Translated from *Uspekhi Khimii*, **60** 1841–1874 (1991) U.D.C. 541.128.13

Problems of the chemical physics of heterogeneous catalysis

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ABSTRACT. A series of fundamental problems of the chemical physics of heterogeneous catalysis are considered: new methods for investigating the mechanism of heterogeneous catalysis making it possible to study the reaction *in situ* with a high degree of time resolution; the dynamics of the elementary step, including energy and electron exchange processes in catalysis; macrodynamics of heterogeneous catalysis, including the formation of dissipative structure; chain mechanisms; heterogeneous-homogeneous catalysis and the role of a multiphase structure in heterogeneous catalysis.

The bibliography includes 245 references.

Contents

I. Introduction 935
II. Methods of study 935
III. Dynamics of the elementary step in catalysis 939
IV. Macrodynamics of the catalytic process 943

I. Introduction

The advances in the theory of heterogeneous catalysis during the last decade are associated both with the rapid development of new physical research methods and the development of computational-theoretical methods, including quantum chemistry, the qualitative theory of differential equations, etc. The theory of the elementary step, the dynamics of the catalytic process, the organisation and self-organisation of complex catalytic processes, the structure of catalysts, and the structure of active centres can be included among the problems of the chemical physics of heterogeneous catalysis.

The present review deals with the dynamics of heterogeneous catalysis and the methods of study associated with it, i.e. the physical methods which make it possible to determine the rates of various processes directly under catalytic conditions. Problems concerning the structure of catalysts and the structure of active centres, which require special analysis, are not discussed.

The present development of the dynamics of catalysis is characterised by two tendencies.

The first (microscopic) tendency is associated with the transition of studies to the atomic-molecular and further the subatomic level, with the use of the advances in quantum chemistry and in surface science for the elucidation of the mechanism of the elementary step in adsorption and in catalysis, and with account being taken of the electron and energy transfer processes in the elementary step and of the role of individual energy levels in the molecule and in the catalyst in effecting the elementary catalytic step.

The second (macroscopic) tendency presupposes the establishment of the features of a complex catalytic process based on the knowledge of the rates of its constituent elementary reactions, the organisation and self-organisation of catalysis, and the construction of a complex catalyst based on the set of data concerning the optimum catalyst for accelerating a particular stage.

The study of the kinetics and mechansm of a catalytic reaction at a microlevel and a macrolevel makes it possible to solve the problem of choosing an active and selective catalyst for a specified reaction. For this purpose, it is necessary to elucidate the structure of the intermediate surface compound in catalysis and to demonstrate the dependence of the rates of reactions on the rates of formation and consumption of such compounds, to establish the relation between the rate of reaction and the structure and chemical composition of the catalyst and the electronic structure of its constituent atoms, and to investigate the changes in the structure of the catalyst under catalytic conditions and the electron and energy transfer processes. In order to meet these requirements, it is essential to apply on a broad front modern physical methods (X-ray diffraction analysis, electron diffraction, various forms of optical and electronic spectroscopy, and laser beam methods) directly under catalytic conditions (*in situ*).

II. Methods of study

The rapid development of the theory of catalysis is impossible without the development of new methods of study, especially *in situ* (under reaction conditions). Optical (IR, UV) and microwave spectroscopic (EPR) methods for the study of the surfaces of catalysts were applied in the 1950's–1960's. X-Ray and photoelectron spectroscopic methods, low energy electron diffraction, secondary ion mass spectrometry, the method based on the fine structure of X-ray absorption (EXAFS), and a number of other methods were applied in the 1970's–1980's. Automatic apparatus for the testing of catalysts and computer techniques have been rapidly improved. New methods are appearing annually.

Unfortunately in the majority of studies the new research methods are used to compare different properties of the catalyst before or after the reaction—at best under catalytic conditions but in a stationary state. Nevertheless, in order to construct a theory of catalysis, it is essential to perform direct measurements of the duration of the dynamic processes on the surfaces. This can be done with the aid of non-stationary methods: the use of the so-called transient regimes, pulsed influences, abrupt changes in the temperature and pressure of the gas, abrupt alteration of the ratio of the components of the catalytic reaction, etc. It is essential to be able to measure both the rate of the catalytic reaction under non-stationary conditions and the rate of change of the concentrations of the absorbed substances and in the structure and various properties of the catalyst itself under the reaction conditions. These processes have to be investigated over all time scales.

Budar[1] drew attention to the fact that the turnover number of the reaction $n = r/N$ (r is the rate of reaction referred to the number N of active centres on the surface) is in the range from 10^{-2} to 10^{2} s^{-1} for many heterogeneous-catalytic reactions. The characteristic reaction times $\tau = 1/n$ are correspondingly between 10^{2} and 10^{-2} s. For such reaction times and turnover numbers, the reaction products are in fact formed in amounts which can be measured analytically in the usual catalytic experiments. In the analysis of the times taken to achieve various elementary stages of the process, it is therefore necessary to examine in the first place whether they fall within the range from 10^{-2} to 10^{2} s, i.e. whether they can influence significantly the rate of catalysis.

We examined[2] the characteristic times of heterogeneous processes occurring in catalysis. Many elementary processes fall within the time range indicated: adsorption and desorption, the majority of chemical stages on the surface, surface diffusion, phase transitions, and electron capture by the so called slow states. The bulk-phase diffusion in the solid catalyst is in most cases a slower process and its rate influences not so much the rate of the catalytic reaction as a whole as the change in the activity of the solid. On the other hand, the exchange of the energy of atoms and molecules with the surface (translational, vibrational, and rotational relaxation, spontaneous phase transition, and electron capture by the so called fast states on the surface) are as a rule faster processes with characteristic times of $10^{-12}-10^{-6}$ s. The electronic excitations can relax even faster, over a period of $10^{-15}-10^{-13}$ s. However, these short characteristic times must also be known in order to construct a complete dynamic picture of the catalytic process.

The methods for the measurement of the characteristic times of all heterogenous processes important for catalysis, both rapid and slow, have therefore assumed major importance. Naturally, the measurement of short times is a more difficult task.

It is necessary to investigate the dynamics of the changes in both the composition of the gas phase and in the concentration of the surface compounds and in the catalyst structure *in situ*. The jump methods are commonest. For example, after the attainment of a stationary state in a flow system, the pressure of one of the components is diminished abruptly and the variation of the pressures of the reactants and reaction products is investigated. In certain cases, it is possible to reject a particular proposed reaction mechanism. The interaction of an alcohol with an aldehyde on MgO,[3] the oxidation of CO on MnO_2 and Cr_2O_3,[4] and the decomposition of HCOOH on ZnO and metals[5] have been studied by this method. The characteristic times amounted to minutes and tens of minutes in the above investigations.

The minimum characteristic times which can be measured using the kinetic flow regime combined with chromatographic analysis are $10-10^{3}$ s. Using cold traps, it is possible to shorten this range somewhat. The pulse type of kinetic study using a katharometer for gas analysis makes it possible to measure times in the range $1-0.1$ s, while without the resolution of peaks in experiments using a katharometer or a flame-ionisation detector it is possible to attain also 10^{-2} s. Mass spectrometric analysis permits the measurement of even shorter times ($0.1-1$ s) in the flow regime at atmospheric pressure and $10^{-3}-10^{-4}$ s in the flow vacuum version.

Further shortening of the measurable characteristic times is limited by the distance from the surface of the catalyst to the sampling site. Unique procedures have been developed for the removal of samples at short distances from the catalyst (less than 1 mm).[6] It has been possible to improve the time resolution to $<10^{-3}$ s. Gleaves et al.[6] called their method the time analysis of products (TAP). The rates of adsorption, desorption, and intracrystal diffusion of acrolein during the oxidation of C_3H_6 on bismuth molybdate and the mechanism of the activation of the reactants in the oxidation of ethylene on silver, in the oxidation of butane on $(VO)_2P_2O_7$, and in the oxidative ammonolysis of methanol on $Mn_2P_2O_7$ were investigated by the TAP method.

In order to understand the mechanism, it is essential to determine simultaneously the composition of the gas phase and the spectroscopic characteristics under the conditions of non-stationary catalysis. Tamaru[7] was one of the first to investigate the rates of reaction of surface compounds on oxide catalysts by IR spectroscopy. Together with the investigation of the dependence of the rate of reaction under stationary conditions on the concentration of a particular surface form, the response of the system to rapid changes in the reaction conditions, for example, the alteration of the isotopic composition of one of the reactants or a change in temperature or pressure, was analysed. Investigators have called this procedure the dynamic approach to the study of chemisorption states.

A set of physical methods for the study of catalysis *in situ* has been developed at the Institute of Chemical Physics of the USSR Academy of Sciences.[8] Catalytic reactors which serve simultaneously as cells for IR, UV, and Raman spectroscopy, as cameras for the study of the X-ray structure, as tubes for EPR measurements, and as cells for the Mössbauer spectrometer were devised. The mechanisms of the interaction of NO with CO on metals,[9] of the oxidation of NH_3 on metals and oxides,[10] and of the partial oxidation of isobutene on complex oxides[11] were investigated with the aid of IR spectroscopy. Raman spectroscopy was applied *in situ* to the study of the high-temperature oxidative condensation of methane on alkaline earth and lanthanide oxides.[12] A new method, namely the spectroscopy of surface electromagnetic waves,[13] has been used to study the oxidation of methane on the same catalysts at a lower temperature. The changes in phase composition in the catalyst on partial oxidation of propene on the Bi–Co–Fe–Mo–O catalyst and in the Fischer–Tropsch synthesis on iron catalysts were studied by X-ray phase analysis and by Mössbauer spectroscopy *in situ*.[14,15] The oxidation of allyl alcohol to acrolein on the V–Mo–O_3 catalyst was investigated by EPR.[16]

In all the studies listed above, the process kinetics were analysed from the change in the intensity of one line in the spectrum (or on the X-ray diffraction pattern). The kinetics of the change in the composition of the gas phase were investigated simultaneously by gas chromatography. This did not ensure satisfactory time resolutions, the measured characteristic times amounting to several seconds and more. The application of mass spectrometric analysis of the gas phase helped to shorten the measured characteristic times.

In the study of reactions of surface compounds alone without the analysis of the gas phase, it is possible to measure also shorter times. The commonest method for the study of surface compounds is IR spectroscopy. It ensures a high resolution with respect to energy and can be used at any pressure of the gas phase. However, the existing versions of IR spectroscopy do not permit the attainment of a time resolution better than to within 1 min.[17] For example, when the FTIR method (Fourier transform IR spectroscopy) was used to study surface compounds in the autooscillatory process involving the oxidation of CO on platinum, the resolution was to within 1 min.

New versions of IR spectroscopy ensure a higher sensitivity, a better time resolution, and in many instances also a better spectroscopic resolution. For example, using the IRAR method (infrared absorption reflection) and sensitive detectors, it has been

possible to increase the sensitivity of the measurement to within 10^{13} cm^{-2} or 0.01 of a monolayer of adsorbed molecules on the face of a single crystal.[19] The method of emission IR spectroscopy permits the investigation with a high sensitivity of catalytic reactions at a high temperature,[10] while diffuse reflectance IR spectroscopy increases significantly the possibility of detecting surface compounds in the spectral range $2000-4000$ cm^{-1}.[20] The spectra obtained by the method of surface electromagnetic waves (SEW) exhibit an unusually high spectra resolution especially if one uses powerful light sources such as lasers.[13] According to Shafranovskii, et al.,[21] the SEW method is at least four times more sensitive than the IRAR method.

A disadvantage of the electronic and photoelectron spectroscopic methods, whose sensitivity is extremely high and which give rise to an extremely good time resolution, is the impossibility of using them at high pressures. The kinetics of reactions on the faces of single crystals were investigated by X-ray photoelectron spectroscopy (XPES) and measurements were made of the changes in the concentrations of surface compounds. The kinetics of the oxidation of NH_3 on platinum were investigated[22] on the basis of the Auger spectra of the adsorbed oxygen. The oxidation of hydrogen on platinum has also been studied by Auger spectroscopy. It proceeds via the formation of surface OH groups.[23] The measured characteristic times of surface processes in the above studies exceeded 1 s.

The application of vibrational LEES (low energy electron scattering) spectroscopy, which is highly sensitive, ensures a satisfactory time resolution and the possibility of measuring the vibrational spectra of isotopically-substituted molecules, to the study of surface reactions is developing rapidly. The disadvantages of the method are a low spectra resolution (compared with IR spectroscopy), a non-linear dependence of the line intensities on concentration, and, what is most important, the necessity to carry out measurements under vacuum conditions. The kinetics of the $C_6H_6 + D_2$ deuterium exchange on Pt(111) were investigated by this method.[24] At $314-346$ K, the characteristic process time was $30-120$ min and the resolution was to within ~ 5 min.

The application of multichannel detectors appreciably increases the sensitivity of the LEES method and hence the time resolution. In the study of the decomposition of N_2O on Si(110) by the LEES method, a time resolution of 5 ms was attained.[25] Similar resolutions were achieved in the study of the adsorption and desorption of CO on Ni(110), Rh(100), and Cu(100), the dissociation of NO on Rh(100), the decomposition of CH_3OH on Ni(100) and Fe(100), and the oxidation of hydrogen on Rh(100).[17] In the adsorption of CO on Ni(111), the resolution was improved as far as 20 μs.[26] The use of electron pulses makes it possible to reduce the resolution time to 1 μs. Owing to the disadvantages of the LEES method mentioned above, there has been a marked diminution of its application in very recent times in the study of the kinetics of reactions of surface compounds, the procedure being replaced by optical methods.

The measurement of even shorter times involves the use of laser techniques. By virtue of the high monochromaticity and high power of the laser radiation one can (1) ensure the independent excitation of various vibrations of the reactant molecules in order to drive the reaction in the required direction, (2) one can detect with a high degree of sensitivity and indentify the reaction intermediates and the energy state of the molecule in the gas phase can be determined with respect to all degrees of freedom—translational, rotational, and vibrational, and (3) the lifetime of the excited states on the surface can be determined.[27]

The laser spectroscopy of species in the gas phase, which has been rapidly developing in recent years, has been used in particular for the determination of the degree of excitation to various energy levels of the desorbed molecules.[28–30] For this purpose, the laser beam is passed in the immediate vicinity of the catalyst. Among the methods employed, we may mention the intracavity laser spectroscopy (ICLS),[31] which is characterised by a sensitivity of 10^8-10^{10} cm^{-3} and a time resolution of 10^{-6} s, laser magnetic resonance (LMR)[32] with a sensitivity of 10^8-10^{10} cm^{-3} and a time resolution of $10^{-2}-10^{-1}$ s, and laser-induced fluorescence (LIF)[33] with a sensitivity of 10^6-10^{10} cm^{-3} and a time resolution of $10^{-8}-10^{-9}$ s. The multiphoton ionisation (MPI) method exhibits the greatest sensitivity (10^3 cm^{-3}) and is most general.[34] Its time resolution is $10^{-8}-10^{-9}$ s and its spectra resolution is 10^{-3} cm^{-1}. The MPI method has been used successfuly to investigate the quantum state of the desorbed molecules.[35,36]

Other laser techniques—coherent anti-Stokes Raman spectroscopy (CARS),[37] opto-acoustic spectroscopy,[31] multiphoton excitation,[38] and high-resolution sub-Doppler laser spectroscopy[39]—still await their application in the study of the quantum kinetics in gas–solid systems. The electron beam-induced fluorescence (EBIF) method, which provides information about electronically excited states, has been used to investigate the desorption of the N_2 molecule.[40] The IR luminescence method involving the application of a Fourier spectrometer, i.e. the emission of radiation characteristic of excited states, has been employed[41] to identify the vibrational and rotational states of CO_2 as the product of the oxidation of CO on platinum. The time resolution of the method is 10^{-6} s.

Laser methods have been used more rarely for the determination of the kinetic constants of surface processes. The laser-stimulated desorption (LSD) method[42] made it possible to determine the constants for a series of catalytic reactions which are difficult to determine by other procedures. In principle it is possible to attain a picosecond (10^{-12} s) time resolution with the aid of the LSD method.[17]

In order to determine the true lifetime of the ultrashort-lived excited state on the surface, the pulsed picosecond laser technique has begun to be used recently. The specimen is usually irradiated by a laser pulse (for example, a pulse from the neodymium laser) lasting several picoseconds and is probed by the laser before, during, and after the laser flash. The lifetimes of the vibrationally excited states of the OH groups on a series of adsorbents[43,44] and of the CO group in the adsorption of CO on metals and complexes[45] have been measured by this (direct) method. It proved to be $10^{-10}-10^{-11}$ s.

The lifetimes of the electronically-excited states on the surface, measured with the aid of laser picosecond photoelectron spectroscopy (LPS),[46] are about 70 ps. There are as yet very few data on the lifetimes of the electronically excited states and they all lie within a very broad range—from 10^{-5} to 10^{-15} s.[28]

A new method for the study of surfaces has appeared recently—the spectroscopy of second harmonic generation of laser radiation (SGSLR).[47–50] When the pulse technique and a photon counter were employed, unique time resolution, amounting to 100 femtoseconds (10^{-13} s), was achieved, i.e. a time of the order of magnitude of the period of a single vibration. The exceptional sensitivity of the SGSLR method is due to the fact that it makes it possible to measure forbidden transitions in a centrosymmetrical system. Within the bulk of a solid, such symmetry predominates, whilst on the surface it is usually disturbed and the restrictions on

the manifestation of the signal are eased. The kinetics of the adsorption of O_2 on Rh(111)[51] and on Si(111),[52] the kinetics of the dehydrogenation of benzene,[53] etc. have been investigated by the SSGLR method. In the study of two-dimensional phase transitions on the Si(111) face, it was found that, as a result of the exposure of the Si(111) surface to laser radiation, the (7 × 7) structure disappears over a period shorter than 150 fs. During this period, the evaporation of atoms cannot take place: it is easy to calculate that the Si atom ejected at a thermal velocity travels only 0.1 nm during this period. The authors[54] justifiably assume that during such a short period only electronic excitation takes place in the forbidden gap of silicon and that Si atoms move slightly away from the ordered positions. In 1989 yet another short wave femtosecond range began to be used in spectroscopy and a resolution as far as 10^{-14} s was achieved. This makes it possible to investigate the properties of the transition state (activated complex) not by calculation but by means of direct measurements. It is difficult to overestimate the importance of transition state spectroscopy for chemical kinetics and catalysis. Although very simple reactions of the type[55]

$$IHg+I^{\bullet}\rightarrow I+HgI^{\bullet},$$

were investigated in the first studies, there are no fundamental obstacles to extention of this method also to complex, including heterogeneous-catalytic, processes.

The rate of transport of current carriers in a semiconductor has been investigated with the aid of laser pulses lasting 6 fs.[56] Laser pulses having an energy of 2 eV and a duration of 200 fs have been used to desorb NO from the Pd(111) face. Translationally and vibrationally excited NO molecules are desorbed. On the other hand, on exposure to nanosecond pulses, unexcited NO molecules are desorbed.[57]

The rates of phase transformations on the surface and in the bulk phase during adsorption and catalysis can be investigated by dynamic structural methods *in situ*. Numerous studies on the structures of two-dimensional phases of adsorbates and adsorbent surfaces have been performed by the slow electron diffraction (SED) method. This method was also used for kinetic purposes[58] and it is then referred to as dynamic SED or video-SED. In the study of the oxidation of CO on Pt(100) by the video-SED method, the movement of diffraction waves on the surface for a constant interconversion of the Co(1 × 1) and CO(*hex*) structures and diffusion of CO between the phases was observed. The time resolution of video-SED method is about 1 s.

Approximately the same time resolution is attained also when scanning tunnel microscopy (STM) is employed.[59–67] This new very highly sensitive method makes it possible to obtain a direct image of the surface atoms with a spatial resolution less than 0.1 nm, i.e. not only at the atomic but also at a subatomic level. The STM method provides a very detailed photographic picture of chemisorption. The high degree of localisation of the method is to some extent a disadvantage, since the minute details of the region investigated thus revealed are difficult to relate to real atoms and surface orbitals.[66] There are no fundamental reasons to prevent the application of electron microscopy *in situ* to investigate catalysts under a controlled atmosphere.[66] The adsorption of H_2 on Si, of S on Re(001),[62] of O_2 on GaAs,[63] and of NH_3 on Si(111)[65] were investigated by the STM method.

In the method based on the extended fine structure of X-ray absorption (EXAFS), a powerful source of X-rays, usually a synchrotron source, with an energy of 1–25 keV is used. With the aid of these X-rays, the fluorescence or emission of Auger electrons is excited, this being accompanied by the formation of holes in deep levels. The EXAFS method reflects fairly accurately the local structure of the surface and makes it possible to measure the distances between the atoms of the adsorbate and the surface or between the surface atoms. The usual time resolution in the EXAFS method is 10^{-6} s. New highly intense sources of soft X-rays (0.1–3 keV) make it possible to obtain nanosecond (10^{-9} s) pulses. Numerous studies on catalysts and their genesis have been carried out with the aid fo the EXAFS method.[68] The application of the method to the study of the real dynamics of a catalytic process is so far in its initial stage[69] and will undoubtedly expand. In one of the latest studies,[70] the spectra of the Pt/Al_2O_3 catalyst were investigated under the conditions of the reforming of hydrocarbons at 20 atm and 400 °C.

Various physical methods have been applied to investigate the changes in the bulk-phase structure of the catalyst during the catalytic process. We have already mentioned the use of the Mössbauer effect for the analysis of the phase composition of the catalyst *in situ*. In the instruments used hitherto,[14] the power of the γ-radiation sources was low and the measurement of a satisfactory spectrum required a long time, which was necessary to accumulate data. For this reason, only very long characteristic times, of the order of minutes and tens of minutes, can be measured by this method.

In many cases the phase transformations of the catalyst take place relatively slowly and determine not so much the rate of the catalytic step proper as the rate of deactivation or activation, i.e. processes involving the formation and ageing of the catalyst. The diffusion of oxygen from the surface into the bulk of the oxide catalyst and back again can be the rate-determining stage of the catalysis proper in oxidation-reduction reactions. This has been demonstrated by the EPR method *in situ* in relation to oxidation reactions on $V-MoO_3$ catalysts.[16] The measured characteristic times are in the range 1–10 s.

The first studies on the application of NMR spectroscopy *in situ* to the investigation of the structure of a catalyst and its changes have been published.[71,72]

Spontaneous phase transitions can occur as a result of the shift of the lattice by fractions of interatomic distances, in which the diffusion of species in the solid plays a subsidiary role. The formation of nuclei and growth of crystals do not take place. A method of measurement of the highest rates of phase transitions has been developed.[73] Using a pulse source of X-rays with a current of tens of kiloamperes, the authors investigated the structural transformations occurring under the influence of a shock wave. In each experiment, the apparatus was completely disrupted. The minimum measurement time was 10^{-8} s and the transformation was completed over a period shorter than 1 μs. The conversion of α-cobalt into another modification was achieved over a period of 2×10^{-8} s. Thus in spontaneous transformations the rearrangement of the entire lattice can be completed over an unusually short time. For this reason, the further development of the X-ray phase analysis (XPA) method requires the development of powerful sources of X-rays and sensitive detectors. The use of synchroton radiation ("X-ray cinema") is promising.

The molecular beam method occupies a special place in studies of the dynamics of the interaction of molecules with surfaces and of the exchange of energy between the molecules and the surface in order to elucidate the elementary stages in chemisorption and catalysis.[28,74,75] A stream of reactant molecules emitted from a high-pressure

chamber via a small aperture into a vacuum chamber strikes a target (the catalyst). In the beam, the collisions of molecules with one another or with the wall are impossible. Diffusional limitations are also excluded. With the aid of the molecular beam method, it is possible to determine (1) the minimum lifetime of the reactant molecule on the surface required for the occurrence of the reaction, (2) the probability of the reaction in a single collision with the surface, (3) the dependence of the rate of reaction on the energy of the molecules in the beam and on the surface temperature, (4) the distribution of the energy (translational, vibrational, and rotational) between the surface, reactant, and the reaction products, (5) the dependence of the rate of reaction on the surface coverage by measured amounts of the adsorbent, (6) the probability of the deactivation of the excited molecules, and (7) the angular distribution of the desorbed and scattered molecules.

The energy of the molecules in the beam is determined by the design of the source. In thermal Knudsen sources, the gas is maintained at a temperature between 77 and 3000 K. These sources yield beams having an atomic flux density of $(2-4) \times 10^{14}$ s^{-1} cm^{-2} and energies from 0.008 to 0.32 eV. The temperature of the beam is frequently also referred to. However, the estimation of the energy of the molecules in the beam in degrees Kelvin is useful only in the case of a Maxwell–Boltzmann distribution.

The application of an ultrasonic beam makes it possible to narrow the distribution with respect to velocity by a factor of 100 compared with the Maxwell distribution in thermal sources. Despite the high density, the molecules in the ultrasonic beam travel parallel to one another and do not collide. By applying a high pressure (>0.1 MPa), it is possible to attain flux densities of $10^{16}-10^{18}$ s^{-1} cm^{-2} for energies of 1–2 eV. By diluting heavy gases with light ones, which move rapidly, for example, helium, it is possible to raise the kinetic energy to 10 eV. By combining the heating of the molecules in the source with ultrasonic flow, it is possible to obtain molecular beams with equal translational and vibrational energies. If a low pressure of a neutral gas is established in the space between the source and the target, it is possible to preserve the vibrational excitation in the molecules having quenched the translational excitation.

The method of modulated molecular beams for the relaxation spectroscopy of molecular beams (RSMB) is used to investigate the kinetics of heterogeneous-catalytic reactions. The interruption of the beam and the application of pulses of the reactants to the target-catalyst greatly increases the signal/noise ratio. The method makes it possible to measure characteristic times up to 10^{-4} s.

The method of molecular beams has found an interesting application in the investigation of real catalytic reactions at a high pressure.[76] The reaction is studied on the face of a single crystal cleaned in an ultrahigh vacuum. After the reaction, the pressure is rapidly reduced and the face of the single crystal is exposed to the molecular beam. Attempts have also been made to obtain high-density molecular beams simulating a high pressure.

Together with the molecular beam method, the method of ion beams has also been developing.[27,77] The theory shows that ion beams are rapidly neutralised on interaction with the surfaces of metals, forming neutral molecules in a vibrationally or electronically excited state. Thus experiments with ion beams can yield information about the interaction with the surfaces of solids of neutral molecules in the ground or weakly excited states, which corresponds approximately to the information obtained by the method of molecular beams. One of the simple ways of studying the interaction of atomic and molecular ions with the surface involves the acceleration of the ions by means of ionic cyclotron resonance.[78]

In our analysis of the research methods listed above, we drew attention mainly to their dynamic and kinetic applications and their time resolution. However, many of the methods being developed are designed primarily for the determination of the structures of catalysts, the structures of the surface and the active centres, and their energy levels.

III. Dynamics of the elementary step in catalysis

Over a long period, the rates of the elementary processes on the surface have come to be estimated from the standpoint of the transition state theory proposed in the 1930's. In this theory, the real dynamics of the motion of nuclei is not considered and account is taken only of the fundamental characteristics of the potential energy surface for the system and of the thermodynamic equilibrium between the reactants and the transition state (activated complex) at the apex of the potential barrier. The ranges of values of the pre-exponential factor k_0 in the Arrhenius equation for different surface processes have been calculated.[79–81]

Very fine experiments are needed for the determination of the exact values of k_0 and clearly there are not enough such experiments. Furthermore, it has been stated recently in a number of instances that transition state theory is inadequate and is subject to limitations when applied to the processes on surfaces: the tunnelling of nuclei at low temperatures, the possibility of a non-adiabatic course of the reaction, and the need to introduce corrections associated with non-equilibrium effects.[81] For example, in adsorption kinetics the factor k_0 is only partly determined by the laws of equilibrium thermodynamics; its other component (the sticking coefficient) is determined by local non-equilibrium effects.[66] The sticking coefficient is usually much smaller than unity.

The non-equilibrium effects in adsorption and catalysis have been examined in a monograph.[28] Several questions have been posed.

1. Are excited molecules formed in exothermic processes on the surface?
2. What is the lifetime of excited molecules on the surface?
3. What is their reactivity?
4. Is the concentration of the active centres related to the characteristics of the mechanism of catalytic reaction?
5. What is the lifetime of the excited states of the solid catalyst?

An accurate answer to the majority of the questions formulated requires a detailed knowledge of the dynamics of the elementary step. In particular, it is necessary to have detailed information about the potential energy surface. Calculations on the dynamics of the interaction have encountered considerable difficulties and can be performed only in the simplest cases. For example, a simplified trajectory method has been used[82] to describe the interaction of NO with the Pt(111) surface. The calculation, in which account was taken of 19 surface platinum atoms, made it possible to find the dependence of the rotational excitation of the desorbed NO molecules on the initial velocity of the molecules incident on the platinum surface. The majority of the answers to the questions posed above have been obtained experimentally.

The most important result of experiments carried out by the molecular beam method is the frequently observed extremely narrow angular distribution of the scattered molecules. The same thing frequently happens in the desorption of the molecules formed in the catalytic reaction. Thus analysis of the angular distribution of the

CO_2 molecules formed in the reaction of the adsorbed CO and O molecules on platinum showed that the intensity varies in accordance with the $\cos^n\varphi$ law, where $n = 6-40$.[83] The very narrow distribution of the desorbed or scattered molecules indicates their translational excitation.

Three reactions have been investigated on platinum by the thermal desorption method:[84,85]

$$N_2O+CO\rightarrow N_2+CO_2,$$
$$2NO\rightarrow N_2+O_2,$$
$$C_{ads}+O_{ads}\rightarrow CO_g.$$

In all three cases, a narrow angular distribution of the reaction products was observed, i.e. they were translationally excited. It is of interest to note that, after the adsorption of the CO molecules on platinum and the subsequent desorption, the angular distribution obeyed the $\cos\varphi$ law, which corresponds to complete thermal accommodation. Evidently the CO molecules desorbed after the equilibrium adsorption and those formed in the C + O reaction on the surface have different structures. In the second case, the CO molecule is not at the bottom of the potential well before escaping into the gas phase. This suggests the need to revise a series of mechanisms of heterogeneous catalysis according to which the reaction proceeds via adsorption interaction on the surface and desorption. Cases in which the reaction of a molecule continues also after its escape from the surface into the gas phase are apparently possible in catalysis.

The application of modern detection methods has made it possible to record the variation of the vibrational and rotational energies of the scattered and desorbed molecules. It was found that in many exothermic catalytic reactions vibrationally excited molecules are formed on the surface. Such reactions include the recombination of H atoms on copper,[86] the oxidation of CO on platinum and palladium,[87,88] the oxidation of carbon on copper,[89] the oxidation of H_2 on platinum,[90] etc. This indicates the energy of the catalytic reaction can be utilised for its possible acceleration.

The formation of vibrationally excited species in the endothermic NH_3 decomposition reaction on platinum has been observed.[91] On excitation of certain N_2 molecules, the 9th vibrational level proved to be occupied (energy of 2.4 eV). When the mechanism of this reaction was considered, only one exothermic stage was discovered:

$$NH_{ads}+NH_{ads}\rightarrow N_2^*+2H_{ads}+2.4\text{ eV}.$$

This may excite the molecule to the 9th vibrational level.

The phenomena involving the "cooling" of the molecule after catalytic reaction were also observed. The formation of translationally cold molecules with a temperature below the surface temperature after the $D_2 + O_2$ reaction on platinum was explained by the fact that the rate of desorption exceeds the rate of the thermal excitation of the reaction product (D_2O) adsorbed on the surface.[92] "Rotational cooling", i.e. a decrease in the "rotational temperature" of the molecules compared with the surface temperature, is frequently observed in the adsorption and desorption of NO on platinum,[93] nickel,[94] and palladium[95] and in the oxidation of NH_3 to NO on germanium.[96] The "rotational cooling" can be explained by the transfer of the energy of the rotation of the NO molecule before desorption to the translational energy on desorption. The interesting phenomenon of the different probabilities of the adsorption of NO from molecular beams oriented with the N or O atoms pointing towards the surface has been investigated.[97]

The explanation of the observed relations is in its initial stage. With the aid of trajectory calculations, attempts have been made[98] to relate the excitation of the molecules on desorption to the characteristics of the potential energy surface. In the thermal desorption of H_2 from Ni(111), one of the observed peaks corresponds to the predominantly vibrational excitation of the desorbed molecule, while the other corresponds to the predominantly translational excitation. In the former case (surface coverage $\theta > 0.5$), the desorption process is limited by the passage of the molecules through the "inlet" potential barrier, while in the latter case ($\theta < 0.5$) it is limited by their passage through the "outlet" potential barrier. Calculations of a similar kind have shown which part of the energy of adsorption and catalysis is transmitted to the surface and consumed on heating the latter and which is distributed in the form of the translational, vibrational, and rotational energies of the reaction product.[99]

On recombination of the N atoms on metals, electronically excited nitrogen molecules were detected.[100,101] The formation of singlet oxygen O_2 ($^1\Delta_g$) was observed in the oxidative dehydrogenation of butane on the Li–Sn–P oxide catalyst.[102]

Thus the formation of excited molecules in catalysis is an established experimental fact. The task for the immediate future is to find the general rules governing this phenomenon and to discover the relation between the formation of excited molecules and the characteristic features of the mechanism of the elementary step.

If during catalysis and desorption excited molecules are formed in conformity with the detailed equilibrium principle, it is to be expected that the excitation of the molecules reacting on the surface will also influence their reactivity. This phenomenon has been investigated in a number of studies on molecular beams.

In a large number of investigations of the interaction of molecular beams having different energies with the surface, a change in the probability of adsorption was observed as a function of the kinetic energy of the molecules in the beam (see, for example, the studies on the adsorption of H_2 on palladium[103] and nickel,[104] of N_2 on tungsten,[105] of O_2 on platinum,[106] etc.). The sticking coefficient s_0 usually increased with increase of the kinetic energy E_i of the molecules in the beam (the usual range is $E_i \simeq 0.5-10$ eV). The sharp changes in this relation for certain values of E_i are usually explained by the existence of an activation barrier to adsorption, while smoother relations are accounted for by the non-uniformity of the surface, i.e. the distribution of the activation barrier with respect to energy.

However, for very low energies of the beam, for example in the adsorption of O_2 on W(100) for $E_i < 0.03$ eV,[106] s_0 diminishes and does not increase with increasing energy. In this case the dependence of s_0 on the surface temperature T_s is much more marked than the dependence of s_0 on T_i. This can be explained by the occurrence not of direct adsorption but of adsorption via a precursor—a presorption state. Before passing to the chemisorbed state, the molecule can exist for a certain time in a weakly bound presorption state and can migrate in this state along the surface. The concept of a precursor and of its role in chemisorption was first put forward by Langmuir and its role in catalysis was examined in detail as early as the 1930's by Roginskii and Zel'dovich.[107] Prolonged debates concerning the question whether the presorption state is a "myth or reality"[106] were terminated, as a result of experiments with molecular beams, by an unambiguous answer: the precursor is real. Controversy continues concerning the nature of the presorption state: some workers believe that it is a physically

adsorbed molecule while others postulate that it is a short-lived excited state. It may be that both cases occur.

Whereas experiments with beams having differing energies have demonstrated incontrovertibly the influence of the translational energy on activated chemisorption, the available data on the translational excitation are fairly contradictory and do not permit a final conclusion. The appreciable increase in the probability of the dissociative adsorption of CO_2 ($\rightarrow CO + O$) on Ni(100) when CO_2 molecules are heated in a source of an ultrasonic beam has been attributed[108] to the involvement of the vibrationally excited molecules in the adsorption process. According to the authors,[108] distorted (bent) CO_2 molecules participate in the dissociation $CO_2 \rightarrow CO + O$.

Controversy concerning the mechanism of the activation of methane and other paraffins in their interaction with metals has continued for a long time. The large isotope effect, observed in the dissociative adsorption of CH_4 and CD_4 on rhodium, has been explained by the translational excitation of these molecules on passing from the presorption state to the chemisorbed state.[109] The subsequent data were fairly contradictory. Lo and Ehrlich,[110] who investigated the adsorption of CH_4 on W(211), adhere to their previous standpoint,[109] i.e. they explain the activation of CH_4 by vibrational excitation. On the other hand, it is believed that the activation of CH_4 on W(110) is caused by translational excitation with subsequent tunnelling of the H atom on chemisorption.[111] The dependence of the sticking coefficients s_0 of methane, ethane, propane, and butane on Ir(110) on the molecular beam energy has been attributed to the direct translational activation of the molecules colliding with the surface.[112] A deficiency of the above studies has been the lack of accurate data concerning the distribution of energy between different levels in the initial molecules.

Direct selective excitation of one of the bonds in the molecule by a laser makes it possible, in principle, to obtain molecules in a definite vibrational state and thus to achieve selective catalysis. The number of studies in this field is extremely large (see the relevant reviews[113–115]), but the results are not so far convincing. Most experiments have been carried out using irradiation by the IR CO_2 laser of various adsorbed compounds with light corresponding to an absorption band of the OH vibrations. The observed desorption was explained by the selective excitation of the bonds in the adsorbed molecule. However, as noted by Chuang,[116] in reality this explanation is doubtful, since there is no clear-cut dependence of the yield on the vibration frequency. The "translational temperature" of the desorbed molecules is usually low and close to T_s. These phenomena have been explained by "indirect" or "resonance" heating.[117] Phonons are emitted from the intermediate vibrational excitation levels, which leads to the heating of the specimen.

These considerations apply also to various data concerning the effect of the laser on catalytic reactions. The reported[118] acceleration of the oxidation of NH_3 on platinum following exposure to the light from a laser at a frequency of 933 cm^{-1} (vibrations of the N–H bond) was not confirmed in a subsequent test.[28]

More definite positive results have been obtained in the study of the electronic excitation of a solid and of adsorbed molecules by laser radiation in the visible and UV ranges. Thus the desorption of oxygen in the form of O_2 and O from the ZnO surface has been observed on exposure to laser light at the frequency corresponding to the forbidden gap in ZnO (λ = 354 nm).[119]

The use of short ($< 10^{-8}$ s) low-power laser pulses and the study of the process at a low temperature are most promising. By applying very short nanosecond (5 ns) laser pulses with a very low power (0.1–1 mW cm^{-2}), with an energy of 4.6–5.3 eV, Natzle, et al.[120] observed the selective desorption of NO from the Ag(111) surface at a low temperature (25–50 K).

The problem of direct detection of vibrationally excited molecules on the surface in chemisorption and catalysis has not so far been solved. Infrared adsorboluminescence might be used as a direct method for their detection. However, experiments and calculations have shown that, during the period taken by adsorption, the molecules have sufficient time to be virtually completely thermalised and the observed glow is simply a result of the heating of the specimen due to the heat of adsorption.[28] An IR laser has been used[121] for the vibrational excitation of physically adsorbed layers of CO on NaCl(100) at 22 K. The infrared adsorboluminescence observed subsequently was characterised by lifetimes of 2–12 μs.

The lifetimes of excited chemisorbed species on the surface have been measured directly in only one group of studies.[43,44] The lifetimes were calculated from the fluorescence decay time by means of the pulse excitation with a laser of the local vibration of the adsorbed molecule. In a number of studies, the lifetime of the vibrationally excited molecules on the surface was also determined by an indirect procedure—from the width of the lines in the IR spectra. For example, the experimental width of the absorption band of CO on Ni(100) and Ni(111), namely $\Delta\nu$ = 10 cm^{-1}, corresponds to the two-phonon breakdown of the C–O vibrations predicted by the theory.[122] The determination of the vibrational relaxation times from SEW spectra has been examined.[123]

Although the measured lifetimes of the vibrationally excited states are fairly short ($\sim 10^{-10}$ s), the excited species presumably participate in catalytic processes.

As regards the stages of the chemical interaction proper in a catalytic reaction, it is usual to distinguish two extreme cases; the Langmuir–Hinshelwood (OH) or surface interaction mechanism and the Eley–Rideal (ER) or impact mechanism. In the former case, the reaction proceeds between the species of two chemisorbed substances, while in the latter it occurs between a chemisorbed species and a species from the gas phase. The oxidation of CO on platinum and palladium has been investigated in greatest detail.[81,124] If the LH mechanism is valid, the elementary stage is the reaction

$$CO_{ads} + O_{ads} \rightarrow CO_2$$

while in the case where the impact (ER) mechanism operates the elementary stage is the reaction

$$O_{ads} + CO_g \rightarrow CO_2$$

or

$$CO_{ads} + O_{2g} \rightarrow CO_2 + O_{ads}.$$

Strictly speaking, both names are incorrect. In reality both the impact and surface mechanisms had been proposed by Langmuir.

The study of the oxidation of CO on Pt(111) by the relaxation spectroscopy of molecular beams[125] showed that the LH mechanism is valid. When CO molecules were admitted onto the Pt(111) surface coated by adsorbed oxygen, an arrest in the release of CO molecules was observed ($< 6 \times 10^{-4}$ s). The lifetime τ of CO molecules on the surface depends not only on the rate of the surface reaction but also on the rate of desorption of CO. On the other hand, when the ER mechanism operates, there should be no arrest and $\tau = 0$. In certain cases, the ER mechanism apparently also operates in a pure

form. Examples of the translational activation of molecules in dissociative reactions following direct impact against the surface (in the presence of the necessary activation energy) were quoted above. Catalytic reactions involving methane proceed as a result of the direct activation of the CH_4 on impact against the surface:[126]

$$CH_4 \rightarrow CH_3 + H_{ads}$$

In reality the LH and ER mechanisms represent certain limiting cases. In the intermediate (and probably the common) version, chemisorbed molecules and mobile weakly adsorbed species in the presorption state (see above) participate in the reaction.

In the oxidation of H_2 on metal single crystals,[127,128] several surface stages were observed:

$$O_{ads} + H_{ads} \rightarrow OH_{ads},$$

$$OH_{ads} + H_{ads} \rightarrow H_2O.$$

The rate of reaction depends on the surface coverage. The repulsive interaction between neighbouring like species exerts the greatest influence. Such interaction has been examined from the standpoint of the lattice gas theory.[81]

Yet another type of elementary process on the surface has been examined.[129,130] In the dehydrogenation of cyclohexane on platinum,[131] the adsorbed labelled benzene readily exchanges with cyclohexane in the gas phase so that labelled benzene is evolved into the gas phase:

$$Pt \cdot {}^{14}C_6H_6 + C_6H_{12} = Pt{:}C_6H_{12} + {}^{14}C_6H_6.$$

A similar exchange of an alcohol with the Al_2O_3 surface hydroxyl has been observed for the dehydration of the alcohol on Al_2O_3:[129]

$$(OH)_{surf} + ROH \rightleftarrows (OHROH)_{surf} \rightleftarrows (OR)_{surf} + H_2O.$$

Thus the dehydration of the alcohol involves adsorption substitution. According to an estimate,[129] the rate of the associative desorption exceeds by many orders of magnitude the rate of the direct desorption (for example, the evolution of water on dehydration of a surface OH group).

An associative complex has been detected by the direct IR spectroscopic method *in situ* in a study of the selective oxidation of isobutene to methylacrolein on a complex oxide catalyst.[11] It has been demonstrated[132] that associative substitution processes and, in a more general form, reactions involving strongly chemisorbed species occur widely. In the reactions mentioned above,[129–131] the activated complex included one strongly and one weakly chemisorbed species. Subsequently this phenomenon was "rediscovered" and was called "adsorption-induced desorption"[133] without referring to earlier investigations.[129,130]

Processes involving the migration of the reactants on the surface (surface diffusion), where one of the reactants diffuses towards the other which is adsorbed more strongly, or towards an active centre at which it reacts also occur extensively in catalytic surface reactions.

It is noteworthy that the surface migration process proceeds as a significantly activated process, its activation energy being appreciably smaller than the activation energy for desorption. Since the species on the surface are far from free in their migrations, in many cases the local concentrations can be replaced by average concentrations when surface diffusion is considered.[28,134]

There exist many examples of the experimental determination of the surface diffusion coefficients by the method of electronic[135,136] and ionic[137] projectors. However, the choice of objects is small and is determined by the possibility of obtaining an image of a section of the surface of the metal in an electronic projector or of individual species in an ionic projector. The diffusion of metal[137] and oxygen[135] atoms and CO molecules[136] on the surfaces of metals has been investigated by this procedure. A method for the determination of the surface diffusion coefficients by studying the desorption induced by the rapid heating of a section of the catalyst has been developed at the Institute of Chemical Physics.[138] Measurements have shown that the activation energy for surface migration is 0.1–0.3 of the activation energy for desorption or 20–60 kJ mol^{-1}, while the pre-exponential factor is between 10^{-2} and 10^{-4} cm^2 s^{-1}.

A model of surface diffusion as a process involving the migration of species both via jumps between centres and in the energy space as a result of the absorption and emission of phonons has been investigated in detail.[134] The possibility of the migration of species over large distances in a single jump has been demonstrated. Allowance for such a jump, which covers many lattice periods, leads to the appearance of characteristic relations in the kinetics of surface reactions, in particular, in the time variation of the rate constant.

The number of measured rate constants for surface diffusion is still very small. It is also essential to know the rate constants for the diffusion of the reaction components into the bulk of the catalyst or into its micropores. In oxidative catalysis, the elementary stage of the process may be the diffusion of oxygen atoms (ions) into the bulk of the oxide catalyst. In selective oxidation catalysts such as bismuth molybdates, the diffusion coefficients of oxygen at the catalytic temperatures can reach $10^{-4}-10^{-6}$ cm^2 s^{-1}. The usual mechanisms of the diffusion of atoms in a solid via vacancies or interstices do not explain such high diffusion coefficients.[139] In order to obtain an explanation of this kind, it is essential to consider cooperative mechanisms (see the next section).

Despite the enormous practical importance of real studies on diffusion in ultraporous catalysts of the type of zeolites, they were begun only recently. At the temperatures of catalytic cracking, the diffusion coefficients of ethane and heptane in the HT-zeolite are respectively $10^{-11}-10^{-12}$ and $10^{-13}-10^{-15}$ cm^2 s^{-1}.[140] MAS–NMR (NMR with magic angle spinning) methods are used to investigate the diffusion in zeolites.[141] Trajectory calculations of the diffusion coefficients of molecules in zeolite pores using data for the real geometry and for the movements of the atoms constituting the zeolites are extremely interesting.[142]

There also exist a further two types of elementary processes in catalysis; electron transfer and proton transfer between two reactants or between reactants and the catalyst.

There have been an enormous number of studies in which the rates of transfer of an electron between the surface and the bulk of a solid were considered, in particular between the adsorbed molecules and a solid. These investigations are in the main associated with the development of microelectronics.[143] "Fast" surface states with capture cross-sections $\sigma \simeq 10^{-13}-10^{-15}$ cm^2 (the corresponding electron or hole capture times are $10^{-8}-10^{-10}$ s) and "slow" surface states with $\sigma \simeq 10^{-18}-10^{-21}$ cm^2 (capture times $10^{-4}-10^{-1}$ s) have been observed. "Ultraslow" traps, characterised by capture cross-sections of $10^{-20}-10^{-30}$ cm^2, which are apparently associated with adsorbed states have also been noted. These ultraslow slow stages in fact determine in many instances the charge and potential of the

surface. The capture times vary in this instance within the range $10^{-1}-10^{3}$ s at low temperatures, i.e. they are equal to or exceed the characteristic times of the catalytic reaction.

It has also been demonstrated[143] that the so called electronic theory of catalysis on semiconductors,[144] in which considerable importance is attributed to the equilibrium Fermi level in the semiconductor as a criterion of its adsorption and catalytic activity, is inconsistent with the experimental data. Owing to the relatively low rate of transport of species on the surface and in the surface layer of the adsorbent and the catalyst, non-equilibrium processes occur.

It has been shown in a number of studies[145,146] that, under the conditions of adsorption and catalysis, the electron and hole transport to adsorbed molecules is effected over large distances from the bulk of the solid. Adsorption requires the obligatory direct overlap of the orbitals of the molecule being adsorbed and the surface atom—active centre. Pure charge transfer is overtaken by the subsequent movement of atomic species, for example, the diffusion of oxygen in the oxide, which frequently limits the rate of the catalytic oxidation.

For example, in the oxidation of allyl alcohol on V/MoO_3, investigated by the EPR method *in situ*,[146] the alcohol molecule initially interacts with the surface oxygen ions O_s^{2-}:

$$CH_2{=}CHCH_2OH+O_s^{2-}\rightarrow CH_2{=}CHCHO+H_2O+\square_s^{2-}.$$

After this, the electron rapidly passes from the surface into the bulk phase, which leads to the reduction of the vanadium ion which is observed by EPR:

$$\square_s^{2-}+V_v^{5+}\cdots O^{-}\rightarrow \square_s^{-}+V^{4+}\cdots O^{-}.$$

Next follows a slow stage—the diffusion of oxygen to the surface (or the reverse diffusion of a vacancy into the bulk of the catalyst):

$$\square_s^{-}+V^{4+}\cdots O^{-}\rightarrow V^{4+}\square_v+O_s^{-}.$$

Under the conditions of stationary catalysis, the movement of electrons into the bulk of the catalyst and from the bulk to the surface and the corresponding movement of oxygen ions reach equilibrium and a surface layer only a few angstroms thick actually "works".

At low temperatures, the electron moves over distances up to 1–2 nm via a tunnel mechanism. The reaction has a low activation energy. At a higher temperature, charge is transferred via the polaron or band mechanism. At still higher temperatures, the main catalyst lattice is oxidised and reduced.

In acid–base catalysis, the most probable elementary stage is proton transfer to the adsorbed molecule with formation of a positive ion (a carbonium ion in the case of hydrocarbons: $C_nH_m + H^+\rightarrow C_nH_{m+1}^+$) or a proton is split off with formation of a negative ion (a carbanion in the case of hydrocarbons: $C_nH_m\rightarrow C_nH_{m-1}^- + H^+$). The carbonium and carbanion mechanims of catalysis have been recognised by most investigators who have studied the reactions of hydrocarbons on oxide catalysts.[147] However, in reality there are very few examples of the spectroscopic detection of carbonium ions on the surface and under catalytic conditions there have been almost none.

Attempts have been made to use the NMR method for this purpose. For example, the kinetics of the conversion of methanol into hydrocarbons on the H-ZSM-5 zeolite were investigated on the basis of the MAS–NMR spectra *in situ*.[141] The formation of protonated methyl ether $(CH_3)_2OH^+$ is apparently an intermediate stage. In the latest study,[148] it was possible to determine the mobility of the protons of the hydroxy-groups of oxides from the width of the NMR line. It was found that the range corresponding to a sharp increase in the mobility of protons on catalysts such as γ-Al_2O_3, Al_2O_3.HF, and others coincides with the region corresponding to the rapid increase in catalytic activity in the dehydration of alcohols. The average residence time of the protons in the equilibrium state is of the order of 10^{-6} s. The authors[148] concluded that the transport of protons ensures more effective interaction with the adsorbed molecules than the transport of the molecules themselves to the hydroxy-groups (under these conditions, we have $\sim 10^{-4}$ s).

The dynamics of proton transfer in the adsorption of molecules with participation of the hydroxy-groups of the surfaces of the oxides has been examined.[149] By analysing the changes in the IR spectra (specially overtones of the OH vibrations) during adsorption, the author[149] concluded that the potential barrier to proton transfer may be lowered.

In subsequent studies, it was shown that proton transfer processes in cyclic complexes of the reactants with the catalyst occur widely in heterogeneous catalysis.[150] The transfer of a proton (or protons) in a single cyclic complex appreciably reduces the activation energy. Such cyclic complexes were first proposed to account for the catalysis of acid reacitons on Al_2O_3 as early as 1938 in studies by Shilov.[151] It remained only to demonstrate their involvement in catalysis by direct spectroscopic measurements.

IV. Macrodynamics of the catalytic process

Together with the concept of chemical kinetics as the science of the rate and mechanisms of chemical reactions, the term "dynamics" of chemical reactions has been increasingly applied in recent times. The term dynamics is applied to the theory of the general evolution of chemical systems on the basis of kinetic equations and dynamic equations of mathematical physics.[152,153] The methods developed by mathematicians for the study of dynamic systems have been vigorously applied in recent years to heterogeneous catalysis.

The kinetic description of heterogeneous-catalytic processes is based on the ideal adsorbed layer model developed by Langmuir.[154] According to this model, all the sections on the surface are uniform and on each of them equilibrium adsorption is observed. The catalytic reaction takes place on interaction of the reversibly adsorbed species. Further development of the formal kinetics of catalytic processes showed that fractional orders, which do not arise from the simple Langmuir kinetics, are frequently encountered in the kinetic equations.

The concept of the kinetics of catalytic processes on non-uniform surfaces was therefore developed in the studied of Roginskii, Zel'dovich, and Temkin.[155] According to this concept, the existence of biographic or induced non-uniformities is postulated and either a distribution function for the centres with respect to heats of adsorption or the law governing the interaction of the species on adsorption is introduced. The idea of a non-uniform surface or of the interaction of the adsorbed species made it possible to explain numerous kinetic relations observed in the study of adsorption and catalytic processes.

Studies in the recent decades have shown that the real picture is still more complex. It has been observed with the aid of physical methods that even on ideal atomically clean single crystal surfaces the kinetics of adsorption and of the reaction are not described by simple Langmuir equations.[156] We may also note the problem of the so called "pressure gap" in studies on catalysis, which are usually carried out at a pressure of 1 atm, and in studies on the physics of surfaces where the kinetics of the elementary heterogeneous processes are investigated under high vacuum conditions ($10^{-6}-10^{-2}$ Pa). In some investigations, attempts have been made to fill this gap. For example, the oxidation of CO on Pd/Al_2O_3 has been investigated[157] in the pressure range from 10^{-4} to 10^4 Pa. The difference between the turnover numbers at low and high pressures of almost an order of magnitude indicates the operation of different mechanisms of the reaction under these conditions.

Numerous studies have shown that deviations from the Langmuir kinetics may be induced not only by the non-uniformity of the surface on interaction between the molecules but also by entirely trivial causes; mass and heat transfer and non-isothermal conditions in the catalyst bed. Among the non-trivial causes associated with the dynamics of the catalytic process itself we may note the following:

(1) phase and structural rearrangement of the catalyst;

(2) phase transformations of the two-dimensional adsorbed layer;

(3) diffusion of the reactants and intermediates between the active centres (kinetics with a precursor);

(4) diffusion of the reactants and intermediates between the different phases in a complex catalyst (spill-over);

(5) exchange of material between the surface and the bulk of the catalyst under the conditions of the catalytic reaction mixture;

(6) the possibility of the extension of the reaction to the gas phase (heterogeneous-homogeneous processes);

(7) the non-equilibrium nature of the process and the influence of the energy exchange on the reaction kinetics;

(8) radical-chain processes on the catalyst surface;

(9) complex autocatalytic and coupled reactions.

For a complete kinetic and dynamic description of the catalytic reaction, it is essential to divide all the relaxation processes into rapid and slow, to elucidate the question of the existence and of the number of stationary states, to carry out studies under conditions remote from equilibrium, and to construct phase portraits of the system (in terms of the "concentration–concentration" or "concentration–temperature" variables).[152] Kinetic models have been devised with three, four, and more independent variables in which account is taken of the catalytic stage proper and the interactions, listed above, which complicate the process dynamics. Even the superposition of two processes with similar characteristics can give rise to a fairly complex overall picture of the dynamic behaviour of the system.[124] The non-linearity arising under these conditions greatly hinder the description of the catalytic reaction.

Theories in which account is taken of the lateral interaction of the nearest molecules on the surface are used for the description of the kinetics of adsorption, desorption, and the reaction on the catalyst surface. These are the Ising[157] and lattice gas[81] models.

The CO oxidation reaction on metals has been subjected to the most comprehensive and detailed investigation. Most workers tend to the view that the main reaction proceeds via the Langmuir–Hinshelwood mechanism. The "non-linearity" of the kinetic equations, caused by the interaction between the adsorbed susbtances, leads to a series of unusual features in the dynamic behaviour of the system.[124,158] Critical phenomena, a multiplicity of stationary states, and autooscillations arise. It has been shown[124] that the slow relaxation, observed in the oxidation of CO on metals, i.e. the anomalously long period of the transition from the initial to the stationary state, can be induced by purely kinetic causes arising from the Langmuir–Hinshelwood mechanism. It had been believed previously that such phenomena are caused by extraneous factors, for example by the slow diffusion of substances on the surface or in the bulk of the catalyst.

At the microscopic level, new approaches to the description of the dynamics of catalytic processes with allowance for the interaction between the reaction medium and the catalyst have been developing on a wide scale. Such processes are considered from the standpoint of the thermodynamics of irreversible processes[159] and synergistic effects.[160]

The application of the concept of reaction affinity, introduced by De Done and borrowed from the thermodynamics of irreversible processes, made it possible to determine the directions of the transformations in a system of complex consecutive reactions.[161] For the occurrence of the reaction, it is essential that the affinities of all the stages in the chain of consecutive reactions are positive. Hence it was concluded that thermodynamic coupling (i.e. the occurrence of a thermodynamically unfavourable reaction after another more favourable one) is impossible. However, in chain or catalytic reactions there is a possibility of kinetic coupling: this requires that the concentration of the intermediate should be higher than the "equilibrium" concentration, if the concentrations refer to the number of reactants (i.e. the species on the left-hand side of the chemical equation of the given stage), or is below the "equilibrium" concentration if the concentrations refer to the number of reaction products (the species on the right-hand side of the equation). At high concentrations of the intermediate, there is a possibility of highly endothermic stages, for example, the desorption stage, which is almost always thermodynamically unfavourable. For example, in the decomposition of NH_3 on tungsten and molybdenum film, the stationary surface coverage by nitrogen atoms under catalytic conditions is much higher than the equilibrium concentration (i.e. the concentration in the absence of catalysis involving the reaction $N_2 \rightleftarrows 2N_{ads}$). The high concentration of nitrogen atoms ensures the occurrence of both the endothermic desorption of N_2 and of the catalytic reaction as a whole.[162]

Thus the widely used concept of the decrease in activation energy on catalysis compared with the non-catalytic reaction as the main cause of catalysis is incorrect or at any rate inadequate. Catalysis is also characterised by the formation of superequilibrium concentrations of intermediates, which is necessary to overcome the endothermicity of the unfavourable stages.

Whereas for small deviations from equilibrium it is possible to make do with linear mechanisms, for large deviations the breakdown of linearity cannot be disregarded. New stationary states arise and are stabilised as a result of energy exchange with the medium. They are organised in both space and time. Prigogine[159] called such structures dissipative. Dissipative structures are formed in open systems under the conditions of exchange of material or energy with the medium and for the cooperative occurrence of microscopic processes.

Four types of dissipative structures have been observed;[163] (1) spatially non-uniform; (2) periodic in time (autooscillations); (3) spatial-temporal (autowaves); (4) bistable or polystable (of the "trigger" type). An increasing number of observations of dissipative structures accumulate in heterogeneous catalysis every year, which

suggests that the observed phenomena are general in character. This applies particularly to complex catalytic systems.

Among spatially non-uniform structures—dissipative structures of the first type, two-dimensional phases have been investigated in greatest detail. In the study of low-temperature adsorption in single crystals of metals and oxides, an enormous number of two-dimensional phases have been discovered.[164,165] Their role in catalysis was also studied, in particular the possibility of a reaction between two adsorbed susbtances forming different phases has been examined. The oxidation of CO on single crystals of platinum group metals has been studied in greatest detail (and continues to be studied). The phases of the adsorbed CO and O on the Pd(111) face and the possible mechanisms of the interaction between them have been investigated by the video-SED method.[165,166] At low coverages, isolated portions of the two-dimensional O_{ads} and CO_{ads} phases are observed and reaction between them is possible as a result of surface diffusion. At moderate coverages, the phases come into contact and the reaction can proceed at the interface. Finally, at coverages close to one monolayer, mixed two-dimensional phases are formed in which each adsorbed CO molecule has a neighbouring O atom and can react with it.

In our studies,[167] the topochemical model of the formation and growth of nuclei was used to describe the kinetics of two-dimensional phase transformations. This model made it possible to explain a series of anomalous phenomena in the kinetics of heterogeneous catalytic reactions. The initial nuclei are formed more readily on dislocations, edges, and other defects. There are also data showing that the reactions of two-dimensional phases can proceed via a cooperative pathway as a result of shifts in linear series. For example, the conversion of the (1 × 1) structure into the hexagonal structure (*hex*) on Pt(100) is a result of the shift of atomic layers through a disordered state.[168]

The so called kinetic phase transitions[169] and their role in heterogeneous catalysis are widely investigated. The ZGB (Ziff, Gulari, and Barshad) model[170] has been used in very numerous investigations. The authors[170] examined similar kinetic transitions in relation to the oxidation of CO on a square uniform lattice. The probability of adsorption in each collision of the molecule with an active centre was assumed to be unity and the probability of reaction in each entry of a CO molecule and an O atom into neighbouring centres was also assumed to be unity. The very fact that the CO molecule occupies one centre on the surface while the O_2 molecule occupies two centres leads to sharp breaks on the curve describing the dependence of the surface coverage on the composition of the gas mixture and to corresponding changes in the reaction rates. Conditions were found under which periodic interaction of the metal alternately with CO and O_2 ensures a higher yield of the product than the interaction with a CO + O_2 mixture. Such sharp breaks were called kinetic first- and second-order phase transitions.

In subsequent studies,[171–174] the ZGB model was developed further: other types of lattices were examined, for example, the hexagonal lattice, and account was taken of the influence of the rates of desorption and diffusion and of the finite probability of reaction (< 1). In all cases, stationary oxidation of CO is possible only in the middle range of coverages θ_{CO} (in the simplest case from 0.33 to 0.52). At the edges of this range, the catalytic activity changes abruptly and a "kinetic phase transition" takes place. Much importance has been attributed to the formation of clusters under the conditions of low coverages θ_{CO} and θ_O and to subsequent percolation in the same CO oxidation reaction on platinum.[175]

The study of the role of two-dimensional and adsorption phases in catalysis is in its initial stages. The application of the video-SED method in catalysis suffers from an evident disadvantage; with its aid, it is possible to determine the structure of the surface only in a high vacuum. Furthermore, the majority of studies have been carried out with an abrupt transformation of the equilibrium phase into a non-equilibrium one by the rapid increase or decrease in temperature, which hinders the study of the initial stage of phase formation. The rapid development of tunnelling electron microscopy, which can be used at a high pressure and even in a liquid, will make it possible to carry out investigations during catalysis *in situ*.

The question of three-dimensional phase transformations and of their role in catalysis has been elucidated to the greatest extent. This problem has been examined in greatest detail in connection with oxidation-reduction reactions of oxidation catalysts. For example, the stability of the catalytic oxidation reactions involving the formation and decomposition of the oxidised and reduced phases has been discussed:

$$M+{}^1/_2O_2=MO, \quad MO+R=RO+M,$$

where M is the metallic phase, MO the oxide phase, and R the oxidised substance. On the basis of the phase rule, some workers[176,177] suggested that under stationary conditions the catalyst should consist of only one phase, M or MO, and that phase transformations cannot serve as stages in a catalytic reaction occurring under stationary conditions.

Further investigations demonstrated that these considerations are erroneous. In reality, during the reaction the catalyst exists in a non-equilibrium state. After oxidation and reduction under catalytic conditions, several phases usually coexist. In particular, it was shown that in the stationary state the oxidised and reduced phases can coexist in the catalyst.[178] On the other hand, under certain external conditions none of these phases can exist.

The existence of non-equilibrium phases in a series of catalytic reactions has been observed at the Institute of Chemical Physics by X-ray phase analysis *in situ*. Thus, in the selective oxidation of propene on the complex Bi–Mo–Co–Fe oxide catalyst, a non-equilibrium iron molybdate phase is formed in which there is a high concentration of vacancies and there iron exists in a state intermediate between Fe^{2+} and Fe^{3+}.[179] After extensive oxidation of methane on Pt/V_2O_5, the formation of a phase having the stoichiometric composition V_2O_4 was observed but with a crystal structure corresponding to that of the initial V_2O_5, i.e. having an enormous number of vacancies.[180] The non-equilibrium phases observed in the above investigations[179,180] facilitate the transport of oxygen via the lattice, which in the given instance is a stage of the overall catalytic process. Under the conditions of the Fischer–Tropsch synthesis on an iron oxide catalyst, a layered structure consisting of alternating fairly thin (20–30 Å) layers of iron oxide and carbide, is formed.[181]

The question of the catalytic transformations occurring in the vicinity of the phase transition point is also of interest. It has been shown that the ferroelectric $BaCO_3$ phase, which is inactive in the oxidation of CO, is converted at the Curie point (403 K) into a catalytically active paraelectric phase.[182] The Curie point of barium titanate shifts by several degrees following the adsorption of various gases; electron acceptors (NO and oxygen) increase it, whilst the electron donor CO and propene reduce it. Hence it follows that not only the phase transition but also, conversely, adsorption and catalysis influence the phase transition point.

Dissipative structures of the second type consist of auto-oscillations. In the 1970's–1980's studies on autooscillations in heterogeneous catalysis developed in an avalanche-like fashion mainly in relation to catalytic oxidation. We may note for example, studies on the autooscillations in the oxidation of cyclohexane on the NaY[183] and KY[184] zeolites, the oxidation of propene on $Co_xMg_{1-x}O$,[185] and the oxidation of CO on palladium-containing zeolites.[186]

Autooscillations are a striking manifestation of the self-organisation and non-equilibrium phenomena in catalysis. In order to account for autooscillations, various kinetic models are used, including negative feedback, non-linearity, and the presence of buffer stages (see the relevant reviews[187,188]). Common explanations include the change in the activation energy for the reaction with surface coverage (for example, as a result of the charging of the surface and the formation of an oxide layer on metals[186]), the thermokinetic mechanism which presupposes the heating and cooling of the system (provided that its heat capacity is high), a heterogeneous-homogeneous mechanism,[189] the existence of two and more surface forms, and the existence of two different phases (for example, oxidised and reduced).

A series of studies in which two-centre and two-phase models of autooscillations in heterogeneous catalysis were confirmed have been published recently. Thus it has been shown that the autooscillations in the H_2 oxidation reaction on different catalysts can be explained by the existence on the surface of Z and Z* centres having different activities and by the transfer of adsorbed species on the surface from one set of centres to another.[190] The autooscillations in the CO oxidation reaction on Pt(100), investigated by means of direct observations of the surface structure using the video-SED method[191] and scanning photoemission spectroscopy,[192] are induced by the coexistence of two structures—a square (1 × 1) structure and a hexagonal (*hex*) structure—of two-dimensional phases. For a coverage $\theta_{CO} < 0.5$, the *hex* structure is stable, whilst for higher values of θ_{CO} the (1 × 1) phase induce a decrease in θ_{CO}, as a result of which the phase transition takes place again and the oscillatory cycle is repeated. The mechanism of this phase transition was investigated with the aid of scanning tunnelling microscopy. It involves the formation of isolated groups (nuclei) comprising adsorbed CO and the subsequent diffusion of the CO species into the layer over the isolated groups.[193] Such isolated groups are much larger than atomic groups but smaller than the area of the single crystal face (90 μm^2).[194]

On Pt(110), autooscillations are observed in the oxidation of CO over a narrower temperature range and are sensitive to small oscillations in pressure. Here too, as on Pt(100), the autooscillations are induced by the presence of two surface phases, but, in contrast to the process on Pt(100), synchronisation is acheived not as a result of the propagation of surface waves of phase transformations but apparently occurs via the gas phase.[195] The synchronisation of autooscillations on the (110) faces of two separate small palladium crystals is achieved very rapidly, over a period of several seconds.[196] On the other hand, on the Pd(111) and Pd(100) faces of the single crystal such synchronisation has not been observed.[197]

The very important problem of the synchronisation of autooscillations in catalysis is still far from being solved. Rigorously periodic autooscillations are frequently observed not only on single crystals but also on powders containing a large number of grains and microcrystals. An attempt has been made[198] to explain the synchronisation of the autooscillations in the oxidation of CO on a palladium-containing zeolite by phase transitions accompanying the oxidation of palladium in combination with thermal effects. The strong heating occurring in the exothermic reaction

$$O_{ads} + CO_{ads} \rightarrow CO_2$$

leads to the diffusion of oxygen and further to the Pd→PdO phase transition. It has been shown[198] that, for small sizes of the palladium crystals, all the oscillations are averaged out and the reaction proceeds in a stationary regime. An increase in the size of the small crystals facilitates the diffusion of O_2 between them and increases the thermal conductivity, which in fact leads to the synchronisation of the autooscillations.[199]

Among other oscillatory regimes in liquid-phase reactions, apparent non-periodic oscillations or chaos have been observed.[200] Deterministic chaos is described in terms of the so called strange attractor in which all the trajectories are attached to a definite region in the three-dimensional phase space. The transition from regular autooscillations to chaotic ones and back again has been observed in the oxidation of CO on Pt(110).[201] The transition to deterministic chaos took place via a stage involving the doubling of the period of the oscillations.

Autooscillations have been observed also in non-oxidative heterogeneous-catalytic reactions: in the interaction of NO with CO on Pt(100),[202] in the decomposition of CH_3NH_2 on platinum,[203] and in the hydrogenation of nitrobenzene on deposited copper and nickel catalysts.[204]

Dissipative structures of the third type—spatial-temporal periodic structures or autowaves—are observed on smooth catalyst surfaces in the same cases as autooscillations.

Travelling waves have been observed in the oxidation of NH_3 on a platinum filament.[205] After brief heating of a small section of the filamental catalyst and after the transition of the reaction on this section from the initial kinetic regime (from a state with a low catalyst activity) to the diffusional regime (to a highly active state), it is possible to obtain a travelling wave in which sections having a high activity alternate with those having a low activity. The travelling wave can be obtained also by the converse procedure involving the rapid cooling of one of the surface sections.

The autowaves arising in the oxidation of CO on the Pt(100) face have been investigated by the video-SED method with scanning of the surface.[206] Autowaves are generated by the alternation of the (1 × 1) and *hex* structures with diffusion of the CO between the phases. Irradiation of a small spot on the Pt(100) surface with laser light induces the desorption of CO in the spot and the propagation of chemical waves at a rate of 2 mm min^{-1} at 480 K.[207]

The problem of the existence of stationary periodic structures or Turing structures in heterogeneous catalysis is separate. In liquid-phase reactions, such structures arise for certain ratios of the rates of reaction and diffusion. They can be observed when the autooscillatory Belousov–Zhabotinskii reaction is carried out in a layer of chromatographic gel.[208]

Dissipative structures of the fourth type, which arise when there are two and more stationary regimes corresponding to the same parameters and with an abrupt transition between them, have long been known in heterogeneous catalysis. The critical phenomena observed in the oxidation of CO and hydrocarbons on metals[209] have been sometimes explained by the self-heating of the catalyst with transfer of the reaction to the diffusional region. Further investigations demonstrated, however, a non-thermal cause of the observed phenomena. The existence of two stationary regimes in the oxidation of CO on platinum—one at high CO concentrations and

the other at high O_2 concentrations—can be explained by the competition between the adsorption and impact mechanisms.[124,153] The ZGB model mentioned above, according to which the critical phenomena in catalysis are caused by kinetic two-dimensional phase transitions, was later used[210] to explain such bistability.

Critical phenomena of this kind have been observed in the study of the oxidation of ammonia on fine platinum filaments.[205,211] The thermographic method developed by Berelko, et al.[205] made it possible to achieve the compensation of the heat evolution in the reaction over a very short period of 10^{-4} s. This procedure made it possible to demonstrate that the rapid transition from the low-temperature stationary regime to the high-temperature regime is induced by kinetic causes and not by a "thermal explosion". Critical phenomena have been observed also in a calorimetric study of the oxidation of propene on the deposited catalyst MoO_3/MgO.[212] The sharp increase in the rate of reaction after the attainment of a certain degree of surface coverage by oxygen was explained by the formation of a more active surface phase.

Hysteresis phenomena have been observed in many critical reactions. These involve the occurrence of the reaction via different stationary states depending on whether the reaction takes place with rising or falling tempertures or depending on the direction in which the reactant concentration varies. Hysteresis has been observed in the oxidation of methane on Pt/V_2O_5 [180] and of NH_3 on platinum.[211] This phenomenon has been usually explained by phase transformations and by changes in the structure of the catalyst on the surface.

In the extensive oxidation of propene on the $CuO/Cu_2O/Cu$ or NiO/Ni catalyst, the hysteresis loop was observed under conditions where the temperature of the O_2 pressure was varied in the forward or reverse directions.[213] These phenomena were attributed to catalyst oxidation and reduction processes. According to Greger, et al.,[213] the removal of oxygen from the catalyst and the absorption of O_2 are independent processes which are influenced by the particle size, the morphology of the particles, and the presence of impurities. Over a wide range of external parameters, two catalyst phases coexist: oxidised and reduced.

The critical phenomena in catalysis have also been attributed to the appearance of a branched chain reaction involving the formation of active centres.[211] An attempt to explain the "catalytic explosion" observed in the decomposition of HCOOH on Pt(110) by the occurrence of a branched chain reaction has in fact been made.[214] However, all the attempts to accelerate the decomposition by introducing the possible intermediate active species formed in the decomposition of HCOOH (hydrogen atoms, CO, and others) yielded a negative result.

There are general relations between catalysis and chain reactions.[215] In heterogeneous catalysis, there is a possibility of the formation of active species: free atoms and radicals escaping from the surface of the gas phase, quasi-free species propagating the chain reaction in the adsorbed layer, and also excited molecules. The commonest case is, however, the formation of non-equilibrium centres of the catalyst itself, similar to the species involved in a gas-phase chain reaction. Examination of the simplest kinetic schemes for A→B catalytic reactions showed that the catalyst activation stage

$$A+Z\rightarrow A+Z^*,$$

where Z is an active centre, is analogous to the chain reaction initiation stage, the catalytic stage proper

$$A+Z^*\rightarrow B+Z$$

is analogous to the propagation of a chain reaction, while the catalyst deactivation stage $Z^*\rightarrow Z$ is analogous to linear chain termination. The possible mechanisms of the formation of new active centres in catalysis, analogous to the occurrence of a branched chain reaction, have also been examined.

The kinetic differences between catalysis and a chain reaction are apparently not very significant. However, there are so far few chain mechanisms in catalysis whose reality has been demonstrated. There have been studies indicating a chain mechanism of the oxidation of CO on V_2O_5/SiO_2,[216] of the isomerisation of olefins on MoO_3,[217] of the Fischer–Tropsch synthesis on iron catalysts,[218] and of the synthesis of hydrocarbons from methanol on zeolites.[219] Further development of physical methods will make it possible to detect more reliably the intermediate species characteristic of chain mechanisms in catalysis.

Here we should like to draw attention to a number of features characteristic of a chain reaction which are frequently observed in catalysis: (a) the alternation of the formation and destruction of active centres (the occupation and liberation of the centres on the surface); (b) the attainment of superequilibrium concentrations of intermediates helping to overcome the endothermicity of unfavourable stages; (c) the attainment of the maximum rate of the reaction after some time has elapsed from its start.

The occurrence of heterogeneous-homogeneous catalysis, where the active species are desorbed from the surface and propagate the chain reaction in space, also constitutes indirect evidence in support of a chain mechanism. The phenomenon of heterogeneous-homogeneous catalysis was discovered in the 1930's and was investigated mainly by the method involving separate calorimetric measurements on the catalyst and the gas phase, which served as the principal means of detecting the homogeneous chain propagation of the heterogeneous-catalytic reaction.[220]

A series of data showing that not only free radicals but also excited molecules can escape from the surface in exothermic catalytic reactions have appeared recently. We have already quoted a number of examples of the narrow angular distribution of the desorbed molecules, indicating their translational excitation. For example, in the decomposition of hydrazine, i.e.

$$N_2H_4\rightarrow N_2+2H_2$$

on Ir(110) the entire evolved nitrogen is distributed within the limits of 7° around the normal to the surface and is translationally hot.[221] In an earlier study[222] of the catalytic decomposition of N_2H_4 by the method of separate calorimetric measurements, the heating of the gas phase relative to the catalyst was explained by the radical-chain propagation in the gas phase of the reaction initiated on the surface. In the light of new data,[221] this result can be explained also by the escape from the catalyst of excited molecules, which are subsequently deactivated in the gas phase with evolution of heat.

In the course of the oxidative dehydrogenation of butene on the Li–Sn–P oxide catalyst, the formation of an electronically excited molecule—singlet oxygen $O_2(^1\Delta_g)$—was observed.[223] It may be that the flow of the gas phase observed in certain catalytic oxidation reactions at 400–500 °C is caused by the formation of electronically excited molecules.

The heterogeneous-homogeneous mechanism of catalysis is apparently the principal mechanism of catalysis at high temperatures. Depending on the nature of the molecules and catalysts, ionic mechanisms of the electrophilic or nucleophilic substitution type, common in liquid-phase organic processes, predominate at low

temperatures (200–500 °C) and acid–base interaction plays an important role. Homolytic mechanisms involving the formation of free radicals and excited molecules predominate at a high temperature.

The transition from the measurement of macrocharacteristics (separate calorimetric measurements, increase in the free volume of the gas over the catalyst) to the direct detection of intermediate species became a new stage in the study of the mechanism of heterogeneous-homogeneous catalysis. The method involving the freezing out of radicals in a matrix beyond the layer of catalyst with their subsequent detection by EPR, which was devised at the Institute of Chemical Physics in Erevan[224] and subsequently developed further,[225] played a major role. The direct detection of free radicals in the gas phase beyond the catalyst without freezing out, for example, by laser magnetic resonance[226] and multiphoton ionisation[227] methods, has given rise to some prospects.

The oxidative condensation of methane on various oxide catalysts has been studied in particularly great detail in recent years:[225,228]

$$2CH_4+O_2=C_2H_4+2H_2O.$$

In this reaction, free radicals are formed on interaction of a methane molecule with the surface oxygen O_s:

$$O_s+CH_4\rightarrow CH_3^{\bullet}+OH_s.$$

The recombination of the radical from the gas phase, i.e.

$$2CH_3^{\bullet}\rightarrow C_2H_6$$

leads to the formation of an ethane molecule (and subsequently, on oxidative dehydrogenation, of ethylene). Although the reactivity is determined by the properties of the catalyst, the selectivity depends on the equilibrium in the gas phase:

$$CH_3^{\bullet}+O_2\rightleftarrows CH_3O_2^{\bullet}.$$

At a low temperature, the $CH_3O_2^{\bullet}$ radical undergoes further extensive oxidation to CO_2 and H_2O, while at temperatures above 600 °C the equilibrium is displaced towards methyl radicals and the selectivity in the formation of their C_2 product increases as the temperature rises. If the activation energy E for the interaction of methane with the catalyst, i.e.

$$CH_4+Cat\rightarrow CH_3^{\bullet}+Cat-H$$

is plotted against the energy Q of the bond between hydrogen and the catalyst Cat–H, then the points corresponding to the case where the acceptor (Acc) is the catalyst lie on a single straight line with the corresponding points for a homogeneous radical reaction:

$$CH_4+Acc\rightarrow CH_3^{\bullet}+Acc-H.$$

The Polanyi–Semenov relation holds:[228]

$$E=E_0-\alpha Q.$$

Heterogeneous-homogeneous radical processes also probably play a definite role in other high-temperature catalytic reactions (vapour phase conversion of methane, oxidation of ammonia, the synthesis of HCN). These should in fact be sought. The study of high-temperature catalysis is in the initial stage and the discovery of new reactions may be expected.

When the macrodynamics of catalytic reactions is examined, it is desirable to pay special attention to the organisation of the process on multicomponent and especially multiphase catalysts. The high reactivity and selectivity of such catalysts is attained as a result of the separation of the process in space: each stage of the catalytic reaction proceeds on a separate phase.

The principle of the separation of a complex reaction into stages each of which is accelerated by its own catalysts was proposed by Lebedev already about 60 years ago;[229] thus a selective catalyst was chosen for the synthesis of butadiene from alcohol:

$$2C_2H_5OH\rightarrow C_4H_6+2H_2O+H_2.$$

Dehydration, dehydrogenation, and condensation stages were isolated in this reaction and for each its own catalyst was selected. Subsequently a complex catalyst consisting of oxide phases accelerating the above stages was devised.

One of the advantages of multiphase catalysis is the possibility of displacing an unfavourable equilibrium as a result of the removal of an intermediate from one phase to another. Weisz,[230] who investigated in detail the conversion of hydrocarbons on the so called bifunctional catalysts, was one of the first to understand this. It was shown that in the reforming reaction on Pt/Al_2O_3 dehydrogenation of n-paraffins (A) is effected on platinum while the subsequent skeletal isomerisation of the n-olefin (B) to the iso-olefin (C) takes place on Al_2O_3 or aluminosilicate: $A\rightleftarrows B\rightarrow C$. By selecting a catalyst, it is possible to accelerate the removal of the substance B from one phase to another and to displace the equilibrium $A\rightleftarrows B$. An increase in the diffusion coefficient and a decrease in the distances between the species promoted the shift of the reaction towards complete conversion. In particular this can be achieved by the mechanical displacement of phases.

The shift of an unfavourable equilibrium can be achieved also in a simple catalytic reaction $A\rightleftarrows B + C$ without intermediates.[231] For this purpose, it is necessary to remove the reaction products constantly to other surface centres, which adsorb it more strongly. The occurrence of the reaction in the so called chromatographic regime was discovered in relation to the dehydrogenation of cyclohexane to benzene. The thermodynamically unfavourable reaction (at a low temperature)

$$C_6H_{12}\rightleftarrows C_6H_6+3H_2$$

can be effected by carrying it out under pulsed conditions with constant removal of products.

In such cases, a multiphase structure is always useful. The activity and selectivity in certain reactions can be increased by using special adsorbents for the reaction products. Thus, zeolites have been used for the removal of water in certain condensation reactions and for the removal of lower alcohols in the exchange of alcohols with esters.[232] Under real conditions of stationary heterogeneous catalysis, not only the concentration gradients of the intermediate compounds diffusing in the pores between the particles of different catalyst phases but also stationary gradients of the catalyst composition within each phase can be established.

The principle of the constant removal of the product from the reaction zone in order to increase the selectivity of the catalysis has been used in metallic membrane catalysts. The application of

palladium alloys in the form of membranes increases their selectivity in the dehydrogenation of butane to butadiene as a result of the removal of hydrogen to the other side of the membrane.[233,234] The involvement of hydrogen in another catalytic reaction (hydrogenation, oxidation) on the other side of the membrane increases the yield of butadiene still further.

The role of the multiphase structure of the partial oxidation catalyst was examined in detail in our investigations[14,235] based on the study of their structure by X-ray phase analysis and Mössbauer spectroscopy *in situ*. It was found that under the reaction conditions the complex Bi–Co–Fe–Mo–O catalyst consists of five main phases: (1) the β-$FeMoO_4$ phase necessary for the adsorption of oxygen; (2) the β-$CoMoO_4$ phase stabilising the β-$FeMeO_4$ phase by virtue of the coherence of the lattices; (3) the non-equilibrium partially reduced $Fe_2(MoO_4)_3$ phase through which oxygen atoms are transported from the oxygen adsorption centres to propene adsorption centres; (4) the $Bi_2(MoO_4)_3$ phase necessary for the adsorption and activation of propene; (5) the MoO_3 phase ensuring the maintenance of stoichiometric relations in the reduction of iron molybdate. The active centres are located near the interface. Non-equilibrium concentrations of vacancies and stationary hydrogen concentration gradients are created in the catalyst.

In oxidative catalysis there is a possibility also of separation in space of centres within a single phase.[236] The study of the oxidation of allyl alcohol to acrolein[16] on the MoO_3 catalyst with added vanadium by EPR *in situ* showed that organic molecules are adsorbed on the outer surface of the catalyst. On the other hand, oxidation and reduction processes occur on the V^{4+}/V^{5+} active centres within the bulk of the catalyst. Constant exchange of oxygen and electrons takes place between the surface and the bulk phase.

The separation of the active centres in space is apparently a general rule for complex catalytic processes. The theory of these processes has been inadequately developed. It must take into account the shifts of the equilibrium, the coupling of stages, and the transport processes between the centres, phases, or particles.

The role of surface and bulk-phase diffusion in heterogeneous catalysis is apparently much greater than has been thought hitherto. The phenomenon of the interphase diffusion of adsorbed species has been called spill-over. The spill-over of hydrogen, first observed in the adsorption of hydrogen on Pt/WO_3,[237] ensures the transfer of hydrogen atoms from the metal to the oxide. In the absence of the metal, there is no adsorption of hydrogen on the oxide. The spill-over phenomenon must play a major role in reactions involving hydrogen, displacing the equilibrium by virtue of the removal of hydrogen atoms.

The mechanism of spill-over is different in different systems. The exchange of D_2 with the hydrogen of the OH groups on Pt/SiO_2 has been investigated[238] by IR spectroscopy with Fourier analysis *in situ*. It was found that deuterium diffuses from the metal to the carrier in a weakly bound state on top of strongly bound OH groups on SiO_2 and exchanges with them. The driving force of spill-over is the concentration gradient between different states of deuterium. The spill-over of hydrogen atoms across an oxide film has been observed.[239] Platinum deposited on silicon and fully coated by a layer of the inert SiO_2 exhibits activity in the dehydrogenation of cyclohexane. The activity of the catalyst decreases exponentially with increase in the thickness of the film from zero to 30 nm and becomes constant for thicknesses in the range 30–2200 nm. The spill-over of hydrogen in the H_2-D_2 exchange and C_2H_4 hydrogenation reactions has been observed without direct contact between the oxide (SiO_2, Al_2O_3) and the metal (Pt/SiO_2, Pt/Al_2O_3), i.e. through the gas phase.[240] According to different data,[241] atomic and ionic species can participate in spill-over. The diffusion coefficients of the H and D atoms in the Pt/SiO_2 and Pt/Al_2O_3 systems proved to be unexpectedly very high: $10^{-3}-10^{-6}$ cm^2 s^{-1}.

The "spill-over of oxygen"—the diffusion of oxygen atoms across an oxide lattice from one active centre to others—was already mentioned above. The phenomenon of the spill-over of the NCO species from the surface of a metal (Pt, Rh) on to a carrier (γ-Al_2O_3) and conversely under the conditions of the reaction of NO with CO has been observed.[242] It has been shown by IR spectroscopy *in situ* that the NCO species participate in the reaction as intermediates.

Synergistic phenomena—the superadditive increase in the activity of the catalyst on mechanical mixing of the components—can be explained by the transfer of material between phases, diffusion, and spill-over. The conversion of propene in its oxidation on the mixed catalyst $CoMoO_4$ + MoO_3 or $CoMoO_4$ + $Bi_2(MoO_4)_3$ was found to be higher than the sum of the conversions on each component separately.[243] This can be explained by the fact that on one or both phases intermediates of possibly free-radical character are formed and after being released into space are adsorbed on another phase and undergo further reaction.

Numerous instances of synergism in partial oxidation reactions have been listed in a review.[244] A new term has been proposed for the designation of the synergistic intensification of catalysis in mixtures—remote control.[245] Synergistic effects have been noted in the hydrogenolysis of thiophene on (MoS_2 + CoS)/γ-Al_2O_3, in the oxidation of isobutene to methylacrolein on SnO_2 + Sb_2O_4, and in the dehydration of *N*-methylformamide on MoO_3 + Sb_2O_4; the influence of platinum on the reduction of Ni is associated with these effects.[245] The operation of the remote control mechanism makes it useful to introduce the catalyst in the form of several layers consisting of different materials.

The overall organisation of the process via parallel or consecutive mechanisms is very important in the dynamics of complex catalytic reactions. This determines, in particular, the selectivity of the catalyst—its ability to accelerate only one of several reactions occurring simultaneously. The principal factors influencing selectivity, namely the bond energy, the ligand effect, the ensemble effect, steric effects, and multiphase structure were examined in the present author's previous review.[235]

References

1. M Boudart *Usp. Khim.*, 1974, **43**(2) 317 [English translation in *Russ. Chem. Rev.*, 1974(2)]
2. O V Krylov *Kinet. Katal.*, 1980, **21** 79
3. M Ya Bykhovskii, O V Krylov *Kinet. Katal.*, 1971, **12** 195
4. H Kobayashi, M Kobayashi *Catal. Rev.*, 1974, **10** 169
5. R J Madix, J Falconer, J McCarty *J. Catal.*, 1973, **31** 316; 1975, **38** 402
6. J T Gleaves, J R Ebner, T C Kuechler *Catal. Rev.*, 1988, **30** 49
7. K Tamaru *Dynamic Heterogeneous Catalysis* Acad. Press, London–New York–San Francisco, 1978, 140 pp.
8. A D Berman, O V Krylov *Usp. Khim.*, 1986, **55**(2) 371 [English translation in *Russ. Chem. Rev.*, 1986(2)]
9. V A Matyshak, M M Slin'ko, R A Gazarov, O V Krylov *Kinet. Katal.*, 1989, **30** 155
10. V A Matyshak, E Lefler, K H Schnabel *Kinet. Katal.*, 1987, **28** 1389

11. V A Matyshak, P V Kurman, M Yu Kutyrev *Khim. Fiz.*, 1984, **3** 1138
12. A A Kadushin, S E Plate, Yu P Tyulenin, et al. *Kinet. Katal.*, 1988, **29** 1518
13. P A Shafranovskii, M Yu Sinev, B R Shub *Kinet. Katal.*, 1988, **29** 1420
14. Yu V Maksimov, M Sh Zurmukhtashvili, I P Suzdalev, et al. *Kinet. Katal.*, 1984, **25** 948
15. O S Morozova, T M Parshina, M M Sakharov, et al. *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii. Moskva* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions. Moscow), Moscow, 1986, Vol. 1, p. 375
16. M A Makarova, B V Rozentuller, O V Krylov *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii. Moskva* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions. Moscow), Moscow, 1986, Vol. 2, p. 32
17. W Ho *J. Phys. Chem.*, 1987, **91** 766; *Surf. Sci.*, 1989, **211/212** 143
18. V A Burrows, S Sunderasan, Y J Chabal, *Surf. Sci.*, 1987, **180** 110
19. W G Golden, D D Saperstein, M V Severson, J Overend *J. Phys. Chem.*, 1984, **88** 574
20. L M Kustov, V A Andreev, V Yu Borovkov, V B Kazanskii *Kinet. Katal.*, 1982, **23** 1161
21. P A Shafranovskii, M Yu Sinev, G N Zhizhin, B R Shub *Kinet. Katal.*, 1988, **29** 1721
22. J Gland, V N Korchak *J. Catal.*, 1978, **53** 9
23. J S Villarubia, W Ho *Surf. Sci.*, 1984, **144** 370
24. M Suhman, S R Bare, P Hofmann, D A King *Surf. Sci.*, 1983, **126** 349
25. W Ho *J. Vac. Sci. Technol., A*, 1984, **3** 1432
26. P A Gurney, W Ho *J. Vac. Sci. Technol., A*, 1985, **3** 1511
27. F Rabentrost, K L Kompa, A Ben-Shaul *Chem. Phys. Lett.*, 1981, **77** 394
28. O V Krylov, B R Shub *Neravnovesnye Protessy v Ktalize* (Non-Equilibrium Processes in Catalysis), Khimiya, Moscow, 1990, 285 pp.
29. D S Kliger (Editor) *Ultrasensitive Laser Spectroscopy* (Translated into Russian), Mir, Moscow, 1986, 519 pp.
30. V S Letokhov *Lazernaya Fotoionizatsionnaya Spektroskopiya* (Laser Photoionisation Spectroscopy), Nauka, Moscow, 1987, 318 pp.
31. V P Zharov, V S Letokhov *Lazernaya Optiko-Akusticheskaya Spektroskopiya* (Laser Optico-Acoustic Spectroscopy), Nauka, Moscow, 1984, 425 pp.
32. Yu M Gershenzon, S D Il'in, O P Kishkovich *Khim. Fiz.*, 1983, **2** 488
33. W M Fairbanks, T W Hänsch, A L Schawlow *J. Opt. Soc. Am.*, 1975, **65** 199
34. P N Johnson *Acc. Chem. Res.*, 1980, (13) 20
35. G D Kubiak, J E Hurst, H G Rennagel *J. Chem. Phys.*, 1983, **79** 5163
36. G D Kubiak, G O Sitz, R N Zare *J. Chem. Phys.*, 1985, **83** 2538
37. S A Akhmanov, N I Koroteev *Metody Nelineinoi Optiki v Spektroskopii Rasseyaniya Sveta* (Non-Linear Optical Methods in Light Scattering Spectroscopy), Nauka, Moscow, 1981, 327 pp.
38. R G Bray, R M Hochstrasser, H N Sung *Chem. Phys. Lett.*, 1975, **33** 1
39. V S Letokhov *Primenenie Lazerov v Spektroskopii i Fotokhimii* (The Application of Lasers in Spectroscopy and Photochemistry), Nauka, Moscow, 1983, 327 pp.
40. R P Thorman, D Andersen, S C Bernasek *Phys. Rev. Lett.*, 1980, **44** 743
41. S C Bernasek *Chem. Rev.*, 1987, **87** 91
42. A V Sklyarov, V V Rozanov, M U Kislyuk *Kinet. Katal.*, 1976, **19**(2) 416
43. E J Heilweil, M P Casassa, R R Cavanagh, J C Stephenson *J. Chem. Phys.*, 1984, **81** 2856; *J. Vac. Sci. Technol., A*, 1985, **3** 1655
44. R R Cavanagh *J. Vac. Sci. Technol., A*, 1987, **5** 469
45. F J Heilweil, J C Stephenson, R R Cavanagh *J. Phys. Chem.*, 1988, **92** 6099; *J. Chem. Phys.*, 1988, **88** 5251
46. R Haght, J Baker, J Staik, et al. *Phys. Rev. Lett.*, 1985, **5** 1302; 1986, **57** 881
47. H W K Thom *Kinetics of Interface Reactions. Proc. Workshop 24–27 IX. 1986, Campobellow* (Edited by M Grunze, H J Kreuzer), Springer, 1987, p. 54
48. Y R Shen *Nature*, 1989, **337**(6207) 519
49. K L Haller, L A Bumm, R J Altkorn, et al. *J. Chem. Phys.*, 1989, **90** 1237
50. E S Peterson, C B Harris *J. Chem. Phys.*, 1989, **91** 2683
51. H W K Thom, C M Mott, X D Zhu, et al. *Phys. Rev. Lett.*, 1984, **52** 348
52. H W K Thom, X D Zhu, Y R Shen, G A Somorjai *Surf. Sci.*, 1986, **167** 162
53. H W K Thom, X D Zhu, G A Somorjai, et al. *J. Chem. Phys.*, 1988, **88** 441
54. S A Akhmanov, N J Koroteev, G A Painton, et al. *Opt. Commun.*, 1983, **47** 202
55. P M Bowman, M Dantus, A H Zewail *Chem. Phys. Lett.*, 1989, **156** 131
56. C V Shank *Solid State Electronics*, 1988, **31** 397
57. J A Prybyla, T F Heinz, J A Misewich, et al. *Phys. Rev. Lett.*, 1990, **64** 1537
58. M P Cox, G Ertl, R Imbihl *Phys. Rev. Lett.*, 1985, **54** 1725
59. D J Smith *Surf. Sci.*, 1986, **178** 462
60. *Proceedings of the 1st International Conference on Scanning Tunnelling Microscopy. Surface Sci.*, 1987, Vol. 181 420
61. R J Calotta *Appl. Surf. Sci.*, 1988, **31** p. 59
62. *Proceedings of the 2nd International Conference on Scanning Tunnelling Microscopy, J. Vac. Sci. Technol., A*, 1988, Vol. 6, p. 257
63. P S Maslova, V I Panov *Usp. Fiz. Nauk*, 1989, **157** 185
64. S Selei, A Cricenti, R Generosi, et al. *Surf. Sci.*, 1989, **211/212** 143
65. P Avouris *J. Phys. Chem.*, 1990, **94** 2246
66. A Zangwill *The Physics at Surfaces* (Russian Translation from English) (Edited by V F Kiselev), Mir, Moscow, 1990, 527 pp.
67. T F Hayden, J A Dumesik, R D Sherwood, R Baker *J. Catal.*, 1987, **105** 299
68. J C J Bart, G Vlaič *Adv. Catal.*, 1987, **35** 1
69. D M Mills *Physics Today*, 1984, (4) 22
70. N S Guyot-Sionnet, D Basin, M Dexport, et al. *Abstracts of the VIth International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis. Pisa, Italy*, 1989, p. 76

71. A D H Claque *Special Periodical Report. Royal Society of Chemistry* (Edited by G C Bond and C Webb), Burlington House, London, 1987, p. 87
72. G W Haddix, J A Reimer, A T Bell *J. Catal.*, 1987, **106** 11
73. O Johnson, A Mitchel, R Norriseeler, L Evans *Phys. Rev. Lett.*, 1970, **25** 1099; 1972, **29** 1369
74. G A Somorjai *Chemistry in Two Dimensions*, Cornell Univ. Press, Ithaca, 1981, Vol. 55, p. 556
75. R B Gerber *Chem. Rev.*, 1987, **87** 29
76. G A Somorjai *Proceedings of the VIII International Conference on Catalysis. West Berlin, 1984*, Weinheim, Basel, 1984, Vol. 1, p. 113
77. A E Bodrov, F I Dalidchik, S A Kovalevskii, B R Shub *Metod Ionnogo Puchka v Issledovanii Protsessov Stolknoveniya Molekul s Tverdym Telom (Metally)* [The Ion Beam Method in the Study of Processes Involving the Collision of Molecules with a Solid (Metals)], Preprint from the Institute of Chemical Physics, 1988, 24 pp.
78. V N Bykov, S A Kovalevskii *Poverkhnost'*, 1986, (9) 140
79. O V Krylov, M U Kislyuk, B R Shub, et al. *Kinet. Katal.*, 1972, **13** 598
80. R C Baetzold, G A Somorjai *J. Catal.*, 1976, **45** 94
81. V B Zhdanov *Elementarnye Fiziko-Khimicheskie Protsessy na Poverkhnosti* (Elementary Physicochemical Processes on the Surface), Nauka, Novosibirsk, 1988, 317 pp.
82. D C Jacobs, R N Zare *J. Chem. Phys.*, 1989, **91** 3182
83. T Matsushima *Surf. Sci.*, 1982, **123** 2663
84. V V Savkin, M U Kislyuk, A V Sklyarov *Kinet. Katal.*, 1987, **28** 1404
85. V V Savkin, T N Bakuleva, L A Boeva, et al. *Kinet. Katal.*, 1989, **30** 1455
86. G D Kubiak, J E Hurst, H G Rennagel, et al. *J. Chem. Phys.*, 1983, **79** 5163
87. D A Mantell, K Kunimori, S B Rialli, et al. *Surf. Sci.*, 1986, **172** 281
88. G W Coulston, G L Haller *J. Chem. Phys.*, 1990, **92** 5752
89. M Kori, B L Halpern *Chem. Phys.* Lett., 1986, **54** 532
90. M A Hoffbauer, D S Y Hsu, M C Lin *J. Chem. Phys.*, 1986, **54** 532; *Surf. Sci.*, 1987, **184** 25
91. S N Foner, R L Hudson *J. Chem. Phys.*, 1984, **80** 518
92. S T Ceyer, W L Guthrie, T H Lin, G A Somorjai *J. Chem. Phys.*, 1983, **78** 6782
93. P C Jacobs, K W Kovalinski, S T Shone, R N Zare *J. Chem. Phys.*, 1989, **91** 3182
94. A V Hamza, P M Ferm, F Budde, G Ertl *Surf. Sci.*, 1988, **199** 13
95. J A Prybyla, T F Heinz, J A Misewich, M M T Loy *Surf. Sci.*, 1990, **250** L173
96. A Mödl, F Budde, T Gritsch, et al. *J. Vac. Sci. Technol., A*, 1987, **5** 522
97. M G Tenner, E W Kuipers, W Y Langhout, et al. *Surf. Sci.*, 1990, **236** 151
98. J T Yates, J N Russel, J Chorkerdorf, S M Gates *Kinetics of Interface Reactions. Proc. Workshop, 1986, Campobello*, (Edited by M Grunze, H J Kreuzer), Springer, Berlin–Heidelberg, 1987, p. 71
99. G D Purvis, M J Redmon, G Wolken *J. Phys. Chem.*, 1979, **83** 1027
100. P Harteck, R Reeves, G Mannela *Can. J. Chem.*, 1961, **38** 1648
101. O Dessaux, P Goodmand, P Matel *J. Quant. Spectrosc. Radiat. Transfer*, 1983, **30** 134
102. J P Guillory, C M Shiblom *J. Catal.*, 1978, **54** 24
103. R L Palmer, J N Smith *Catal. Rev.*, 1975, **12** 279
104. H J Robota *Surf. Sci.*, 1985, **155** 1011
105. C T Rettner, E K Schweizer, M Stein *J. Chem. Phys.*, 1990, **93** 1442
106. C T Rettner, D J Auerbach *Kinetics of Interface Reactions. Proc. Workshop, 1986, Campbello* (Edited by M Grunze, H J Kreuzer), Springer, Berlin–Heidelberg, 1987, p. 145
107. S Roginskii, Ya Zel'dovich *Acta Physicochimica l'USSR*, 1934, **1** 556
108. C E Gdowski, A V Hamza, M P D'Evelyn, R J Madix *J. Vac. Sci. Technol., A*, 1985, **3** 1561; *Surf. Sci.*, 1985, **167** 451
109. C N Stewart, G Ehrlich *J. Chem. Phys.*, 1975, **62** 4672
110. T S Lo, G Ehrlich *Surf. Sci.*, 1987, **179** L18; 1988, **205** L813
111. C T Rettner, H E Pfnur, D J Auerbach *J. Chem. Phys.*, 1986, **84** 4163, 6782
112. A V Hamza, A P Steinruck, R J Madix *J. Chem. Phys.*, 1986, **85** 7494; 1987, **86** 6506
113. T J Chuang *Surf. Sci. Repts.*, 1983, **3** 3
114. T F George, J Lin, A C Beri, W G Murphy *Progr. Surf. Sci.*, 1984, **16** 139
115. T J Chuang *Surf. Sci.*, 1986, **178** 763
116. T J Chuang *J. Chem. Phys.*, 1982, **76** 3828; *Phys. Rev. Lett.*, 1982, **49** 382
117. J Hussla, H Schu, T J Chuang, et al. *Phys. Rev., B*, 1985, **32**, 3482
118. A P Belikov, V D Borman, B I Nikolaev, et al. *Khim. Fiz.*, 1985, **4** 1030
119. I P Moiseenko, A A Glebovskii, A A Lisachenko *React. Kinet. Catal. Lett.*, 1985, **28** 117
120. W C Natzle, D Padowitz, S I Sibener *J. Chem. Phys.*, 1988, **88** 106
121. H C Chang, G F Ewing *J. Phys. Chem.*, 1990, **94** 7635
122. B N Person *J. Phys.*, 1984, **17** 4741
123. P A Shafranovskii, A S Prostnev, L A Kuzin, et al. *Dokl. Akad. Nauk SSSR*, 1990, **311** 87
124. G S Yablonskii, V I Bykov, V I Elokhin *Kinetika Model'nykh Reaktsii Geterogennogo Kataliza* (Kinetics of Model Heterogeneous Reactions), Nauka, Novosibirsk, 1984, 224 pp.
125. C T Campbell, G Ertl, H Kuipers, J Segner *J. Chem. Phys.*, 1980, **73** 5862
126. M Yu Sinev, V N Korchak, O V Krylov *Usp. Khim.*, 1989, **58** 38
127. P R Norton *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Elsevier, Amsterdam, 1982, Vol. 4, p. 27
128. J L Gland, G B Fisher, E B Kollin *J. Catal.*, 1982, **77** 263
129. V V Sadovnikov *Dokl. Akad. Nauk SSSR*, 1974, **217** 872
130. V V Sadovnikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, (6) 1220; *Dokl. Akad. Nauk SSSR*, 1977, **235** 637
131. J J McCarroll, S J Thomson *J. Catal.*, 1970, **19** 144
132. A Ya Rozovskii *Kinet. Katal.*, 1989, **33** 533
133. T Yamada, T Onishi, K Tamaru *Surf. Sci.*, 1983, **133** 533
134. A S Prostnev, M A Kozhushner, B R Shub *Khim. Fiz.*, 1985, **5** 85
135. J R Chen, R Gomer *Surf. Sci.*, 1979, **79** 413
136. J R Chen, R Gomer *Surf. Sci.*, 1980, **81** 589
137. G Ehrlich, F G Hudda *J. Chem. Phys.*, 1966, **44** 1039
138. M U Kislyuk, I I Tret'yakov, R K Nartikoev *Kinet. Katal.*, 1982, **23** 1191
139. O V Krylov *Kinet. Katal.*, 1981, **22** 15

140. B Weisz *Proceedings of the VIII International Congress on Catalysis. Tokyo, 1980. Preprints of Plenary Lectures*, p. 1
141. T Tsiao, D R Corbin, C Dybowski *J. Am. Chem. Soc.*, 1990, **112** 7140
142. J M Thomas *Chemistry and Physics of Solid Surfaces* (Edited by R Vanselow, et al.) Springer, Berlin—Heidelberg, 1986, Vol. 5, p. 107
143. V F Kiselev, O V Krylov *Elektronnye Yavleniya v Adsorbtsii i Katalize na Poluprovodnikakh i Dielektrikakh* (Electronic Phenomena in Adsorption and Catalysis on Semiconductors and Dielectrics), Nauka, Moscow, 1979, 234 pp.
144. V I Volkenshtein *Elektronnaya Teoriya Kataliza na Poluprovodnikakh* (Electronic Theory of Catalysis on Semiconductors), Fizmatizdat, Moscow, 1960, 187 pp.
145. B V Rozentuller, K N Spiridonov, O V Krylov *Kinet. Katal.*, 1981, **22** 797; *Dokl. Akad. Nauk SSSR*, 1981, **259** 893
146. M A Makarova, B V Rozentuller, O V Krylov *Kinet. Katal.*, 1987, **28** 1143, 1395
147. J Abbot, B W Wojcechowski *J. Catal.*, 1989, **115** 1
148. V N Makatun A K Potapovich, V A Shestakov *Trudy Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the All-Union Conference on the Mechanisms of Catalytic Reactions), 1978, Vol. 1, p. 128
149. V B Kazanskii *Kinet. Katal.*, 1980, **21** 159
150. V B Kazanskii *Problemy Sovremennogo Kataliza. Trudy Mezhdunarodnoi Konferentsii Pamati G K Boreskova. Novosibirsk* (Problems of Modern Catalysis. Proceedings of the International Congress Commenorating G K Boreskov. Novosibirsk), Nauka, Novosibirsk, 1988, Vol. 1, p. 237
151. E A Shilov *Dokl. Akad. Nauk SSSR*, 1938, **18** 643
152. M G Slin'ko, G S Yablonskii *Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis), Vol. 17, *Nestatsionarnye i Neravnovesnye Protsessy v Geterogennom Katalize* (Non-Stationary and Non-Equilibrium Process in Heterogeneous Catalysis), Nauka, Moscow, 1978, p. 154
153. G S Yablonskii, V I Bykov, A N Gorban' *Kineticheskie Modeli Kataliticheskikh Reaktsii* (Kinetic Models of Catalytic Reactions), Nauka, Novosibirsk, 1933, 251 pp.
154. I Langmuir *Trans. Faraday Soc.*, 1922, **17** 607
155. S Z Roginskii *Adsorbtsiya i Kataliz na Neodnorodnykh Poverkhnostyakh* (Adsorption and Catalysis on Non-Uniform Surfaces), Izd. Akad. Nauk SSSR, Moscow, 1948
156. M W Roberts, C S McKee *Chemistry of the Metal—Gas Interface* (Russian translation from English) (Edited by V M Gryaznov), Mir, Moscow, 1981, 539 pp.
157. S M Landry, R A Dalla Betta, J P Lu, M Boudart *J. Phys. Chem.*, 1990, **94** 1203
158. Yu K Tovbin *Kinet. Katal.*, 1979, **20** 1225
159. I Prigogine *From the Existing to the Incipient. Time and Complexity in Physical Sciences* (Translated into Russian), Nauka, Moscow, 1985, 324 pp.
160. H Haken *Synergetics* (Translated into Russian), Mir, Moscow, 1980, 405 pp.
161. M Boudart *Ind. Eng. Chem., Fundam.*, 1986, **25** 70
162. M Boudart *J. Phys. Chem.*, 1983, **87** 2786
163. W Ebeling *The Formation of Structures in Irreversible Processes* (Translated into Russian), Mir, Moscow, 1979, 271 pp.
164. G A Somorjai, M A Van Hove *Adsorbed Monolayers on Solid Surfaces. Structure and Bonding*, Springer, Berlin—Heidelberg, 1979, Vol. 38, p. 146
165. G Ertl, J Küppers *Low Energy Electrons and Surface Chemistry*, VCH Verlag, Munich, 1985, p. 374
166. H Conrad, G Ertl, J Küppers *Surf. Sci.*, 1978, **76** 323
167. A D Berman, O V Krylov *Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis), Vol. 17, *Nestatsionarnye i Neravnovesnye Protsessy v Geterogennom Katalize* (Non-Stationary and Non-Equilibrium Processes in Heterogeneous Catalysis), Nauka, Moscow, 1978, p. 102
168. K Heinz, E Lang, K Strauss, K Müller *Surf. Sci.*, 1982, **120** L401
169. R F Willis *Ber. Bunsenges. Phys. Chem.*, 1986, **90** 205
170. R M Ziff, E Gulari, J Barshad *Phys. Rev. Lett.*, 1986, **56** 2553
171. P Meakin, D J Scalapino *J. Chem. Phys.*, 1988, **87** 731
172. P Fischer, U M Titulaer *Surf. Sci.*, 1989, **221** 409
173. H P Kaukoner, R M Nieminer *J. Chem. Phys.*, 1989, **91** 4380
174. M Dumont, P Dufour, B Sante, R Dagonnier *J. Catal.*, 1990, **122** 95
175. M Colb, Y Boudeville *J. Chem. Phys.*, 1990, **92** 3935
176. G K Boreskov *Zh. Fiz. Khim.*, 1940, **14** 1337
177. C Wagner, K Hauffe *Z. Elektrochem.*, 1938, **44** 172
178. C Wagner *Berichte Bunsenges. Phys. Chem.*, 1970, **74** 401
179. O V Krylov, Yu V Maksimov, L Ya Margolis *J. Catal.*, 1985, **95** 289
180. V Yu Bychkov, M Yu Sinev, B N Kuznetsov, et al. *Kinet. Katal.*, 1987, **28** 665
181. O S Morozova, Yu V Maksimov, G N Kryukova, et al. *Proceedings of VIII Soviet-French Seminar on Catalysis. Novosibirsk*, 1990, p. 111
182. B V Rozentuller, K N Spiridonov, O V Krylov *Kinet. Katal.*, 1981, **22** 797; *Dokl. Akad. Nauk SSSR*, 1981, **259** 893
183. I L Tsitovskaya, O V Al'tshuler, O V Krylov *Dokl. Akad. Nauk SSSR*, 1973, **112** 1400
184. A A Ukharskii, M M Slin'ko, A D Berman, O V Krylov *Kinet. Katal.*, 1981, **22** 1353
185. A A Kadushin, V A Matyshak, O V Krylov *Izv. Akad. Nauk SSR, Ser. Khim.*, 1979, (5) 944
186. M M Slin'ko, N I Jaeger, P Svensson *J. Catal.*, 1989, **118** 349
187. M M Slin'ko, M G Slin'ko *Usp. Khim.*, 1980, **49** (4) 567; *Kinet. Katal.*, 1982, **23** 1421
188. N J Jaeger, P Möller, P J Plath *J. Chem. Soc. Faraday Trans.*, 1986, **82** 3315
189. A D Berman, A V Elinek *Dokl. Akad. Nauk SSSR*, 1979, **248** 643
190. A N Ivanova, G A Furman *Khim. Fiz.*, 1984, **3** 93
191. G Ertl, P R Norton, J Rustig *Phys. Rev. Lett.*, 1982, **49** 171
192. H H Hotermund, S Jakubith *J. Chem. Phys.*, 1990, **91** 4942
193. W Hösler, E Ritter, R J Behm *Ber. Bunsenges. Phys. Chem..*, 1986, **90** 205
194. P Möller, K Wetze, M Eiswirth, G Ertl *J. Chem. Phys.*, 1986, **85** 5328
195. M Eiswirth, P Möller, K Wetze, et al. *J. Chem. Phys.*, 1989, **90** 510
196. M Ehsasi, et al. *Chem. Phys. Lett.*, 1990, **165** 115
197. A Palazov, G Kadinov, Ch Bonev, et al. *Surf. Sci.*, 1990, **225** 21
198. N J Jaeger, et al. *J. Chem. Soc., Faraday Trans. 1*, 1986, **82** 3315
199. L D Schmidt, L Aris *Unsteady State Processes in Catalysis. Proceedings of International Conference*, 1990. Novisibirsk (Edited by Yu Matros), USPC, Utrecht, 1990, p. 203
200. X Wu, Z A Schelly *React. Kinet. Catal. Lett.*, 1990, **42** 303

201. M Eiswirth, K Krieschmar, G Ertl *Surf. Sci.*, 1988, **202** 565
202. S B Schwartz, L D Schmidt *Surf. Sci.*, 1987, **183** L269; 1988, **206** 453
203. S Y Hwang, L D Schmidt *J. Catal.*, 1988, **114** 230
204. L Petrow, C Vladov, A Eliyes *J. Mol. Catal.*, 1989, **51** 237
205. V V Berelko, et al. *Dokl. Akad. Nauk SSSR*, 1976, **229** 898
206. M P Cox, G Ertl, K Imhihl *Phys. Rev. Lett.*, 1985, **54** 1725
207. T Fink, R Imbihl, G Ertl *J. Chem. Phys.*, 1990, **91** 5002
208. A M Zhabotinsky, A B Rovinsky *React. Kinet. Catal. Lett.*, 1990, **42** 201
209. M G Slin'ko, V S Beskov, N A Dubyaga *Dokl. Akad. Nauk SSSR*, 1972, **204** 1174
210. M Ehsasi, M Mitloch, O Franck, et al. *J. Chem. Phys.*, **91** 4944
211. V V Barelko, Yu E Volodin *Kinet. Katal.*, 1976, **17** 683
212. E L Aptekar', O V Krylov *Trudy Vsesoyuznoi Konferentsii po Mekhanizmu Geterogenno-Kataliticheskikh Reaktsii. Moskva* (Proceedings of the All-Union Conference on the Mechanisms of Heterogeneous-Catalytic Reactions. Moscow), Moscow, 1974, Preprint No. 77
213. M Greger, B Ihme, M Kotter, L Rieckert *Ber. Bunsenges. Phys. Chem.*, 1984, **88** 427; 1987, **91** 1007
214. J Falconer, R Madix, J McCarty *J. Catal.*, 1974, **31** 320
215. O V Krylov *Kinet. Katal.*, 1985, **26** 273
216. M Ya Kon', V A Shvets, V B Kazanskii *Dokl. Akad. Nauk SSSR*, 1972, **203** 624
217. O V Krylov, K M Spiridonov, D Gati *Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis), Vol. 17, *Nestatsionarnye i Neravnovesnye Protsessy v Geterogennom Katalize* (Non-Stationary and Non-Equilibrium Processes in Heterogeneous Catalysis), Nauka, Moscow, 1978, p. 144
218. A T Bell *Catal. Rev.*, 1981, **23** 203
219. H H Nijs, P A Jacobs *J. Catal.*, 1983, **84** 43
220. Ya B Gorokhovatskii, T P Kornienko, V V Shalya *Geterogenno-Homogennye Reaktsii* (Heterogeneous-Homogeneous Reactions), Tekhnika, Kiev, 1972, 200 pp.
221. H H Sawin, R P Merrill *J. Chem. Phys.*, 1980, **73** 996
222. O V Krylov *Dokl. Akad. Nauk SSSR*, 1960, **130** 1063
223. J P Ghillory, C M Shiblom *J. Catal.*, 1978, **54** 24
224. A B Malbandyan, A A Mantashyan *Elementarnye Protsessy v Medlennykh Gazofaznykh Reaktsiyakh* (Elementary Processes in Slow Gas-Phase Reactions), Izd. Akad. Nauk Arm. SSSR, Erevan, 1975, 259 pp.
225. T Ito, J H Lunsford *Nature*, 1985, **319** 721
226. Yu M Gershenzon, S V Il'in, et al. *Khim. Fiz.*, 1983, **2** 488
227. E E Gulcicak, S D Colson, L D Pfefferle *J. Phys. Chem.*, 1990, **94** 7069
228. M Yu Sinew, V N Korchak, O V Krylov *Proceedings of IX International Congress on Catalysis. Calgary*, 1988, Vol. 2, p. 968
229. S V Lebedev *Zh Obshch. Khim.*, 1933, **3** 898
230. P B Weisz *Catalysis. Polyfunctional Catalysis and Complex Reactions* (Translated into Russian), Mir, Moscow, 1965, p. 10
231. S Z Roginskii, M I Yanovskii, A D Berman *Osnovy Primeneniya Khromatografii v Katalize* (Principles of the Application of Chromatography in Catalysis), Nauka, Moscow, 1972, 370 pp.
232. V Ponec *Disc. Faraday Soc.*, 1981, (72) 93
233. V M Gryaznov, M G Slinko *Disc. Faraday Soc.*, 1981, (72) 35
234. V M Gryaznov, M M Armilova, N V Orekhova, N A Makhota *V Mezhdunarodnyi Simpozium po Geterogennomu Katalizu. Varna*, 1983, (The Vth International Symposium on Heterogeneous Catalysis. Varna, 1983), Izd. Bol'g. Akad. Nauk, Sofia, 1983, Vol. 1, p. 225
235. O V Krylov *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Modern Problems), Khimiya, Moscow, 1986, p. 41
236. D Cordischi, M LoJacono, G Minelli *J. Catal.*, 1986, **102** 1
237. W C Neikam, M A Vannice *J. Catal.*, 1971, **20** 210
238. E C Conner, J F Cevallos-Candan, N Shah, W Haensel *Spillover of Adsorbed Species* (Edited by G M Pajonk, S J Teichner), Elsevier, Amsterdam, 1983, p. 287
239. J M Cogen, K Ezaz-Nikrau, et al. *Angew. Chem.*, 1987, **26** 1182
240. D H Lenz, W C Conner *J. Catal.*, 1984, **104** 288
241. *K H Steinberg* (Editor) *Proceedings of II International Conference on Spillover. Leipzig, 1989*, p. 262
242. V A Matyshak, M M Slin'ko, et al. *Kinet. Katal.*, 1986, **27** 167
243. O V Isaev, O V Udalova, O V Krylov *Kinet. Katal.*, 1984, **25**(4) 1016
244. O V Krylov, L Ya Margolis *Inter. Rev. Phys. Chem.*, 1983, **3** 305
245. B Delmon, H Matralis *Proceedings of the International Conference on "Unsteady State Processes in Catalysis", 1990. Novosibirsk* (Edited by Yu Matros), VSP, Utrecht, 1990, p. 29