rate of oxidation of the complexes with the rate of the catalytic reaction. The rate of oxidation of the complexes was calculated from the formula

$$w = \epsilon D_{st} k, \qquad (2)$$

where D_{st} is the stationary optical density in the catalytic experiments, k the rate constant for the oxidation of the corresponding complexes, and ε an experimental coefficient.

Table 1. The activation energies E and the pre-exponential factors for the oxidation of the surface complexes.

Complexes (spectral band)	E, kJ mol^{-1}		k_0, s^{-1}	
	thermal desorption	isothermal experiments	thermal desorption	isothermal experiments
Carbonyl (1710 cm^{-1})	92	92	$1.1 \cdot 10^7$	$6.1 \cdot 10^6$
Formate (1620 cm^{-1})	75	75	$5.3 \cdot 10^4$	$5.3 \cdot 10^4$
Acetate (1580 cm^{-1})	63	63	$3.4 \cdot 10^2$	$2.2 \cdot 10^2$

For low degrees of conversion, the flow cell can be regarded as a differential reactor and the rate of extensive oxidation was therefore calculated from the equation

$$W = F c_{CO_2}, \qquad (3)$$

where F is the flow rate and c_{CO_2} the concentration of carbon dioxide in the gas phase.

The results of the comparison of the rates of the catalytic reaction (w_{CO_2}) and of the oxidation of the surface compounds—the carbonyls (w_{1710}), the formates (w_{1620}), and the acetates (w_{1570})—are presented in Table 2. Their comparison shows that the overall rate of oxidation of the surface compounds w_Σ is close to the rate of the catalytic reaction. One may conclude that the extensive oxidation of cyclohexane proceeds via the formation and oxidation of the carbonyl and carboxylate complexes and that the carbonyl complexes make the greatest contribution. A kinetic model, all stages of which have been demonstrated directly, has been proposed[64] on the basis of the results. The model reproduces correctly the changes in the concentrations of the surface compounds and the CO_2 concentration under non-stationary conditions; the stationary rates of reaction and the concentrations of the surface compounds also agree satisfactorily with the experimental values. The kinetic parameters of all the stages have been determined.

Table 2. Comparison of the rates of the catalytic reaction and of the oxidation of the surface compounds (cm^3 min^{-1}).

T, K	w_{1700}	w_{1620}	w_{1570}	w_Σ	w_{CO_2}
493	0.07	0.02	0.007	0.09	0.13
513	0.13	0.03	0.08	0.17	0.13
533	0.22	0.04	0.01	0.27	0.27
568	0.32	0.06	0.013	0.4	0.34

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In conclusion we may note that new vibrational spectroscopic methods are developing rapidly, including the characteristic slow electron loss spectroscopy (EELS), the inelastic electron tunnelling spectroscopy (IETS), and Raman spectroscopy with a laser source (laser-Raman), which is widely used in the study of surface compounds. However, the number of examples involving the use of these types of spectroscopy in studies directly under the conditions of catalysis is as yet small. Studies of catalysis *in situ* by infrared-Fourier spectroscopy have begun to be published recently.[53,65]

The experimental techniques for the investigation of catalysis by spectroscopic methods are developing rapidly. It is to be expected that the role of spectroscopic methods in the investigation of catalysis *in situ* will increase sharply as the sensitivity and rapidity of the response of the apparatus are improved.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow