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Heterogeneous free-radical reactions in oxidation processes

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Abstract. The role of heterogeneous reactions of free radicals in oxidation processes of various types is analysed: homogeneous gas-phase, stabilised combustion, and heterogeneous-catalytic processes. It is shown that in all cases the observed kinetics and product compositions may be determined by the set of heterogeneous and homogeneous stages having the same nature, occurring in the systems simultaneously and as interdependent reactions. The possible mechanisms of the heterogeneous formation of free radicals and of their subsequent reactions are discussed. The methods for the investigation of heterogeneous radical reactions are examined. The bibliography includes 198 references.

I. Introduction

Oxidation processes (extensive and partial oxidation) are traditionally considered independently both in the theory of gas-phase reactions and in heterogeneous catalysis. There are a number of reasons for this, associated with the overall kinetic features, the mechanism of the activation of the reactants, and the chemistry of the elementary stages, which are different in homogeneous and heterogeneous processes. Furthermore, even the systems of concepts, terminology, and general approaches to the analysis and description of the processes in these two fields of chemical kinetics differ significantly.

There exist experimental facts and theoretical concepts according to which heterogeneous processes involving the reactor walls or the surface of solid packing can determine the characteristics of gas-phase oxidation processes. However, in heterogeneous-catalytic oxidation processes there is a possibility of the formation of species carrying an excess of free energy (the active and excited molecules, free atoms and radicals). The release of such species into the gas phase may lead to a homogeneous continuation of the process. Under these conditions, the reactions of the radical species play an especially important role. They are highly reactive in homogeneous processes and can also give rise to surface compounds which are intermediates in oxidation reactions.

Various aspects of the mechanisms and kinetics of heterophase processes involving free radicals have been surveyed in a number of publications.[1-13] The hypothesis of heterogeneous–homogeneous reactions, according to which chain carriers are initiated on the surface of the reaction vessel or catalyst, has been formulated in a review.[1] The release of these carriers into space leads to the continuation of the process in which the bulk-phase and surface reactions occurring simultaneously are closely interrelated and are independent.

The reactions including homogeneous and heterogeneous stages have been classified, the possible mechanisms of the heterogeneous formation of radicals have been analysed from the standpoint of thermochemistry, methods for the recording of active species and for the investigation of heterogeneous–homogeneous reactions have been described, and data concerning the mechanisms and kinetics of specific processes have been examined in a monograph.[2]

The possible variants of the combination of homogeneous and heterogeneous stages of a complex process have been discussed and examples of their occurrence in the oxidation reactions of substances belonging to different classes have been presented in a book.[3]

The differences in the description of gas-phase radical-chain processes have been analysed[4] within the framework of the traditional ideas of the chain theory, which do not take into account the possible participation of the surface in the chain propagation and branching stages, and also within the framework of the approach developed by the author, which does take into account such a possibility. It has been shown in relation to the hydrogen oxidation reaction that allowance for heterogeneous factors permits a more complete description of the phenomenology and kinetics of the process.

Analysis of the mechanism of the partial oxidation of methane showed that the formation of the methyl radical on interaction with an oxidative centre on the surface of the oxide catalyst represents the stage involving the activation of the CH_4 molecule in the catalytic process.[5,6] The selectivity of the process as a whole depends on the subsequent reactions of the CH_3 radical both in the gas phase and in heterogeneous reactions.

The study of Driscoll et al.[7] was largely devoted to the employment of instrumental methods for the detection of free radicals formed in heterogeneous processes. Specfic procedures, which permit the application for this purpose of various modifications of mass-spectrometry, matrix isolation of radicals combined with measurement of IR and EPR spectra, photoelectron spectroscopy, and multiphoton and resonance ionisation methods, have been examined. Examples illustrating the role of free radicals in catalytic reactions have been presented.

Data on the generation of free radicals, obtained mainly by the 'freezing out' (or matrix isolation) of radicals in a matrix of

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reagents and reaction products with recording of EPR spectra, have been analysed in recent reviews.[8,9] It was shown that radicals form in many heterogeneous processes, including catalytic oxidation reactions.

Analysis of the reactions of the $OH^{\cdot}$ and $HO_2^{\cdot}$ radicals in the atmosphere showed that heterogeneous reactions of the radicals may be a significant factor determining the gas composition of the troposphere and the stratosphere.[10,11]

The kinetics of the catalytic reactions accompanied by the release of active species into space have been examined in two communications.[12,13] The conditions for the appearance of nonstationary regimes, the possible multistage mechanisms of such reactions, and the kinetic equations for the stationary and nonstationary conditions as a function of the nature of the reaction propagated in the gas phase, as well as the role of the mass transfer processes in the catalyst grain were analysed.

In recent years, the number of studies devoted to the heterogeneous reactions of free radicals has continued to grow. Some of the postulates formulated previously require rethinking in the light of the results. Unfortunately, a systematic consideration of the entire set of available data is not available in the literature. This has stimulated their survey and analysis from a single standpoint and the determination of the direction in which further progress in the understanding of the mechanisms of the oxidation processes may be attained.

II. Heterogeneous factors in homogeneous gas-phase oxidation processes

In the traditional theory of gas-phase radical-chain processes (RCP), the involvement of the surface (as a rule the walls of the reaction vessel or the surface of the packing introduced into the reactor) in the chain initiation and termination stages is considered.[14-16] The presence of a lower ignition pressure limit is associated with the decisive role of the heterogeneous termination. Within the framework of this approach, a significant feature is the regime in which the chain carriers are destroyed — in the diffusional or kinetic regime (in the latter case, an important factor is the probability of their destruction in collisions). On the other hand, the destruction itself is considered only as the disappearance of a species in the gas phase, no attention being devoted to the chemistry of the process and its detailed mechanism.

The need to take account of heterogeneous factors exists also when the chain initiation mechanism is considered. Since the work of van't Hoff,[17] the influence of the material and of the preliminary treatment and relative surface area of the reaction vessel walls on the kinetics of the oxidation processes in the gas phase has been frequently noted.

Considerable progress in the study of the role of the surface and radical-chain processes has been associated with the creation of a method for separate calorimetric measurements,[18] the essential feature of which consists in the measurement of the differences between the temperatures at different points in the reaction volume, for example near the walls and at some distance from them. Depending on the location of the process or of its individual stages, the magnitude and sign of these differences may differ. If heterogeneous stages are completely absent, heating takes place in the centre of the cylindrical vessel, and

$$\Delta T_v = \frac{Q_v}{4\pi\lambda},$$

where Q_v is the heat evolved in the volume reaction per unit time and λ is the thermal conductivity of the gas.

If the reaction takes place wholly on the surface of a cylindrical reactor having a radius R with a thermocouple-containing capillary having a radius r placed along the axis of the reactor, then

$$\Delta T_s = \frac{Q_s}{4\pi\lambda}\frac{r}{R+r}\ln\frac{R}{r},$$

where Q_s is the heat evolved in the heterogeneous reaction per unit time.

Finally, if the process takes place partially on the walls and partially in space, then

$$\Delta T = \frac{Q_v}{4\pi\lambda} + \frac{Q_s}{4\pi\lambda}\frac{2r}{R+r}\ln\frac{R}{r}.$$

Expressions similar to those quoted above may be obtained for fully homogeneous or fully heterogeneous reactions.[19]

In essence, the method involving separate calorimetric measurements has been the first direct experimental method for the investigation of heterogeneous–homogeneous processes. Numerous examples of its successful application to the study of the mechanisms of various processes, including gas-phase oxidation, have been quoted.[1,2,19] An evident limitation of the method is associated with the impossibility of using it to investigate the detailed mechanisms of the heterogeneous formation and subsequent reactions of active species. For this reason, until recently the principal conclusions concerning the mechanism of the heterogeneous stages have been reached on the basis of the analysis of the kinetics of the RCP (Radical Chain Process).

Thus the decrease in the effective activation energies for the thermal and oxidative pyrolysis of methane ($E_{ef} = 85-335$ kJ mol^{-1}) has been attributed to the involvement of the surface in the chain initiation.[20] It has been noted that, under conditions ruling out the influence of the surface (shock waves, adiabatic compression, and jets of a heated carrier gas), higher values of E_{ef} (>370 kJ mol^{-1}) are observed. If the primary step involves the chemisorption of methane, i.e.

$$[S] + H-CH_3 \rightarrow [H...S...CH_3], \qquad (1)$$

then the energy of the dissociation of the C–H bond and of the formation of the primary radicals $CH_3^{\cdot}$ diminishes. In a heterogeneous process involving a carbon surface (any initial surface under cracking conditions is of this kind), the energy E_{ef} decreases compared with its value in a purely homogeneous process approximately by 210 kJ mol^{-1} and approaches the experimental values.

There is serious evidence (see, for example, the study of Garibyan et al.[21]) in support of the heterogeneous chain initiation in the oxidation reactions of hydrogen and C_1-C_3 hydrocarbons in a quartz reactor. A break in the Arrhenius relation for the reaction

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}, \qquad (2)$$

is observed in the temperature range 450–715 °C. The low-temperature section ($E_{ef} = 100$ kJ mol^{-1}) is attributed to a heterogeneous process, while the high-temperature section (200–240 kJ mol^{-1}) is attributed to a homogeneous process.

The possibility of the occurrence of heterogeneous chain branching, propagation, and transfer stages and not merely chain initiation and termination has been discussed.[15,22] This hypothesis makes it possible to explain many facts established in the study of the gas-phase oxidation processes (activation energies, nonlinear variation of the rate of reaction as the concentrations of the reactants are varied, dependence of the composition of the product on the coating of the reactor walls). Nevertheless, specific mechanisms involving heterogeneous stages in the reactions of specific radicals have been scarcely considered until recently in the RCP theory.

The analysis of the influence of heterogeneous factors on the rate of RCP was based on the following postulates:[23]

1. When the first ignition limit is stable and the kinetic curves for the variation of the concentrations of the components of the reaction mixture are reproducible, the rate coefficient for the heterogeneous radical destruction reaction is constant.

2. The heterogeneous chain carrier destruction reaction is a first order process.

3. The adsorption of chain carriers is identical with chain termination.

However, there are a whole series of characteristic features of the RCP kinetics which cannot be described without a more detailed allowance for the role of heterogeneous stages. These features include the following:[24] continued acceleration of the isothermal process after the concentrations or pressures of the reactants reach values below those characteristic of the first ignition limit; expansion of the range of self-ignition under the influence of species preadsorbed on the reactor walls; heterogeneous self-inhibition of the chain combustion; hysteresis phenomena; vibrational combustion regimes in a closed volume.

A series of studies, in which the new approach to the role of heterogeneous factors in gas-phase reactions has been developed, have been devoted to the analysis of these features.[23-38] It was shown that the kinetics of many processes, traditionally regarded as homogeneous, are determined by the presence of a feed-back between heterogeneous reactions and RCP in the gas phase. This is associated to a large extent with the involvement of heterogeneous stages not only (and not so much) in the initiation and destruction of chain carriers but also in the propagation and branching of chains. The reactor surface is regarded as a 'reservoir' providing a store of active species (or their precursors) in the reaction zone and ensuring their involvement in the process (in particular their influence on the branching stage).

One of the possible variants of such influence is the increase in the branching factor during the process as a result of the decrease in the effective rate of the heterogeneous destruction of the chain carriers.[25] This may be induced by a decrease in the probability of the destruction of the radicals in their interaction with the surface as the degree of coverage of the latter by various species increases during the reaction.[26] The fact that during the combustion of H_2 and CO the reaction does not stop when the concentration of the reactants falls below the first ignition limit, i.e. the observed degrees of conversion are much higher than might have been expected for a constant rate of chain termination, has also found an explanation.[23]

In certain cases, it has been possible to determine the nature of the active species concentrated on the surface and to put forward a mechanism of their influence on characteristic features of the process. In particular, it has been shown[29] that, under the conditions of the hydrogen oxidation reaction, the walls of the quartz reactor are capable of adsorbing considerable numbers of hydrogen atoms: one adsorbed hydrogen atom is formed per H_2 molecule converted into water, while at a reactor temperature of 450–650 K the coverage of the reactor wall may be 6.5×10^{13} atoms cm^{-2}.

Hydrogen atoms with similar properties, generated by an incandescent tungsten filament in a hydrogen atmosphere, are adsorbed on quartz. The lifetime of the hydrogen atoms on the surface under the conditions of reduced pressure at the reaction temperature (at least tens of minutes at ~500 °C) exceeds by several orders of magnitude the characteristic lifetimes (tens of seconds). However, when molecular hydrogen is supplied, the surface is rapidly cleaned.

The ability of oxygen to clean the surface by removing the adsorbed hydrogen atoms has been demonstrated in a study of the recombination of hydrogen atoms on the surface of a Chromel–Alumel thermocouple.[28] Whereas at 500 °C at a pressure of 3 Torr the stationary recombination temperature rise in a jet of atomic hydrogen was 2–5 °C, after the treatment of the thermocouple for 10 min with oxygen it rose to 30–50 °C.

The $-\rangle Si-OH$, $-\rangle Si-H$, and $SiH_x(OH)_{2-x}$ groups have been detected by IR spectroscopy during the oxidation of monosilane on a silica gel surface. In the absence of oxygen, they did not appear, i.e. these surface compounds are formed during oxidation and are intermediates.[34]

It has been postulated[23] that the stages involving the formation and reactions of the hydrogen atoms on the reactor surface play an important role in the mechanism of the oxidation of hydrogen. It is suggested (in contrast to the traditional point of view) that the collision of a hydrogen atom from the gas phase with the surface leads not to chain termination by recombination but to the formation of an adsorbed hydrogen atom (H_s), the reaction of which with molecular oxygen leads ultimately to chain branching.

$$H_s + O_2 \rightarrow HO_2, \quad (3)$$

$$H + HO_2 \rightarrow 2\ OH, \quad (4)$$

$$H + HO_2 \rightarrow H_2O + O, \quad (5)$$

$$O + HO_2 \rightarrow OH + O_2. \quad (6)$$

It is suggested that in the above scheme reaction (3) is heterogeneous whilst reactions (4)–(6) may be both heterogeneous, i.e. they proceed with participation of adsorbed atoms, and homogeneous.

In considering the possible mechanism of the heterogeneous chain self-ignition of $SiH_4 + O_2$ mixtures, Azatyan and Aivazyan[35] suggested that, in addition to reactions (3)–(6), the following process leads to chain branching:

$$H_s + O_2 \rightarrow OH_s + O. \quad (7)$$

On the basis of the proposed scheme, it has been possible to construct a kinetic model and to obtain an equation describing the kinetics of the oxidation of hydrogen over a wide range of pressures of the reactants, including the conditions on either side of the lower ignition limit.[23,32,37]

Important evidence for the involvement of heterogeneous stages in chain propagation and branching is provided by nonstationary phenomena. The appearance of, for example, hysteresis phenomena and oscillatory regimes under static conditions without self-heating, detected in the oxidation reactions of CO and P_4 and SiH_4 vapours and also in the decomposition of NCl_3,[23] may be caused only by chemical factors, in particular by the reactions of the adsorbed chain carriers.[30-32,34-36,38] For example, in the oxidation of silane the propagation of the process as a function of time and also the variation of the first ignition limit are described by curves with hysteresis, which is associated with the reversible variation of the properties of the surface during combustion.[31]

The existence of decaying oscillations in the isothermal combustion of CO in a closed volume is due to the involvement in the reaction of adsorbed atoms and radicals:[29] repeated filling of the reactor containing MgO with a 'dry' $CO + O_2$ reaction mixture leads to a decrease in the number of pulsations, but, after the $H_2 + O_2$ reaction has been carried out in the same reactor, the initial nature of the oscillations is restored.

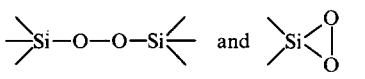
Repeated isothermal ignition in a closed volume has been observed also in the reaction of monosilane with oxygen. Azatyan and Aivazyan[38] were able to show that successive flashes occur at different distances from the reactor wall, have different spectral compositions, and correspond to different overall processes.

The results of kinetic analysis indicate[12] that the presence of several stationary states, including two unstable states responsible for the occurrence of autooscillations, may be associated with the reversible adsorption-desorption of radicals.

The studies considered above have not only created a new approach to the understanding of the kinetics of the RCP but have also posed the question of the chemical behaviour of the 'wall', which is important. Unfortunately, nothing has been said in the above communications concerning the nature of the surface centres of quartz responsible for the strong adsorption of hydrogen atoms and also the possibility of the occurrence of reaction (3), which is a key process in the chain branching induced by the surface.

The results of the study of the surface centres of oxides subjected to mechanical activation[39-45] and of 'reactive silica', obtained by the heat treatment of the large surface area of silica subjected to preliminary methoxylation,[46] have thrown some light on this question. Centres of various types are present on such surfaces and may be converted into one another and modified by means of special chemical treatment.

Centres of the paramagnetic and diamagnetic types, such as the $-\rangle Si^{\bullet}$, $-\rangle Si-O^{\bullet}$, and $-\rangle Si-OO^{\bullet}$, doubly coordinated silicon atoms $=Si:$, strained $-\rangle Si-O-Si\langle-$ bridges, and the peroxide groups

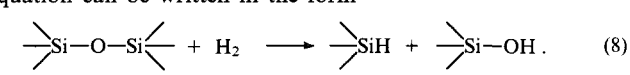


have been identified by EPR and optical spectroscopy. Their structures and reactivities have been investigated and it has been shown that some of them may induce the dissociation of the C–H and H–H bonds. Quantum-chemical calculations and comparison of the activation energies for the reactions of various surface centres of mechanically activated quartz with H_2, D_2, CH_4, C_2H_6, and C_3H_8 molecules have demonstrated the applicability of the Polanyi–Semenov correlation,

$$E = E_0 + \alpha|\Delta H| ,$$

to the reactions of surface centres with gas phase molecules.

It has been suggested[29] that the siloxane bonds are 'opened' under the influence of hydrogen atoms on the surface of quartz and hydroxy-groups are formed. Bystrikov et al.[40] were able to demonstrate by the NMR and IR spectroscopic methods and by the thermal desorption method in combination with quantitative chemical analysis that, when quartz is ground under a hydrogen atmosphere, $-\rangle SiH$ groups are formed, i.e. the overall reaction equation can be written in the form



(8)

According to the data obtained by Bobyshev and Radtsig,[44] the X–H bond dissociation energies in the surface compounds $-\rangle SiH$, $-\rangle SiOH$, and $-\rangle SiOOH$ are 419, 510, and 389 kJ mol^{-1} respectively. The first two values are comparable with the Si–O bond strength in quartz and, if analogous surface compounds are formed in the interaction of the surface of the quartz reactor with hydrogen atoms under the experimental conditions,[29] then the hydrogenation of the surface by hydrogen atoms is entirely probable. For such bond energies, the lifetime of the hydrogen on the surface should be extremely long even under evacuation at elevated temperatures. The probability of reaction (3) increases with decrease in the hydrogen bond energy. This question will be examined in greater detail below.

We shall consider specially the 'stabilised combustion' process, which will be understood (in accordance with Pfefferle and Pfefferle[47]) as gas-phase combustion occurring in the presence of a catalytically active surface of a solid. This makes it possible to carry out the process in 'weak' mixtures of a fuel with an oxidant at much lower temperatures, with a much lower yield of impurities contaminating the environment (in the first place nitrogen oxides), and with an increased efficiency of utilisation of the heat evolved under these conditions.[48]

Various catalysts, the macrokinetics of the processes, and the design of the reactors employed to achieve the stabilised combustion of various fuels (hydrocarbons, hydrogen, and CO) have been considered in a series of reviews.[47,49–51] Direct measurements of the concentrations of the active species (OH$^{\bullet}$ radicals[52–54] and oxygen atoms[55]) showed that, depending on the conditions and the nature of the surface, they can both decrease monotonically on moving away from the surface (in this case the process apparently proceeds as a heterogeneous reaction or is concentrated in the near-surface layer) and can pass through a maximum. The latter case probably indicates directly the occurrence in space of a chain process initiated by the reaction on the surface.

It is of interest that in the combustion of hydrogen the concentrations of the OH$^{\bullet}$ radicals ($\sim 10^{15}$ cm^{-3}) and the profiles of their concentrations along the normal to the surface are virtually identical for platinum and quartz at 1170 K.[47,52] For the combustion of methane[55] and ethane,[54] the oxygen atom concentration profiles depend on temperature in the case of the platinum catalyst: the concentration of oxygen atoms decreases monotonically on moving away from the surface below 1570 K (methane) and 1450 K (ethane), while at higher temperatures a concentration maximum ($\sim 10^{16}$ cm^{-3}) is attained at distances of 0.5–3.0 mm. In the case of a quartz surface, the concentration of oxygen atoms passes through a maximum, reaching $\sim 4 \times 10^{15}$ cm^{-3} (1580–1665 K, methane) and $\sim(1-2) \times 10^{15}$ cm^{-3} (1315–1560 K, ethane).

A wider range of metals has been investigated in the combustion of hydrogen.[56] The activity of the metals increases in the sequence Pt > Pd > Rh > Ir > Ni. With increase in pressure in the range 0.005–0.2 Torr in the temperature range 950–1300 K, the yield of the OH$^{\bullet}$ radicals passes through a maximum at 0.7 ± 0.1 Torr, but the maxima in the rate of reaction as a whole and in the rate of formation of the radicals may not coincide. The activation energies for the formation of radicals vary in the range from 1150 (Rh) to 172 (Pt) kJ mol^{-1} and are not correlated with the activities of the metals. The OH$^{\bullet}$ radicals are also formed in the reaction of hydrogen with a preoxidised metal in the absence of oxygen from the gas phase, i.e. they may be a product of the reaction of hydrogen with adsorbed oxygen atoms.

The data obtained in the above investigations[47–56] make it possible to return to the analysis of the influence of heterogeneous factors in gas-phase combustion processes at a new level. However, one should note yet again that even the early investigations (see, for example, Polyakov[1] and Gorokhovatskii et al.[2]) demonstrated in relation to the oxidation of hydrogen and hydrocarbons that the 'slow homogeneous' and explosive heterogeneous initiated oxidation processes obey the same rules. The results of the above investigations[47–56] show that the behaviour and role of the surfaces of the traditional 'wall-type' (quartz) and classical catalytic materials (Group VIII metals) in combustion processes may be similar.

III. Free radicals in heterogeneous-catalytic oxidation processes

It is clear from the preceding section that, whilst recognising the important role of the heterogeneous reactions of radicals in gas-phase oxidation processes, the RCP theory does not deal with the detailed mechanisms of these reactions, being restricted to a macrokinetic and in a number of instances a stoichiometric description. The details of the interaction of species with the surfaces of solids have been investigated traditionally in heterogeneous catalysis, resorting to data derived from solid state chemistry and surface science.

Out of the entire wide variety of processes in which both the surface of a solid and the surrounding bulk phase play a significant role, in heterogeneous catalysis one usually considers heterogeneous–homogeneous reactions which begin on the surface and pass to the surrounding space as a result of the release of active intermediate species into the gas phase, where the reactions involving them continue or are terminated.[13] In the present review, only processes with participation of radical species are considered, although there is a possibility that saturated molecules capable of reacting in the gas phase at a high rate[2] as well as molecules in an excited state[57] are released into space.

Generally speaking, the radicals formed in the heterogeneous stages may play yet another role in the process — they may be trapped by another active centre on the surface. In this case, the majority of the radicals are converted into the final reaction products within the catalyst grain or layer and only a small proportion of them, largely generated by the outer surface, may be detected experimentally in the free volume of the reactor.[58,59] There are also grounds for classifying these processes as heterogeneous–homogeneous because, firstly, the nature of the radical generation stage may be different in the two cases and, secondly, the radical may undergo reactions in homogeneous

stages between each generation on one centre and chemisorption on another, which again necessitates the joint consideration of heterogeneous and gas-phase processes. Furthermore, in the 'classical' heterogeneous – homogeneous catalysis it is likewise not permissible to rule out the possibility of a secondary interaction of the radicals with the surface, so that all the important stages in the chemical processes are of the same nature in both cases.

Thus all the reactions, the significant stages of which occur both on the surface and in space regardless of the role of these stages in the process as a whole (activation of the reactants, conversion of the intermediates, formation of the final products), should apparently be regarded as heterogeneous – homogeneous reactions.

This approach may prove to be too broad, but it makes it possible to consider related processes from single standpoints without emphasising the formal difference between them.

Before proceeding to the consideration of the individual stages of heterogeneous – homogeneous catalytic reactions, we shall consider general features. One may postulate that the probability of the formation of radicals should increase with decrease in the probability of the 'adhesion' of the reactant molecules to the catalyst surface, i.e. the heterogeneous – homogeneous character of the process should be more pronounced (a) in the oxidation of saturated molecules (hydrogen, alkanes) compared with alkenes, aromatic hydrocarbons, or organic compounds with functional group substituents, (b) in the case of compounds of one class — organic compounds with a smaller number of carbon atoms, (c) for oxide catalysts compared with metals, (d) for oxides without transition metal ions, and (e) at higher temperatures.[2]

Analysis of the literature data (Table 1) shows that the transfer of the reaction into space has been detected in a wide variety of processes with participation of compounds of different classes and molecular masses on catalysts of different nature. This is also indicated by the compilation of all the data presented by Gorokhovatskii et al.[2] Thus one may conclude that the presence of a homogeneous component in catalytic oxidation reactions is a common phenomenon. Despite the fact that the available literature data refer to catalytic systems and reactant conditions which are difficult to compare, in considering them it is possible to differentiate a series of common key aspects including common kinetics of heterogeneous – homogeneous catalytic reactions, a common mechanism of the formation of free radicals in heterophase processes, and common reactions of the radicals, including their interaction with the surface.

1. Kinetic features of heterogeneous – homogeneous catalytic processes

In a number of cases, the conclusion that heterogeneous-catalytic reactions undergo homogeneous propagation has been based on the analysis of the process kinetics (Table 1). Indeed, the presence of two reaction zones in a heterogeneous – homogeneous process may lead to the appearance of specific characteristics of the kinetics. In a number of cases, it is possible to differentiate the heterogeneous and homogeneous components.

The previously widely used kinetic method for demonstrating the heterogeneous – homogeneous nature of the process by varying the ratio of the surface of the catalyst or an 'inert' material to the free volume of the reactor (S/V) (see, for example, Refs 1, 2, 12, and 13) is based on the variation of the relative sizes of the reaction zones. Such demonstration is more reliable if the selectivity in the formation of various products varies simultaneously with the rate of the process as the S/V ratio is varied. For example, in the oxidation of propene on a bismuth – molybdenum oxide catalyst, it was demonstrated by this method[77] that epoxypropane is formed in a homogeneous process from the radicals released into space, while acrolein is formed in a process occurring on the surface. Similar experiments at higher temperatures have demonstrated that biallyl is a product of the homogeneous reactions of allyl radicals.[97]

The procedure used to demonstrate the involvement of radicals in the reaction, which consists in varying the direction of the flux of reactants in the presence of a large free volume along only one direction from the catalyst bed,[80] may be regarded as a variety of the method examined above. The nonadditivity of the rate of the oxidative dehydrogenation of propane in the free volume and on a thin bed of a V – Mg oxide catalyst has been demonstrated[80] and the observed proportions of the products have been accounted for by the occurrence of a chain reaction in the free volume.

The method involving the variation of the free volume has been used widely also at the present time, but, when applied to catalytic reactions, it can lead to erroneous conclusions. This is associated with the fact that, when the S/V ratio is varied, the rate and selectivity of the process may vary significantly only when the specific rates of the heterogeneous generation and destruction of the radicals are relatively low. Otherwise, the probability of the destruction of the radicals within the grain is close to unity (see the estimates made in a number of investigations[13,59,60]), the degree of conversion of the reactants on the catalyst is also high, and the homogeneous reaction occurring in the free volume does not contribute significantly to the process as a whole.

The nonmonotonic nature of the dependences of the reaction rates on the reactant concentrations has also been attributed to the heterogeneous – homogeneous course of process. Thus it has been assumed[61] that the extremum in the dependence of the rate of the catalytic oxidation of hydrogen on the concentration of oxygen cannot be accounted for within the framework of the equations obtained by the stationary concentrations and active surfaces methods. Since the maximum rate of reaction was attained with mixture compositions corresponding to the explosion limit, the observed features were accounted for by resorting to the concept that the hydrogen combustion is a chain reaction.

In a study of the oxidation of methane on MgO, an abrupt change in the composition of the products was observed when the contact time was varied.[98] The authors suggested that this can be accounted for by the difference between the concentrations of the methyl radicals in the gas phase and by the occurrence of their recombination reaction at higher concentrations (second order with respect to $CH_3^{\bullet}$ radicals) and of the addition of an oxygen molecule, i.e.

$$CH_3 + O_2 \Longleftrightarrow CH_3O_2,$$

at their lower concentration and subsequent formation of the extensive oxidation products (first order with respect to $CH_3^{\bullet}$ radicals).

A similar effect has been observed by other investigators[98,99] in the oxidation of methane on phosphate catalysts: a decrease in temperature and an increase in the oxygen concentration led to the preferential formation of formaldehyde, while the opposite change in conditions resulted in the growth of selectivity with respect to ethane. At a constant temperature, the overall selectivity with respect to $HCHO + C_2H_6$ remained almost unchanged, while the fraction of formaldehyde increased in proportion to the oxygen concentration, differing significantly on different catalysts. The authors postulate that this effect is due to a combination of the following factors: the dependence of the equilibrium position in the reaction involving the addition of oxygen to CH_3 on temperature and oxygen concentration and also the differences in the elementary interactions of the radicals with the surfaces of different catalysts.

The generalised formal kinetic models for heterogeneous – homogeneous reactions have been examined in a number of studies.[12,13,100] It was shown that, when the simplest multistage mechanisms operate, the forms of the kinetic equations for heterogeneous and heterogeneous – homogeneous nonchain reactions may be identical.[13]

Table 1. The release of species into the free volume in catalytic oxidation reactions.

Substance oxidised	Catalyst	Lower temperature limit of release into space/°C	Method of detection[a]	Ref.
H_2	$V_2O_5-MoO_3$	400	KA	60, 61
	Pt	500	LIF	62
	Pt	–	RFM	63
NH_3	Pt	525		64
CO	Pt	180	KA	65
	Pd	200	KA	66, 67
CH_4	SiO_2, Al_2O_3	650	KA, RFM	68
	MgO, Li/MgO, lanthanide oxides	500	RFM	69, 70
	metal oxides	500	KA	71
	K/Al_2O_3, Al_2O_3	550	RFM	59
	Sr/La_2O_3	700	PIMS	72
	MgO, Sm_2O_3	450	TAP	73
C_1-C_4	MgO	>25	IR, TPD	74
C_1-C_3	MgO, PbO, Bi_2O_3, $Bi_2O_3-MoO_3$	500	RFM	75
C_2-C_8	Al_2O_3, Cr_2O_3	400	SC	76
C_3H_6	$Bi_2O_3-MoO_3$	650	KA	77
	$Bi_2O_3-MoO_3$	450	RFM	78
	MgO, deposited Co and Mo oxides	450	RFM	60
C_3H_8	V_2O_5	570	KA	79
	V and Mo oxides	560	KA (SC)	80
C_6H_{12}	NaX zeolite	220	KA	81
	Pd	320	KA	82
C_6H_{14}	Pd	250	KA	83
$C_{11}H_{24}$	MgO	650	KA	84
C_6H_6	Pt	130	KA	85
	Pt	<80	KA	86
	Pd	220	KA	87
$C_6H_5CH_3$	Pt	180	KA	88
$C_6H_5CH=CH_2$	Pt	240	KA	89
CH_3OH	Ag	500	RFM	90, 91
C_3H_7OH	transition metal oxides	500	RFM	92
iso-$C_5H_{11}OH$	Ag	300	KA	93
HCHO	SiO_2, Al_2O_3	650	KA, RFM	68
ROH	Al_2O_3, Pt/Al_2O_3, transition metal oxides	315	RFM	94–96
RNH_2	transition metal oxides	350	RFM, MS	96

Note. Kiperman's data[13] were used in the compilation of the table.

[a] The following designations have been adopted: KA = kinetic analysis; IR = infrared spectroscopy; RFM = radical 'freezing out' (matrix isolation) method combined with measurements of EPR spectra; MS = mass spectrometry; SC = separate calorimetric measurements; TAP = temporal analysis of product; TPD = thermoprogrammed desorption; PIMS = photoionisation mass spectrometry; LIF = laser indiced fluorescence.

A more complex mechanism, postulating that the heterogeneous conversion of the surface compound into the reaction products takes place via a first order reaction and that the formation of radicals from this product is a second order process (chain branching, propagation, and quadratic termination reactions are possible in the gas phase), has been examined by Berman and Margolis.[12] Analysis of the kinetic equations describing the process shows that one or several stable stationary states with different contributions by the homogeneous component can exist. For other reactions orders, the stationary state becomes unstable and there is a possibility of the occurrence of auto-oscillatory regimes. It also follows from this analysis that smooth or abrupt changes in the reaction rate in the isothermal regime are possible when the reactant concentrations are varied monotonically.

The multiplicity of stationary states may be manifested by the appearance of hysteresis in the rate of reaction when the temperature is varied cyclically. This type of kinetics, observed in the oxidation of cyclohexane on the NaX zeolite, has been attributed to the partial transition of the reaction to the gas phase.[81]

Concluding the brief analysis of the kinetic features of heterogeneous–homogeneous catalytic processes, we may note that, on the basis of their analysis alone, it is impossible to reach a final conclusion concerning the presence or absence of the homogeneous component of the reaction. However, in certain cases such analysis may be fairly informative.

2. Methods for the investigation of heterogeneous–homogeneous radical reactions

The methods based mainly on the analysis of the kinetics and used in the investigation of heterogeneous–homogeneous reactions before the wide scale employment of various physical methods in chemical kinetics have been surveyed.[2] The majority of instrumental methods for the investigation of radical processes in the gas phase can be adjusted in principle to the study of heterogeneous radical reactions. Unfortunately, nowadays only a few of them are employed for such purposes, while in other cases it is still necessary to overcome significant technical difficulties. Here we shall describe briefly the characteristics of certain instrumental methods and new approaches without repeating, as far as possible, what has already been stated in the review[7] concerning the use of mass spectrometry, matrix isolation of radicals combined with measurement of IR and EPR spectra, photoelectron spectroscopy, and multiphoton and resonance ionisation for the study of the role of the free radicals in catalytic reactions.

3. Method involving separate calorimetric measurements

The separate calorimetric measurement method (SC method) was mentioned above when the role of heterogeneous factors in gas-phase reactions was considered. This method has also been employed in the study of the transfer of the reactions on heterogeneous catalysts into free space (see, for example, Ganieva et al.[76] and Nguyen and Kung[80]). One of the modifications of the SC method involves the carrying out of two series of experiments: in the first series, the catalyst in the form of a thin layer is deposited on the walls of the reaction vessel with a radius R, while in the second it is deposited on a capillary with a radius r in which a thermocouple is enclosed, the capillary being placed along the axis of a cylindrical reactor. The ratio of the heats evolved on the surface and in the reactor volume is defined by the relation[19,20]

$$\frac{Q_s}{Q_v} = \frac{\Delta T_2 - \Delta T_1}{2\Delta T_1 \ln(R/r)}.$$

As already mentioned, the limitation of the SC method consists in the impossibility of determining with its aid the nature of the species responsible for the bulk propagation of the process. Furthermore, in the study of processes occurring on granular porous catalysts the SC method makes it possible to differentiate only the fraction of the heat evolved in the free volume of the reactor and the latter may be very small even if the contribution of the volume reaction is high but the reaction itself is localised within the pores of the grain or in the space between the catalyst grains. More informative methods, permitting the direct detection of the active species and the determination of their form and concentration (or the rate of their generation), are therefore needed.

a. The method involving the 'freezing out' of radicals

The method in which the free radicals are isolated in a solid matrix from frozen reaction products, initial reactants, or substances specially added to the gas stream in order to form the matrix with subsequent measurement of the EPR spectra is used widely to investigate radical processes in the gas phase.[100] In the Russian literature, this method is referred to as the radical freezing-out method (RFM). Its description, scope, and specific examples of its application in the study of different processes, including heterophase processes, can be found in a series of reviews and monographs (see, for example, Refs 7–9 and 101). We shall consider only certain modifications of the method, which have given rise to fundamentally new possibilities.

It has been frequently noted (see, for example, Ermolaev et al.[97]) that, depending on the composition of the matrix and its temperature, the form of the EPR spectrum of the radicals frozen out may vary markedly, which hinders their identification. It is particularly difficult to distinguish the spectra of the $RO_2^{\bullet}$ radicals (R = hydrogen atoms or organic fragments) if their mixture is formed in the reaction and the matrix contains a large amount of water. In the presence of oxygen in the reaction mixture, the majority of the radicals are converted into $RO_2^{\bullet}$ in the cold part of the reactor or on the way to the freezing out trap. By employing liquid helium for cooling and argon as the matrix and by carrying out the process at low temperatures or in the absence of oxygen, the problem may be solved.[69,70,75] However, in most cases it is impossible to carry out the reaction under oxygen-free conditions and the use of liquid helium significantly complicates the technique.

A method has been proposed for the identification of radicals stabilised in a solid matrix involving their photolysis by UV light and the re-recording of the EPR spectrum.[95,97–99,102] The authors suggest (see the discussion of the paper of Ismagilov et al.[95]) that the photolysis involves the dissociation of the R–OO bond in the $RO_2^{\bullet}$ radical and that the $R^{\bullet}$ radical remains in the matrix. The spectra of the radicals $R^{\bullet}$ are more informative and the new radicals formed in the reaction can be identified in principle on their basis. This approach has been used in the study of extensive oxidation reactions of alcohols[97–99,102] and amines[96] on oxides and deposited platinum catalysts.

However, it is known that, when various peroxy-radicals $RO_2^{\bullet}$ (R = alkyl, allyl, vinyl, acyl, etc.) are irradiated, the primary step is the dissociation of the O–O bond and not of the C–O bond.[103] Furthermore, the reaction investigated leads to the formation of a mixture of radicals, so that the EPR spectrum obtained after photolysis is a result of the superposition of the spectra of all the paramagnetic species formed, which greatly complicates its analysis.

As already mentioned, in the gas-phase oxidation reactions, in catalytic processes, and in the chemistry of the atmosphere, the role of the stages involving the interaction of radicals with various surfaces is considerable. As a rule, the rate constants for these stages (or the probabilities of the reactions on collision of the radical with the surface) are high and methods with a high time resolution are needed for their investigation.

In the traditional RFM scheme when the entire gas stream is directed to the freezing out trap (direct sampling), the velocity of the gas jet is restricted by the considerable convective heat exchange which impairs the regime under which the matrix is frozen and the radicals are stabilised within it. As a result, the interaction of the radicals with the solid substance investigated,

deposited on the wall or placed along the axis of a cylindrical reactor, takes place in the diffusional regime.[104,105]

The time resolution can be increased by means of diffusional sampling,[106-108] in which the freezing out trap is placed in the vicinity of the axis of the gas stream but outside it, so that the gas should not heat it convectively. In order to increase the rate of the diffusional removal of radicals to the freezing out trap, helium is employed as the carrier gas. Since only a proportion of the radicals enter the matrix under the conditions of diffusional sampling, the sensitivity of the method is reduced by a factor of 5-6 compared with direct sampling. However, the velocity of the jet can then be increased to 30 m s^{-1} and the time resolution can be raised to $\sim 10^{-3}$ s, which renders the reactions of radicals with a surface, whose probability is close to unity, susceptible to measurement. This method has been employed to investigate the interaction of $HO_2^{\cdot}$ radicals with the surfaces of ice, carbon black, Al_2O_3, and various salts,[105] of the $CH_3^{\cdot}$ and $CH_3O_2^{\cdot}$ radicals with the surfaces of quartz and NaCl,[107] and of the $HO_2^{\cdot}$, $CH_3O_2^{\cdot}$, and $FO_2^{\cdot}$ radicals with the surface of quartz.[108]

b. Mass spectrometry

Repeated attempts to employ the mass-spectrometric (MS) method in the study of heterogeneous-homogeneous oxidation reactions have been made.[28,109-111] However, the problem is that in the usual method the fragments of saturated molecules generated on exposure to an ionising electron beam can give rise to the same peaks (m/z) in the spectrum as the radicals present in the system. The concentration of the latter is then usually several orders of magnitude lower, which virtually precludes their differentiation from the overall spectrum in practice.

The possibility of studying reactions involving free radicals increased sharply when photoionisation mass spectrometry (PIMS) was employed.[112] The ionisation thresholds of radicals are generally much lower than for the saturated molecules from which they are formed. Therefore the use of, for example, a UV radiation source with a set of filters designed for different light wavelength ranges or of lasers (multiphoton ionisation processes are then most often employed[113]) permits the selective ionisation of species (radicals) of one kind without ionising others (saturated molecules). This method has been used to investigate the generation of $CH_3^{\cdot}$ radical on the Sr/La_2O_3 catalyst for the oxidative condensation of methane (OCM)[72] and the interaction of these radicals with the surface.[114]

Time-of-flight mass spectrometry with multiphoton ionisation by laser radiation has been employed[115] for the detection of the methyl radicals formed in the OCM reaction on the Ca/Al_2O_3 and Sr/La_2O_3 catalysts. The use of mass spectrometry with chemical ionisation (MSCI) may also prove to be promising, but we are not aware of any examples of the application of this method in the study of heterogeneous-homogeneous processes.

A study has been published recently[73] in which the detection of radical species by mass spectrometry was combined with the TAP technique which make it possible to investigate processes on heterogeneous catalysts with a high time resolution.[116] This aspect is also extremely promising.

Hitherto it has been possible to consider the rates of reaction of radicals with a surface in only a small number of instances. The high sensitivity and selectivity ensured by the PIMS and MSCI methods make it possible to solve one of the most complex problems — the elucidation of the stoichiometry of heterogeneous radical reactions.

c. Molecular beams

The general term 'molecular beam method (or technique)' (MB) is usually understood as the set of methods for the investigation of the kinetics and mechanisms of reactions (both homogeneous gas-phase and heterogeneous reactions) in which the reactants and/or products are investigated and in which the directions of their velocities are rigorously specified (see, for example, the relevant reviews[117,118]). The methods for the generation and detection of the beam may be varied. For example, the distribution of the species with respect to different energy modes can be varied under these conditions from the Maxwell-Boltzmann equilibrium distribution to a fairly narrow distribution, which is different for different partner species. This makes it possible to investigate not only the reaction kinetics but also the dynamics of the energy transfer processes during collisions or the form of the potential energy surface for the system.

An additional advantage of the MB technique when applied to the study of heterogeneous processes is associated with the possibility of monitoring precisely the surface coverage and also of investigating the steric effects (the distribution of the species reflected by the surface or arising from it, the possibility of interaction as a function of the angle of incidence of the beam).[119] The combination of the MB technique with the methods for the simultaneous investigation of the surface and surface compounds (thermoprogrammed desorption and photoelectron spectroscopy,[120] IR spectroscopy with isotope substitution[121,122]) is particularly fruitful in the study of the reactions of radicals with various surfaces.

d. Laser induced fluorescence

The detection and the determination of the concentrations of species by the method based on the laser induced fluorescence (LIF) are based on the measurements of the emission by the excited species. The greatest advance in the application of fluorescence methods in the study of atoms and radicals was achieved when the excitation sources employed comprised pulsed or continuous broad-band and frequency-tunable dye-based lasers, which could be tuned to the narrow absorption bands of the test species.[123]

An advantage of the LIF method applied to heterogeneous-homogeneous processes is the possibility of measuring the concentration of species with a fairly high spatial resolution. This is in fact why it has been possible to determine the spatial profiles of the concentrations of $OH^{\cdot}$ radicals and O atoms in stabilised combustion processes.[52,55-57,124,125]

The use of the LIF method in the study of OCM process made it possible to demonstrate[126] that $OH^{\cdot}$ radicals are formed under the conditions of this reaction and also in the 'oxidation of water'.

e. Other methods

The method for the detection of species from the disappearance of a metallic mirror, used to confirm the involvement of radicals in the OCM reaction,[127] is based on the formation of volatile organometallic compounds in the interaction of, for example, thin films of metallic lead (a 'mirror' deposited beforehand on the reactor surface) with radicals (in the given instance tentatively identified with $CH_3^{\cdot}$). Although according to the data of Rice and Tweedell[128] certain mirrors (for example, tellurium or antimony mirrors) disappear only on exposure to radicals of a particular type ($CH_3^{\cdot}$, $C_2H_5^{\cdot}$), this method [as well as the low-temperature reduction of copper and tungsten oxides by hydrogen at a certain distance from the catalyst (Pd, Pt) employed in early investigations[129-131] and the disappearance of the glow in the gas under analogous conditions[132]] can serve as only a qualitative indication of the release of active species into the free volume.

Various modifications of IR spectroscopy have been employed to investigate the radical generation processes and the repeated interaction of the radicals with the surface of oxides.[74,133-136] However, one should note that only surface compounds (alkoxy- and hydroxy-groups), appearing as a result of the interaction of the active surface centres with hydrocarbons and with the radicals formed, were detected spectroscopically in the above investigations. Like other methods for the investigation of the surface and surface compounds, IR spectroscopy yields most information when it is combined with methods for the direct

detection of free radicals, as happens for example in the MB technique.

4. The mechanism of the heterogeneous formation of free radicals

As already mentioned, heterogeneous free radical formation reactions may play the role of chain initiation stages in RCP and of reactant activation stages in heterogeneous-catalytic processes. Therefore the elucidation of the mechanisms of such reactions is extremely important for the understanding of the process as a whole. Here we shall consider the energy relations of the interaction of reactant molecules with the active surface centres and the available data on the detailed mechanisms for these reactions.

a. Thermochemistry of the interaction of molecules with active surface centres

It follows from Table 1 that the propagation of heterogeneous-catalytic processes in the free volume occurs widely in the oxidation of substances of different classes. This indicates the existence of a universal cause which makes the formation of radicals in heterogeneous processes extremely probable.

Two cases in which the heterogeneous formation of radicals may become energetically more favourable than their homogeneous formation have been analysed.[2]

1. In the dissociative adsorption of a molecule with subsequent desorption of one of the adsorbed fragments:

$$AB + 2Z \rightarrow ZA + ZB, \quad (9)$$

$$ZA \rightarrow Z + A^{\cdot} \quad (10)$$

2. In the binding to the surface of only one of the fragments of the activated molecule (the second fragment escapes into the free volume under these conditions).

$$AB + Z \rightarrow ZB + A^{\cdot}. \quad (11)$$

In the first case, the bond dissociation energy in the initial molecule decreases more the higher the energy of the bond between its fragments and the surface centres Z; however, under these conditions the activation energy for the abstraction of a radical from the surface increases.

In the second case, the bond dissociation energy diminishes less, but there is no need for additional energy consumption on the abstraction of a radical from the surface. According to the authors,[2] the formation of radicals via the second mechanism in one stage is more probable.

On the other hand, when one considers the probability of the release of radicals into the free volume in a particular reaction, then a different assessment must be made, namely one must compare the energy relations for the formation of radicals in the interaction of various molecules with the surface of the solid with the energy relations for other possible types of interaction leading to the activation of the reactants. Such analysis may be performed on the basis of the available thermochemical literature data (see, for example, Refs 137–139).

Table 2 presents estimates of the energy expenditure ($\Delta H + E_{st}$, where ΔH is the overall enthalpy change and E_{st} is the energy evolved in the stabilisation on the surface of an activated molecule or its fragment) in the following processes leading to the activation of certain molecules in catalytic reactions on the surface: (1) abstraction of a hydrogen atom from the RH molecule by a powerful oxidative centre on the oxide surface $[O]_s$ or by a surface metal atom [M] with formation of a radical $R^{\cdot}$:

$$[O]_s + RH \rightarrow [OH]_s + R^{\cdot}, \quad (12)$$

$$(\Delta H_1 + D_{O-H}) = D_{R-H},$$

Table 2. Energy expenditure (kJ mol^{-1}) on the activation of molecules via different mechanisms.

Molecule	Energy expenditure in processes			
	12 (or 13)	14	15	16
H_2	431	1668	1668	1484
CH_4	431	1630	1308	1250
C_2H_6	410	1584	1183	1120
C_3H_8	398	1609	1162	1078
n-C_4H_{10}	393	1605	1154	1037
iso-C_4H_{10}	389	1601	1120	1016
C_2H_4	435	–	1275	1012
C_3H_6	322	1421	1033	936
C_6H_6	427	–	1258	886
CH_3OH ($R = CH_2OH$)	385	–	1099	1049
HCHO	314	–	1195	1045
NH_3	439	1630	1463	991

or

$$[M] + RH \rightarrow [M-H] + R^{\cdot}, \quad (13)$$

$$(\Delta H_1 + D_{M-H}) = D_{R-H};$$

2) Heterolytic dissociation with abstraction of a proton from a strong basic centre $[O^{2-}]_s$ with formation of an anion R^-:

$$[O^{2-}]_s + RH \rightarrow [O^{2-}...H^+]_s + R^-, \quad (14)$$

$$\Delta H_2 + Q_{H^+} + Q_{R^-} = D_{R-H} + I_H - I_{R-R^-};$$

(3) Heterolytic dissociation into a hydride ion, which is bound to the cation $[M^{n+}]_s$ and the cation R^+:

$$[M^{n+}] + RH \rightarrow [M^{n+}...H^-]_s + R^+, \quad (15)$$

$$\Delta H_3 + Q_{R^+} + Q_{H^-} = D_{R-H} + I_R - I_{H-H^-};$$

4) Ionisation of the molecule with formation of a molecular ion RH^+, whereupon

$$\Delta H_4 + Q_{RH^+} = I_{RH}. \quad (16)$$

In the above equations, ΔH_i represents the enthalpy changes in the corresponding processes, D_{R-H} is the energy of the homolytic association of the R–H bond, I_j represents the ionisation potentials of the species, and Q_j are the heats of adsorption of the species.

It is easy to demonstrate that in all these processes the sign and magnitude of the heat change depend on the compensation of the energy by binding the fragments of the activated molecule to the surface centres. The energy which has to be compensated is as a rule minimal for the first process. For example, in the case of oxide catalysts one may expect that the energy of the O–H bond formed in this process is comparable to the energy expenditure on the homolytic dissociation of the R–H bond, i.e. its compensation does not require the binding of the second fragment. In the heterolytic dissociation of bonds [reactions (14) and (15)], the energy expenditure is so large that its compensation requires the binding of both fragments, which must occur synchronously in a single reaction step, i.e. the activation of the molecule requires the presence of paired centres with unusual configurations and energy relations. For process (12) [or (13)], it is sufficient to have single oxidative centres.

The above analysis shows that the formation of free radicals in the interaction of molecules of substances of various classes with the surfaces of metals and oxides may prove to be energetically preferable compared with other mechanisms of their activation. Furthermore, this process requires only one type of single centres and it takes place in a single stage. The combination of these factors may render such a process the most

favourable. This conclusion is the opposite of that arrived at by Gorokhovatskii et al.,[2] but it is based on quantitative thermochemical data. It may be that this in fact explains the more common employment of the approach based on the homogeneous propagation of oxidative heterogeneous-catalytic reactions (Table 1).

b. Generation of free radicals in catalytic reactions

The considerable progress in the study of heterogeneous–homogeneous radical reactions in recent years has been due to the considerable attention devoted by investigators to the catalytic oxidative condensation of methane (OCM) to higher hydrocarbons on oxide catalysts, which proved to be a convenient model in the study of such reactions.[5–8]

The formation of radicals in the presence of OCM catalysts under catalytic conditions (or close to such conditions) has been demonstrated by means of a whole series of methods (Table 1). The rates of formation of the radicals are close to the rates of reaction of the reactants.[59] According to current ideas, the overall mechanism of this reaction is the same on all oxide catalysts. The primary OCM product (ethane) is formed as a result of the recombination of the methyl radicals generated by the oxide surface. The differences between the catalysts, which determine their different efficiencies, are themselves determined by the properties and concentrations of the radical-generating active centres and also by the specific surface, porosity, and morphology, on which the relative rates of the secondary heterogeneous and homogeneous radical reactions depend. Results important for the understanding of the mechanisms of the generation and secondary reactions of the radicals in heterogeneous processes have in fact been obtained precisely in the study of the OCM process (the discussion below is based mainly on these results).

One of the mechanisms of the formation of free radicals in oxidation processes on oxide catalysts most frequently discussed in the literature presupposes the homolytic dissociation of the bond in the RH molecule when it collides with a strong oxidative surface centre $[O]_s$ with the simultaneous formation of a free radical and a surface hydroxy-group $[OH]_s$ in a single stage:[59,60,69–71,74,75]

$$[O]_s + RH \rightarrow [OH]_s + R^{\cdot} \qquad (17)$$

There exists an alternative point of view, according to which the process proceeds via dissociative adsorption and the key factor is the presence on the oxide surface of strong basic centres $[O^{2-}]_b$, which ensure the heterolytic dissociation of a C–H bond in the hydrocarbon molecule:[140–146]

$$[O^{2-}]_b + RH \rightarrow [O^{2-}...H^{+}] + (R^{-})_{ads} . \qquad (18)$$

The conversion of the anion R^{-}_{ads} produced into a radical requires that it should lose an electron on interaction with an electron-accepting (hole) centre $[h^{+}]$:

$$[h^{+}] + (R^{-})_{ads} \rightarrow [h^{0}] + R^{\cdot}_{2}. \qquad (19)$$

A model of the heterolytic dissociation of the C–H bond was initially formulated for the activation of alkenes and aromatic hydrocarbons in their partial oxidation reactions; subsequently it was transferred to the activation of methane.[140,147,148] This was based on the presence in many catalysts of the OCM process of alkali, alkaline earth, and lanthanide ions. In certain cases, the efficiency of the catalyst increases after the introduction of an alkaline modifying agent.

It follows from the data in Table 2 that the heterolytic bond dissociation in lower alkanes is energetically extremely unfavourable. It has been suggested that the role of the basic centres $[O^{2-}]_b$ actually consists in compensating for the energy expenditure on the dissociation of the C–H bond by binding the proton. If the energy of the interaction of these centres with Lewis acids (proton, CO_2) is adopted as a measure of the basicity, then its increase would entail an increase in the efficiency of the catalyst.

The rates of formation of the OCM products on different oxide catalysts (M/Al_2O_3 and M/MgO, where M = Li, Na, K, Cs, Pb, or Nd) have been compared[149,150] with the numbers of active centres and their strengths, which were determined from the adsorption of CO_2 by programmed thermal desorption and calorimetric methods. There is no direct correlation between the rate of formation of the OCM product and the basicity, but in a number of cases (the Pb/Al_2O_3 and Nd/MgO catalysts with different contents of the deposited component and MgO–alkali metal cation systems) an inverse correlation has been observed between the rate and the heats of adsorption. The introduction of alkaline components into oxide systems apparently leads not only (or even not so much) to an increase in their basicity but also to the modification of the oxidative properties of the lattice oxygen.[151]

Indeed, it has been shown[150] that an increase in the Na content in the Li/MgO and and Nd/MgO catalysts leads to an increase in the concentration of the oxidative centres. At the same time the rate of formation of the OCM product increases. Similar results have been obtained also for other oxide catalysts.[151–153] Furthermore, the interaction of oxide systems containing strong oxidative centres with methane leads to the formation of OCM products even in the absence of oxidants from the gas phase.[115,152–158]

Thermochemical studies have shown[153,157] that the relation between the activation energy for the formation of C_2 hydrocarbons in the interaction of methane with these oxides and the O–H bond energy in the hydroxy-group formed simultaneously corresponds to the Polanyi–Semenov relation obtained for the homolytic abstraction of a hydrogen atom from a methane molecule by various species in the gas phase:

$$CH_4 + X^{\cdot} \rightarrow CH^{\cdot} + XH , \qquad (20)$$

where X = F, OH, H, CH_3, O, Cl, Br, I, HO_2, CH_3O, CH_3O_2, etc.

Data concerning the applicability of the Polanyi–Semenov relation to the dissociation of the C–H and H–H bonds in hydrocarbon and hydrogen molecules on the active centres arising in the mechanical treatment of quartz and aerosil were presented above.[42,43] Although the formation of free radicals was not recorded directly in the above investigations, analysis of the kinetic isotope effects and the characteristics of the formation and reactions of the surface compounds, which according to the authors are products of radical capture, enabled them also to drawn an analogy between heterogeneous and the gas-phase reactions of type (12) [or (13)] and (20).

Similar conclusions concerning the mechanisms of the processes under consideration were reached in a study of the interaction of various molecules with irradiated (in the visible, UV, X-ray, and γ-ray ranges) oxides – MgO,[74,159,160] TiO_2,[161–163] and others,[164,165] as well as SiO_2 and Al_2O_3, modified by vanadium, molybdenum, and tungsten ions.[161,166–168] Irradiation, which leads to the formation of hole O^{-} centres with powerful oxidative properties, induces a sharp increase in the reactivity of the oxides. As a result, in the reaction of methane, for example, it is possible to detect the formation of ethane even at room temperature.[162] According to Kotova's data,[165] the process proceeds via the homolytic dissociation of a C–H bond with formation of excited surface OH groups. The presence of molecular hydrogen in the system inhibits the reaction of methane.

Thus the combination of the available data on the mechanism of the interaction of hydrocarbons and hydrogen with oxides confirms the conclusion reached earlier on the basis of thermochemical data that free radicals may be formed as a result of the homolytic dissociation of R–H bonds under the influence of oxidative surface centres. We may add only that the oxygen ions bound to the readily reducible cations,[115,155] the radical-ions $O^{\cdot -}$,[69,70,74,75,169,170] the surface oxygen ions O^{2-}_{LC} with a lower coordination,[70] and peroxide ions O^{2-}_{2} [156–158,170,171] are included in the literature among the centres possessing such properties.

However, one cannot rule out the possibility that at elevated temperatures all these types of active oxygen are converted into a single type, most probably the radical-ion $O^{\cdot -}$.[170,172-174]

$$O^{2-} + [h^+] \text{ (or } M^{n+}) \rightarrow O^{\cdot -} + [h^0] \text{ [or } M^{(n-1)+}], \quad (21)$$

$$O_2^{2-} \rightarrow 2\ O^{\cdot -}. \quad (22)$$

The results of quantum-chemical calculations[175-180] confirm the high probability of the formation of methyl radicals in the interaction of methane with $O^{\cdot}$ surface centres. On different oxide systems (MgO, MoO_3, $CuMoO_4$), the $O^{\cdot -}$ centres are equally active and have similar properties regardless of the pathways leading to their formation (their appearance as a consequence of the nonstoichiometry of the oxide or as a result of electron transfer under the influence of radiation).[181] Hole centres, having similar electronic properties but present in other systems (for example N^{2-} and AlN), possess also a similar activity in relation to the generation of radicals.[182]

Hitherto we have dealt with the mechanism of the formation of radicals in the interaction of the molecules of the substances being oxidised with the surface centres of catalysts. However, the available experimental data show that, apart from such 'primary' radicals which are products of the abstraction of a hydrogen atom from the RH molecule, and $RO_2^{\cdot}$ radicals, species can also be detected in the gas phase the products of which must be a series of far reaching consecutive transformations of the initial molecules.

As regards the $OH^{\cdot}$ radicals and oxygen atoms formed in stabilised combustion processes,[47,52-57] the available data are insufficient to consider the mechanism of their formation. In particular, it has been suggested[57,124,125] that $OH^{\cdot}$ radicals are formed on recombination of the oxygen and hydrogen atoms adsorbed on the metal surface, but one cannot rule out also their formation in secondary homogeneous reactions. On the other hand, according to some data, in the OCM reaction the generation of secondary $OH^{\cdot}$ radicals is important for the dynamics of the active centres of the catalysts.[128] We shall therefore consider their generation in greater detail.

In one of the first studies devoted to the formation of radicals in the OCM reaction,[69] it was shown that, when molecular oxygen is used as the oxidant, the rate of generation of radicals in the presence of the Li/MgO catalyst is constant, whilst in the case where N_2O is employed it decreases monotonically. The differences in the occurrence of the OCM in the presence of O_2 and N_2O are also indicated by the results obtained on the Sm_2O_3 catalyst:[183] and replacement of O_2 by N_2O lowers significantly the rate of the process.

Studies of the kinetic isotope effect occuring when CH_4 is replaced by CD_4 showed that, in the oxidation by oxygen, one cannot postulate the existence of a single stage determining the rate of the process,[184] whilst in the oxidation by N_2O such a stage is the reoxidation of the catalyst active centres.

The study of the oxidation–reduction properties of the Li/MgO catalyst showed that its reduction by hydrogen-containing reductants is not accompanied by the evolution of water, or at least that the dehydration of the reduced surface is a very slow process.[153,185] However, when oxygen is supplied to a specimen reduced by hydrogen or hydrocarbons, a rapid evolution of water is observed. When N_2O is introduced, the specimen is reoxidised at temperatures below 700 °C solely by the molecular oxygen formed to a small extent in the catalytic decomposition of N_2O. This led to the conclusion that the traditional mechanism of the oxidation-reduction processes, according to which stage (17) is followed by the dehydroxylation stage

$$2\ [OH]_s \rightarrow [O^{\cdot -}]_s + [O]_s + H_2O, \quad (23)$$

and the oxygen vacancies $[O^{\cdot -}]$ formed are filled as a result of the chemisorption of oxidants from the gas phase, i.e.

$$[O^{\cdot -}]_s + \tfrac{1}{2}O_2 \rightarrow [O]_s, \quad (24)$$

or

$$[O^{\cdot -}]_s + N_2O \rightarrow [O]_s + N_2, \quad (25)$$

does not operate in oxide systems with a high lattice oxygen $[O]_s$ bond energy because stage (23) is reversible and the equilibrium is greatly displaced to the left. This conclusion has been confirmed by thermochemical data.[186] Naturally, in the absence (or at a very low concentration) of oxygen vacancies, the reoxidation via reaction (24) or (25) is impossible. However, molecular oxygen is nevertheless capable of reoxidising a surface coated by hydroxy-groups via the overall reaction

$$4\ [OH]_s + O_2 \rightarrow 2\ H_2O + 4\ [O]_s. \quad (26)$$

According to the data of Sinev et al.,[185] this unusual 'oxidative dehydrogenation' of the catalyst active centres can proceed via the following stages:

$$[OH]_s + O_2 \rightarrow [O]_s + HO_2^{\cdot}, \quad (27)$$

$$[OH]_s + HO_2^{\cdot} \rightarrow [O]_s + H_2O_2, \quad (28)$$

$$H_2O_2 \rightarrow 2\ OH_2^{\cdot}, \quad (29)$$

$$[OH]_s + OH^{\cdot} \rightarrow [O]_s + H_2O. \quad (30)$$

The sum of stages (27)–(30) gives rise to the oveall equation (26). Among the heterogeneous stages leading to the reoxidation of the active centres, stage (27) is slowest. Its rate constant is higher the lower the O–H bond energy in $[OH]_s$.

The modelling of the reoxidation process via the proposed mechanism using the rate constants for stages (27), (28), and (30), estimated from Sinev's thermochemical data,[187] and the known rate constant for the homogeneous decomposition of hydrogen peroxide demonstrated a satisfactory agreement with experimental kinetic data.[186] There is so far no direct evidence that the reoxidation proceeds via the proposed mechanism. However, the data[126] indicating the presence of $OH^{\cdot}$ radicals in the gas phase may serve as indirect evidence for the validity of the mechanism (27)–(30) and hence for the heterogeneous–homogeneous radical nature of the reoxidation of the reduced oxide surface.

It is important to note that reaction (27), which is of key importance in the mechanism (27)–(30), is stoichiometrically identical with reaction (3), which, according to Azatyan,[23] is responsible for many of the characteristics of the RCP involving the oxidation of various hydrogen-containing compounds or mixtures (see Secion II). This confirms yet again the close relation between heterogeneous processes (in the given instance, the transformation of the active surface centres on oxide catalysts) and radical reactions.

In conclusion of this Section, we may note that there are numerous publications in the literature devoted to the mechanism of the formation of radicals under the conditions of oxidation reactions on oxide catalysts. Unfortunately, this cannot be said about metallic catalysts, although fairly extensive factual data on the release of radicals from the surfaces of metals into the free volume have accumulated.

5. The mechanism of the interaction of radicals with the surface of a solid

One can postulate that the subsequent fate of the radicals formed in particular heterogeneous reactions depends in the general case on the relation between the number of collisions of the radicals in the gas phase and with the surface and also on the nature and reactivity of the surface centres.

The reactions of radicals in the gas phase have been investigated widely by various methods and for many of them reliable kinetic data have been obtained and have been treated systematically in numerous monographs, reviews, and data banks (see, for example, Refs 188–190). Unfortunately, this cannot be said about the heterogeneous reactions of radicals, for which, as already mentioned, it is frequently difficult to specify even their stoichiometry. On the other hand, if the catalyst pores are

sufficiently narrow and tortuous and the species diffuse in them in Knudsen or transitional regimes, then the number of collisions of the radicals with the surface is large and the contribution of these reactions to the overall formation of the catalytic reaction products and to the process selectivity may be decisive.

The influence of the porosity on the heterogeneous radical destruction processes has been investigated.[191] The radicals ($CH_3O_2^{\bullet}$, $C_4H_9O_2^{\bullet}$, $C_3H_5^{\bullet}$, and $C_3H_5O_2^{\bullet}$) were generated in the first part of a two-section reactor and were then directed to SiO_2 and Al_2O_3 specimens having different specific surfaces and porosities. The peroxy-radicals proved to be more reactive than the corresponding hydrocarbon radicals. An increase in pore radius leads to an increase in the rate of destruction of the radicals, which indicates easier permeation of the radicals into the grain and an increase in the effective area of the surface on which their destruction takes place. The recapture of the radicals formed from C_1-C_4 hydrocarbons on irradiated MgO [74] leads to the surface alkoxy-groups $[OR]_s$. Their decomposition under the conditions of programmed thermal desorption results in the formation of the corresponding alkenes from the C_2-C_4 alkanes:

$$[OC_nH_{2n+1}]_s \rightarrow [OH]_s + C_nH_{2n}, \quad (31)$$

and of CO and H_2 from methane:

$$[OCH_3]_s \rightarrow CO + \tfrac{3}{2}H_2. \quad (32)$$

In view of the unusual importance of the heterogeneous radical reactions for the OCM process, numerous studies have been devoted to the interaction of methyl radicals with various oxides. The types of reactions of the $CH_3^{\bullet}$ radicals on different surfaces are apparently determined by the differences between the properties of the active centres and in the first place the surface oxygen. Depending on the electronic properties of the oxide and on the cation in the coordination sphere of which the oxygen ion is present, the probability of the formation of methoxy-groups and their reactivity may vary greatly.

The kinetics of the accumulation and consumption of the $[OCH_3]_s$ groups formed on recapture of the methyl radicals by the oxidised Al_2O_3, CaO, and BaO surfaces have been investigated[133-136] by the IR spectroscopy of surface electromagnetic waves and by reflection-absorption IR spectroscopy. The activation energy for the formation of methoxy-groups from methane varied in the range from 63 (BaO) to 126 (Al_2O_3) kJ mol^{-1}, while the activation energy for their subsequent conversion into formate groups was 21 – 33 kJ mol^{-1}.

Quantum-chemical calculations for the interaction of $CH_3^{\bullet}$ radicals with MoO_3 showed [175,176] that methoxy-groups of two different types may be formed: with $O-CH_3$ bond energies of ~38 and ~272 kJ mol^{-1}. The methoxy-groups of the first type may be formed when the radicals are captured by the O^{2-} or O^- ions formed on irradiation. The presence of stable (chemically generated) O^- ions on the surface was responsible for the strong binding of the radicals and the formation of stable methoxy-groups (second type).

The study of the reactivities of various oxides in the relation to the $CH_3^{\bullet}$ radicals generated catalytically in the CH_4+O_2 reaction showed that the typical OCM catalysts (MgO, Li/MgO) are almost 'transparent' towards the radicals, while the catalysts for the extensive (ZnO, NiO, CeO_2) and partial (MoO_3/SiO_2) oxidation capture them effectively.[192,193] An electron is transferred when the $Mo^{6+} \rightarrow Mo^{5+}$ transition takes place in the interaction of the methyl radical with MoO_3/SiO_2; in the case of CeO_2, an electron is transferred to an adsorbed oxygen molecule with formation of O_2^-. The methoxy-group is successively converted into a formate group, which ultimately leads to the formation of carbon oxides.

A similar investigation but with azomethane as the source of radicals and a Knudsen cell as the reactor showed that at 650 °C the probability of the capture of $CH_3^{\bullet}$ radicals by the surfaces of typical OCM catalysts (La_2O_3, Li/MgO, Sr/La_2O_3) in the absence of oxygen from the gas phase is ~10^{-7}, increases to ~10^{-6}, and remains unchanged at $P_{O_2} = (1-18) \times 10^{-4}$ Torr.[194] The absence of a dependence of the probability of capture on the oxygen pressure in this range shows that the species interacting with the surface is the $CH_3^{\bullet}$ radical and not $CH_3O_2^{\bullet}$, the concentration of which increases in proportion to P_{O_2}. On ZnO and CeO_2, the probability of capture in the absence of oxygen is close to 10^{-5}, diminishing somewhat with increase in P_{O_2} from 0 to 1.8×10^{-3} Torr. The introduction of N_2O into the gas phase does not affect the process. The activation energy for the capture of the radicals on different oxides is 13 – 33 kJ mol^{-1}.

An attempt has been made[195] to determine the types of the reactions of the $CH_3^{\bullet}$ radicals obtained by irradiating different oxides under a methane atmosphere. In the absence of a catalyst, the formation of any kind of product has not been detected; on the other hand, in the presence of catalysts ethane and CO appear, the rates and selectivities of the formation on different oxides differing significantly and depending on the preliminary treatment. The authors suggest that irradiation promotes the generation of $CH_3^{\bullet}$ radicals and their capture by the surface oxygen ions leads to the formation of methoxy-groups, which decompose with evolution of CO and H_2.

Whereas the capture of methyl radicals by the surfaces of the OCM or extensive oxidation catalysts leads to the formation of carbon oxides, in the case of vanadium, molybdenum, and possibly tungsten oxides the conversion of the methoxy-groups into partial oxidation products has been postulated.[161] This has been demonstrated[196] by direct experiments involving the interaction of the $CH_3^{\bullet}$ radicals, obtained as a result of the decomposition of azomethane, with the MoO_3 and MoO_3/SiO_2 catalysts. In the presence of water vapour, the authors observed the formation of methanol, while under a dry atmosphere formaldehyde was formed, which confirms the possibility of the partial oxidation of methane on MoO_3-containing catalysts via the formation and recapture of a surface methyl radical:

$$Mo^{VI}O^{2-} + CH_3^{\bullet} \rightarrow Mo^{V}OCH_3^{-}. \quad (33)$$

Depending on the presence or absence of water in the gas phase, either the hydrolysis of the methoxy-groups with formation of methanol or their decomposition with formation of formaldehyde may take place.

There are also data showing that the methoxy-groups can themselves be a source of methyl radicals.[197,198] In particular, the formation of methyl radicals has been observed in the temperature range 525 – 650 K on programmed heating of a molybdenum single crystal, on the (110) face of which initially oxygen (0.15 – 0.50 of a monolayer) and then methanol (at 120 K) are adsorbed.[197] This may indicate the reversibility of reaction (33) and the validity of the quantum-chemical calculations.[175,176]

The results of studies on the interaction of $CH_3^{\bullet}$ radicals with clean and oxidised metal surfaces have been published recently.[120-122] The molecular beam method combined with methods involving the simultaneous investigation of the surface and surface compounds were employed in these studies.

On the oxygen-modified (100) face of a molybdenum single crystal, the adsorption of radicals is observed even at room temperature.[120] If the surface coverage by oxygen is incomplete, then the dehydrogenation and disproportionation of the methyl fragments take place on heating with evolution of methane and hydrogen into the gas phase and the formation of surface carbon, which reacts in its turn with the oxygen present on the surface, affording CO. The maximum rates of evolution of methane, hydrogen, and CO are attained at ~500 K; the CO evolution curve has a second maximum at 950 K. If no free metal atoms (not coated by oxygen) remain on the surface, then the second CO evolution peak is absent and the rate of evolution of methane diminishes, tending to a constant value on the surface the composition of which corresponds to MoO_2. Hence it follows that the dehydrogenation and disproportionation processes takes place more vigorously on a metal surface than on an oxide surface.

Programmed thermal desorption and reflection-absorption IR spectroscopic methods have been used[121] to investigate the interaction of methyl radicals with the (111) face of a platinum single crystal. The formation of the $Pt-CH_3$ and Pt_3CCH_3 groups (at a much lower concentration) was observed at 150 K. On heating, the liberation of ethene is observed, but ethane is not formed. The authors suggest that the methyl fragments dissociate partially to CH_2 and, tentatively, that ethene is formed in the course of one of two reactions:

$$CH_3 + CH_2 \rightarrow C_2H_5 \rightarrow C_2H_4 + H, \quad (34)$$

$$CH_2 + CH_2 \rightarrow C_2H_4. \quad (35)$$

Hall et al.[122] investigated the interaction of methyl radicals with the clean and oxidised (100) and (111) faces of a nickel single crystal. If the surface contains hydrogen or a preadsorbed hydrocarbon (for example, ethane), then methane is rapidly evolved when radicals are introduced. The adsorption of radicals on the (100) face and subsequent heating lead to the recombination of the methyl fragments with the hydrogen atoms and the evolution of methane at 220 K. On the (111) face, this process is much more vigorous. It has been shown in experiments that isotope-substituted molecules that at 240 K the methyl groups abstract a hydrogen atom from the adsorbed species and no longer from the surface. The oxidation of the surface alters completely the type of reactions: at temperatures of about 300 K, the adsorbed methyl fragments recombine with formation of ethane and the desorption of $CH_3^{\bullet}$ radicals is also observed.

Overall, one has to conclude that, although the reactions of the radicals with the solid surface are extremely important in both homogeneous gas-phase and heterogeneous-catalytic oxidation processes, their kinetics and mechanisms have not yet been investigated adequately.

IV. Conclusion

Analysis of the literature data shows that it is difficult to find examples of purely homogeneous oxidation processes in the gas phase, which are not influenced by heterogeneous factors. On the other hand, the reactions on heterogeneous catalysts are frequently accompanied by the release of free radicals into the gas phase and this is not a side process in relation to the main reaction pathway in the adsorbed layer but is an essential stage leading to the formation of the final products in homogeneous or secondary heterogeneous stages.

Taking into account the data obtained in recent years in the course of intensive investigations of the OCM and stabilised combustion processes, one may ask the question what is the meaning of the expression 'proportion of the reaction occurring in the free volume (or on the surface)' if the heterogeneous and homogeneous stages are equally inseparable components of the conversion of the reactants into products?

Another question also arises: how fundamental is the difference between the 'gas-phase' reactions, on the one hand, and 'heterogeneous–homogeneous catalytic' reactions, on the other, if in either case both the rates of the elementary processes in the gas phase and the entire set of factors determining the rates of heterogeneous processes (the chemical nature and morphology of the solid, the surface area, the purity of the surface, etc.) are equally important?

In the light of the above analysis, these differences are completely indeterminate. Refraining from more wide scale generalisations, we may venture to express the view that the boundary between the gas-phase and heterogeneous-catalytic oxidation is arbitrary and its existence is associated mainly with the fact that the studies in these two fields developed almost independently for decades. Such isolation had to some extent also a positive aspect, since it made it possible to concentrate on the 'main' process and to differentiate and investigate the characteristic features of the elementary reactions in the gas phase or on the surface of a solid, refraining from dealing with 'side' factors. However, the combination of the efforts of specialists dealing with the study of the kinetics and mechanisms of reactions in the gas phase, heterogeneous catalysis, solid state chemistry, and surface phenomena appears extremely promising. The greatest progress is to be expected in this connection as regards the development and adaptation of highly sensitive methods for the study of radical processes in heterogeneous reactions, the creation of kinetic models of complex heterophase processes, and ultimately a deeper understanding of the mechanisms of the oxidation reactions and the possibility of controlling them.

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