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Interaction of hydrocarbons with partial oxidation catalysts

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Contents

I.	Introduction	1073
II.	Activation of hydrocarbons by the oxygen of the surface	1074
III.	Activation of hydrocarbons by the oxygen and cations of metal oxides	1075
IV.	The influence of the acid – base properties of catalysts on the activation of hydrocarbons	1077
V.	The influence of structural defects in the catalysts on the activation of hydrocarbons	1078
VI.	The selectivity of the partial oxidation and activation of hydrocarbons	1079
VII.	Conclusion	1080

Abstract. The interaction of hydrocarbons having different structures with catalysts for their partial oxidation is considered. The activation of the hydrocarbon molecules on the surface can lead to the formation of adsorption complexes or radicals. This process depends on the structure of the hydrocarbons and the energy of the bonds in them, the temperature and nature of the surface of the solid (structure, the valence state of the elements entering into its composition, and the form of oxygen and its mobility). The possible mechanism of the activation of hydrocarbons on different catalytic systems is discussed. The bibliography includes 149 references.

I. Introduction

The catalytic oxidation of organic substances is a complex multistage process. Numerous studies have been devoted to its mechanism. The interaction of organic substances and solids, in particular catalysts, is known to be accompanied by the formation of intermediate surface compounds which are converted into reaction products on further oxidation. The composition of the products, *i.e*. the direction of the process, are determined to a large extent by the nature of the intermediate compounds and also by the active form of oxygen participating in the oxidation process. The first stage of the catalytic oxidation is the activation of the molecules of organic compounds. Unfortunately, little attention has been devoted to the study of this stage, although in our view it exerts a significant influence on the subsequent oxidation stages.

The interaction of hydrocarbons with the catalyst is accompanied by the formation on its surface of adsorption complexes or radicals. The role of radicals in the oxidation reactions and their influence on the selectivity have been examined in a review.[1] The formation of surface compounds in the interaction of hydrocarbons with various heterogeneous catalysts has been described.[2] Questions of the interaction of hydrocarbons with partial oxidation catalysts have been examined in a monograph,[3] but only the results published up to 1975 were discussed. It is useful to analyse the current literature data on the oxidation mechanism. Evidently such a task cannot be performed within the framework of a single communication. In the present review, attention is concentrated on the nature of the activation of hydrocarbons and the influence of the chemical properties and structure of the catalysts on the activation.

The development of new spectroscopic methods, such as IR Fourier spectroscopy, laser Raman spectroscopy, *etc*., made it possible to determine the structures of many surface compounds formed in the interaction of hydrocarbons with the catalyst.[3] The energies of the bonds in the intermediate compounds formed when hydrocarbons are adsorbed on the active surface centres have been calculated by quantum-chemical methods.[4] In the calculations of the structures of the surface compounds and of the nature of the bonds between the adsorbed hydrocarbons and the catalysts, many properties of the surfaces of the solids are usually disregarded,[5, 6] so that an appreciable proportion of the mechanisms of the catalytic reactions and of the activation of hydrocarbons are of a formal character.

The interaction of hydrocarbons with the active centres of the catalysts is accompanied by the deformation [7 – 11] and the subsequent dissociation of individual bonds in the reacting molecules. The C – H bond in hydrocarbons may be dissociated homolytically or heterolytically. In the homolytic dissociation, a surface OH group and a free radical are formed on the catalyst surface:

$$RH + (O_s) \longrightarrow (OH) + R^{\bullet},$$

where O_s is surface oxygen.

The heterolytic reaction is accompanied by the binding of a proton on an alkaline surface centre:

$$RH + (O_s^{2-}) \longrightarrow (O^{2-}\cdots H^{+}) + R^{-}.$$

The heterolytic dissociation of the hydrocarbon molecule with formation of a hydride on the acid surface centre (Lewis centre) is also possible:

$$RH + (M^{n+}) \longrightarrow (M^{n+}\cdots H^{-}) + R^{+},$$

where M^{n+} is the Lewis centre.

In the homolytic dissociation of a C – H bond, the radicals formed on the catalyst surface can be desorbed into the gas phase, initiating the homogeneous propagation of the process, or can remain on the surface and participate in the stages leading to the formation of the reaction products.[12] The characteristics of the

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heterogeneous-homogeneous oxidation reactions of hydrocarbons have been described in a review.[1]

In considering the dependence of the reactivity of hydrocarbons on their structure, the activation energies (E_a) for the dissociation of various bonds can be compared.[7] For example:

Bond	E_a /kJ mol^{-1}	Bond	E_a /kJ mol^{-1}
CH_3-H	456.7	$CH_2=CHCH_2-H$	368.7
CH_3CH_2-H	410.6	C_6H_5-H	460.9
$(CH_3)_2CH-H$	398.0		

Alkenes exhibit a higher reactivity than alkanes. Comparative study of the oxidation of various alkenes on a palladium single crystal showed that the allyl C–H bond in the hydrocarbon molecule is less reactive than the vinyl bond.

Saturated hydrocarbons may be activated in two ways:[2]

(1) cleavage of a C–H bond by electrophiles with formation of a carbonium ion or a carbanion and subsequent dissociation of a C–C bond;

(2) dissociation of a C–C bond in the interaction with a low-valence metal.

The ability to cleave a C–C bond depends on the oxidation state of the transition metal. In redox processes, there is a possibility of the formation of catalytic *ensembles* and the role of the catalyst then consists in transforming one-electron processes into processes involving two and more electrons. Thus the structure of the hydrocarbons and the nature of the bonds in the molecules constitute one of the main factors influencing the way in which they are activated on interaction with catalysts.

Various mechanisms of the activation of butane have been considered in a review.[7] The dissociation energies of the bonds between hydrogen and the primary, secondary, and tertiary carbon atoms have been compared with the rates of abstraction of one or two hydrogen atoms from the hydrocarbon. Various mechanisms of the activation of hydrocarbons and of the formation in this process of radicals and complexes (carbonium ions and carbanions) have been described in communications [7–9] devoted to the study of the partial oxidation of alkanes, in particular propane.

The composition of the catalyst exerts a major influence on the activation of hydrocarbons. For example, on the V_2O_5 catalyst one hydrogen atom is abstracted from the CH_3 group of toluene, whereas following the introduction of the PO_4 group into the catalyst a new active centre ($V^{\delta+}\cdots O^{\delta-}\cdots P$) is formed on the surface and this time two hydrogen atoms are abstracted simultaneously from the hydrocarbon molecule on this centre. Under these conditions, a surface compound different from that on vanadium pentoxide is formed and a different reaction product is therefore obtained. The activation mechanism depends on the nature of the active surface centres, on which different forms of oxygen may be present. The centres for the adsorption and activation of hydrocarbons consist of cations, acid – base centres, free electrons, and defects and vacancies in the solid. The possible versions of the interaction of hydrocarbons with catalysts will be examined below in relation to olefins (ethene and propene), alkanes (ethane, propane, and butane), and aromatic compounds (benzene and toluene).

II. Activation of hydrocarbons by the oxygen of the surface

It is very difficult to discover a process in which only the oxygen of the catalyst surface participates. One of the few examples for which it is possible to trace the activation of hydrocarbons by precisely such oxygen is the oxidation of ethene on silver.[13,14] Ethene is known not to be sorbed on pure silver.

Korchak and Tret'yakov's study [14] was devoted to the kinetics of the oxidation of ethene on silver foil cleaned in an ultrahigh vacuum. The formation of an oxide phase on the surface of silver during the experiment can be virtually completely avoided if the oxygen pressure is below 10^{-2} mm Hg while the catalyst temperature does not exceed 523 K. In order to obtain reproducible kinetic data, the catalyst had to be treated in hydrogen at 773 K to eliminate traces of the oxide phase. Under these conditions, the oxidation of ethene afforded only CO_2 and H_2O.

By observing the above conditions, it was possible to investigate in detail the kinetics of the oxidation of ethene on silver free from a surface oxide phase. At an oxygen pressure of $2\times10^{-4}-10^{-2}$ mm Hg and a catalyst temperature of 400 – 523 K, the principal stages of the mechanism of the extensive oxidation of ethene are described satisfactorily by the following scheme:

$$O_2 + 2Z \overset{a}{\rightleftharpoons} 2ZO, \quad (1)$$

$$C_2H_4 + ZO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2H_4OZ, \quad (2)$$

$$C_2H_4OZ \xrightarrow{k_3} CH_3CHOZ, \quad (3)$$

$$CH_3CHOZ + 5ZO \xrightarrow{k_4} 2CO_2 + 2H_2O + 6Z, \quad (4)$$

where a is the adsorption coefficient and Z a catalyst active centre. Stage (4) represents the overall complete oxidation reaction of acetaldehyde, which proceeds at a high rate and does not limit the overall process.

Korchak and Tret'yakov [14] established that silver free from an oxide layer or oxygen dissolved in the bulk phase is 2×10^4 times more active in the extensive oxidation of ethene than the oxidised form of the catalyst. When the catalyst is saturated with oxygen, the rate of the extensive oxidation falls, which leads to the equalisation of the rates of the extensive and mild oxidation and hence to an increase in the selectivity in the formation of epoxyethane.

In order to increase the process selectivity, in industry the catalyst is activated in a stream of air. Taking into account the data presented above, one can postulate that the activation takes place as a result of the saturation of the catalyst with oxygen and the formation of an active phase on the surface.

The specific catalytic properties of pure silver can be explained by the fact that the dissociative adsorption of oxygen proceeds at a high rate on this metal. Because of this, extensive coating of the surface by oxygen atoms is achieved, such atoms oxidising ethene rapidly to CO_2 and water.

When oxygen is dissolved in silver, the strength of its bond with the metal diminishes and there is a sharp increase in the activation energy for the dissociative adsorption of oxygen (from 14 to 28 kcal mol^{-1}).[15] As a result, the coating of the surface by atomic oxygen decreases in the course of the reaction, which actually entails a fall in the rate of the extensive oxidation of ethene.

The decrease in the amount of atomically adsorbed oxygen is accompanied by an increase in its molecular adsorption, particularly at elevated O_2 pressures, which should increase the rate of formation of epoxyethane. The principal conclusions reached as a result of the study of the kinetics and mechanism of the oxidation of ethene on pure silver have been confirmed by the results of other investigations. Thus it has been established that the adsorption of ethene on silver becomes possible only after the latter has been treated with oxygen.[13]

The mechanism of the formation of surface oxygen has been described in detail in a series of communications and monographs (see, for example, Margolis [3]). The oxygen on the surfaces of oxide systems is known to undergo consecutive transformations:

$$O_{2\,(gas)} \longrightarrow 2O^- \longrightarrow 2O^{2-}.$$

The oxygen ion formed (O^-) is inserted in the lattice of the solid in the form of O^{2-}. The oxygen may dissolve in the near-surface layers of metals.

In the adsorption of oxygen on the surface of silver, the quasi-oxides Ag_2O and Ag_2O_3 are formed, *i.e.* metallic silver is converted into the Ag^+ cations. The study of the interaction of silver

with oxygen also enabled investigators [16–18] to reach the following conclusions:

1. Depending on the conditions, the oxygen on the surface of silver is adsorbed in different forms. The dimeric oxide Ag_2O with ionic type of bonding is formed at temperatures below 470 K and this form participates in the extensive oxidation of ethene.

2. If silver is treated with a mixture of ethene with oxygen, weakly bound covalent oxygen appears on the surface of the metal in the form of single atoms, such form corresponding to the structure Ag–Ag–O.

It has been suggested that the 'ionic' oxygen creates surface sites for the adsorption of ethene,while the 'covalent' oxygen participates in the formation of epoxyethane. The disposition of oxygen on different faces of the silver lattice depends on the structure of the catalyst surface. This influences the catalyst activity and the selectivity in the ethene oxidation reaction and hence also the structure of the surface compounds.

It has been shown by IR spectroscopy that the adsorption of ethene entails the dissociation of the double bond in the ethene molecule and the formation of various surface compounds.[19,20] With the aid of improved IR Fourier spectroscopy, strongly bound acetaldehyde and the complex Ag·CO have been detected on the Ag/Al_2O_3 catalyst.[21] It has been established [22–24] that ethene is activated with participation of the atomic surface oxygen. When ethene is oxidised on silver, acetaldehyde, formate, oxalate, and CO_2 are formed in addition to epoxyethane.[25] The epoxyethane conversion products have been investigated by IR spectroscopy and NMR and also by an isotope method involving the use of ^{13}C.[26]

The degree of dispersion of silver on various supports (SiO_2, Al_2O_3, TiO_2) is very important for the conversion of ethene into epoxyethane.[27,28] However, since the heats of adsorption of the reaction components on silver with different degrees of dispersion have not been determined and the coexistence on silver of various adsorbed forms of oxygen has not been confirmed, the question of the influence of the degree of dispersion on the activation of ethene remains open.

The atomic structure of the silver surface (nanoclusters) has been discovered with the aid of a tunnelling microscope and the migration of the metal particles on the surfaces of supports has been observed.[29]

There is no information in the literature about the influence of the rearrangement of the silver surface on the activation of ethene and the formation of surface complexes. In quantum-mechanical calculations of the energy parameters of the ethene conversion process, simplified models are therefore used [30] in which a stationary silver atom bound to oxygen or entering into the composition of the cluster is considered. The calculation has been performed [31] for the interaction of oxygen, hydrogen, chlorine, hydroxy groups, and ethene with silver clusters on supports. Depending on the mode of coordination to a silver atom, the chemisorbed oxygen (an atomic oxy-radical) can participate in the formation of epoxyethane or can be converted into an inactive form. Additives introduced into the silver influence the ratio of the radical forms of oxygen.

Thus ethene is activated with participation of different forms of oxygen. The oxygen dissolved in the silver lattice influences the process occurring the catalyst surface.

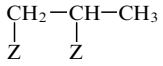
Data concerning the migration of silver atoms on the catalyst surface under the influence of the medium (the formation of clusters of different size, surface diffusion) are not taken into account in the models employed in calculations for the ethene activation process. The mechanisms of the conversion of ethene into epoxyethane are therefore formal in character: although they are in fact used in kinetic analysis, they do not reflect the true reaction mechanism.

III. Activation of hydrocarbons by the oxygen and cations of metal oxides

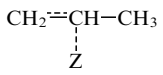
1. Olefins

The most thoroughly investigated stage in the process involving the oxidation of hydrocarbons is their adsorption on oxide systems. Depending on the structure, olefins can be adsorbed in the following forms on the surface of the catalyst:[32,33]

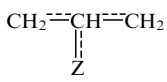
(a) two-centre forms with σ-bonds:



(b) associative π-complex:



(c) dissociative π-allyl complex:



Extensive experimental data on the formation of σ-, π-, and allyl complexes on the surfaces of various oxide systems in the adsorption of propane have been accumulated.[32–35]

Formal mechanisms have been proposed for the adsorption and the reactions, in which it is postulated that such surface compounds are formed when olefins are activated on the cations of the metal oxide lattices. For example, when propene is adsorbed on MoO_3 it forms a bond with Mo^{6+}, as a result of which a π-complex is formed and the Mo^{6+} ion is simultaneously converted into Mo^{5+}. The structure of molybdenum oxide has been investigated with the aid of an electron microscope and also by X-ray phase analysis and UV and Raman spectroscopy.[36,37] In the course of the oxidation of propene, MoO_3 is reduced to MoO_2 and MoO. More complex structures — Mo_8O_{20} and Mo_9O_{26} — have also been detected. When MoO_3 was deposited on silica gel, the formation of molybdates was observed.[36] The structure of MoO_3 has been investigated in detail [37,38] and the existence of different forms of oxygen on its various faces has been demonstrated.[39–42]

Particular attention has been devoted to the Bi–Mo–O system,[32,33] consisting of three different phases: $Bi_2O_3 \cdot 3MoO_3$ (α-phase), $Bi_4O_3 \cdot 2MoO_3$ (β-phase), and $Bi_2O_3 \cdot MoO_3$ (γ-phase).[43] The study of the structures of these phases and of their catalytic activities in the oxidation of propene led investigators to the conclusion that, when propene interacts with the catalyst surface, the abstraction of a hydrogen atom from the methyl group is followed by the formation of π- and σ-complexes. The olefin molecule is activated by a bismuth cation. It has been demonstrated in numerous experiments that the active oxygen necessary for the conversion of these complexes into acrolein originates from MoO_3. The characteristic features of the transport of the active oxygen in a Bi–Mo–O catalyst have been investigated.[42]

In order to increase the rate and selectivity of the oxidation of olefins, catalysts with more complex compositions have been used. Several molybdates (multiphase systems) may be present in them, for example $CoMoO_4 + Bi_2MoO_4 + Fe_2(MoO_4)_3$.

The mechanism of the action of such complex catalysts has been established with the aid of various methods (IR, UV, EPR, and Mössbauer spectroscopy).[44,45] The fundamental principle is the separation of the functions of the separate system components. Propene is adsorbed on the Bi–Mo–O component and is activated on bismuth ions, while the oxygen necessary for the conversion of the complexes is supplied by the iron molybdate phase $Fe_2(MoO_4)_3$. This phase is converted into the divalent iron molybdate $FeMoO_4$.

The propene and oxygen adsorption and activation centres are separated. The study of complex systems showed that, when bismuth molybdate is mixed with the Fe–Co–Mo solid solution, epitaxy of the crystals of one phase on another is observed and the transport of oxygen participating in the oxidation of propene is facilitated.[46,47] Unfortunately there are no literature data on the adsorption and activation of propene on other complex systems and it is not clear which of the cations 'abstract' a hydrogen atom from the olefin molecule.

If an alkene (for example, isobutene) is adsorbed on a complex multiphase catalyst, it is not possible to establish by the thermoprogrammed desorption (TPD) method which of the phases participates in the process.[48] The interaction of isobutene with oxygen on the Co–Mo–Bi–Fe catalyst has been investigated by IR Fourier spectroscopy and it has been shown that an anhydride-like compound is formed in the adsorption process. Other forms of the interaction of the olefin with the catalyst have not been observed. Unfortunately, the mechanism of the activation of an alkene on such complex systems could not be elucidated.

A model has been developed for the action of catalysts consisting of several phases (Bi–Mo, Sn–Sb, Mo–Fe), among which oxygen donors and acceptors are present.[49,50] Oxygen migrates from the donor to the acceptor *via* spill-over. The reaction mechanism on such systems has been called 'remote control'. It has been suggested that hydrocarbons are adsorbed on the acceptor phase, but there is no experimental confirmation of this. Unfortunately, the elementary mechanism of the activation of alkenes on multicomponent systems still remains unelucidated.

2. Alkanes

The activation of alkanes on oxide catalysts occurs in many cases *via* a heterogeneous-homogeneous mechanism. This applies particularly to the oxidation of methane, which, in contrast to other hydrocarbons, is not adsorbed on the catalyst surface at the reaction temperature. It is activated on impact against the surface, being converted into a methyl radical, which is desorbed and forms a methoxy-compound as a result of a secondary interaction with various forms of oxygen on the surface or with a OH group. The mechanism of the activation of methane, the kinetics of the process, and its energy characteristics have been described in a series of communications (see, for example, Refs 51–57) and will not therefore be considered in the present review.

The oxidation of C_2-C_5 alkanes can proceed *via* two mechanisms — heterogeneous-homogeneous and heterogeneous.[53] Ethane, propane, and butane are adsorbed on catalysts and are either oxidised to aldehydes, anhydrides, and acids or are dehydrogenated to alkenes.[8,9] The alkane oxidation catalysts are molybdenum and vanadium oxides, compounds of the type of molybdates or vanadates, or V–P–O systems.[7–9,58–60]

The activation of alkanes is ensured by the ability of the catalysts to propagate redox processes and by the presence on their surfaces of atomic oxygen and acid–base centres. The conversion of alkanes into various adsorbed forms — radicals, complexes, and carbonium ions — is possible by virtue of these properties of the catalysts.

A mechanism has been proposed[61,62] for the activation of ethane on MoO_3 and alkali metal molybdates. The interaction of ethane with atomic oxygen and the Mo^{5+} and $Mo^{6+}-O^-$ (ethane activation centre) active centres entails the abstraction of a hydrogen atom and the conversion of the hydrocarbon molecule into the $C_2H_5^{\bullet}$ radical. The interaction of $C_2H_5^{\bullet}$ and O^- leads to the formation of the ethoxide $C_2H_5O^-$, which is converted into acetaldehyde with participation of a hydroxy group of the catalyst surface. Ethene is formed on decomposition of this ethoxide (oxidative dehydrogenation).

The activity of alkali metal vanadates in the oxidation of ethene depends on the catalyst structure.[62] The influence of vanadium pentoxide on the activation of ethane has been investigated and a relation has been demonstrated between characteristics such as the degree of dispersion of the oxide and the yield of acetaldehyde.[61] The oxidation of methane and ethane on iron phosphate has also been studied.[63]

Numerous studies have been devoted to the oxidative dehydrogenation of propane and the results have been surveyed in reviews.[8,9] Following adsorption and activation, propane is converted into propene or oxidation products (acrolein, acetaldehyde, *etc.*). These two aspects of the conversion of propane have a common stage — the abstraction of a hydrogen atom from the methyl group of the molecule. According to Michalakos *et al.*,[64] in the activation of propane a propyl radical is formed and is then converted into propene. The vanadium-containing catalysts Mg–V–O, V–Sb–O, *etc.* are used to effect this process.

Mechanisms for the conversion of propane on Bi–Mo–O, Sn–Sb–O, and other catalytic systems have been proposed in a review.[9] According to these mechanisms, the oxidation of the intermediate reactive forms, which are the products of the interaction of propane with the catalyst, involves the formation of oxygen-containing surface complexes.

Investigators have devoted much attention to the study of oxidation reactions and oxidative dehydrogenation of butane.[6,7] It has been established that the mechanism of the activation of butane with participation of different forms of oxygen on the surface of the catalysts is similar to the mechanism of the oxidation of propane.[65–67]

The oxidation of butane on the V–P–O catalysts leads to the formation of a centre ($V^{5+}\cdots O$) on which the hydrocarbon is activated,[68,69] some of the V^{5+} ions being reduced to V^{4+}. If there are no V^{4+} ions in the catalyst, butane is not activated. It has been found[70–72] that, in the activation of a butane molecule on the $V^V=O$ active centre, two hydrogen atoms are abstracted from it.

On the V–P–O catalyst, butane is converted into oxygen-containing products,[73] whilst on other vanadium systems, for example on V–Mg–O, it gives rise to butadiene (oxidative dehydrogenation).[74]

Thus the activation of C_2-C_4 alkanes on various catalysts entails the formation of various surface forms of these compounds (radicals, complexes).

3. Aromatic hydrocarbons

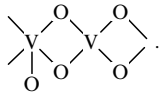
The oxidation reactions of aromatic hydrocarbons may be of two kinds: oxidation of the side chain of alkyl-substituted aromatic compounds without disruption of the structure of the ring and oxidation with degradation of the aromatic ring. Different forms of oxygen — electrophilic and nucleophilic — participate in these processes. Diverse vanadium systems, containing added molybdenum oxide and alkali metals in addition to the vanadium ions, are used as the catalysts.

The catalytic oxidation of aromatic hydrocarbons to maleic and phthalic anhydrides has been studied in fair detail using modern experimental methods. Quantum-mechanical calculations for these systems have also been carried out.[4] A series of studies have been devoted to the structure, the nature of the surface, and the valence state of the vanadium ion in vanadium catalysts.[75–78]

Much attention has been devoted to the investigation of supported vanadium catalysts. The role of supports (for example a zeolite, quartz, SiO_2, and aerosil) in the state of the vanadium ion has been investigated resorting to the EPR method. The formation of polyvanadates and oligomers as well as bridges comprising vanadium ions has been observed on silica gel and aluminium oxide.[77] The structure of vanadium oxide depends on the type of support.[79] Meta- and deca-vanadates are formed on aluminium oxide, while octahedral vanadium pentoxide is formed on silica gel. The $V_2O_5-TiO_2$ system merits special attention. Monolayer catalysts are the most active in the partial oxidation of aromatic hydrocarbons.

Bond and Tahir[80] examined the properties of catalysts obtained by different methods. The state of vanadium ions was

investigated by various spectroscopic methods (IR Fourier spectroscopy, laser Raman spectroscopy, EPR, XPES, NMR). The following types of active centres on the surfaces of vanadium catalysts were established by analysing the data obtained:

V=O, VH^+, V–OH, .

The structure of the V_2O_5/TiO_2 catalysts has been investigated by NMR using the ^{129}Xe isotope and it has been shown that vanadium ions form large domains and individual V_2O_5 crystals contain large pores.[81]

Analysis of the ^{51}V NMR data obtained in a study of vanadium catalysts deposited on aluminium and titanium oxides showed that the structure of vanadium oxide depends on the degree of coverage of the support and the nature of the latter.[82] The symmetry of the octahedra in the layers on the outer surface of the support is disturbed to a greater extent than the symmetry of the tetrahedra in the crystal. When vanadium oxide is inserted in titanium oxide, surface defects are formed and the specific surface of the catalyst changes.[83] Particularly interesting data have been obtained in a study of the influence of the support (titanium oxide) on the state of the vanadium ion.[84] In this system, vanadium can exist in the following forms: V^{4+} (forms a solid solution with rutile); V^{5+} (is inserted in the rutile surface and forms a monolayer); VO^{2+} (is formed during the reaction on reduction of V^{5+} in the monolayer); deformed V_2O_5 crystals.

The EPR study of V–Ti catalysts showed that the number of spins and the *g*-factor depend on the degree of surface coverage of the support by vanadium ions.[85] Two types of ions were discovered: the tetrahedral V^{4+} and the vanadyl ion. The structure of the active centre of a vanadium catalyst has been described.[86,87] The vanadium ions on TiO_2 (rutile and anatase) are in different states: an amorphous vanadium layer is formed on anatase, whereas separate regions with partly reduced vanadium ions are produced on rutile.[88] Analysis of data on the state of vanadium ions on the surface of the catalyst showed[89] that, depending on the concentration and the method of preparation of the catalyst, mono- or poly-layers are formed and the ratio of the V^{4+} and V^{5+} ions changes.

The wide variety of the possible states of vanadium on TiO_2 led to special interest of investigators in the mechanism of the activation of aromatic hydrocarbons having different structures. A cluster incorporating vanadium ions was chosen as the model. The changes in the energy of the C–H bonds in the methyl group on activation were discovered from the results of a quantum-mechanical calculation for the interaction of toluene with isolated vanadium cluster[90–92] and it was shown that oxygen plays the role of an adsorption centre if it adjoins the vanadium ion. The approach of the CH_3 group to the cluster results in the deformation of the C–H bonds. The structure of the surface compound and its further transformation into different products depend on the orientation of the toluene molecule relative to the cluster (*via* the ring or the CH_3 group).

The following mechanism of the oxidation of toluene has been proposed on the basis of an IR spectroscopic study: (1) abstraction of a hydrogen atom from the CH_3 group on chemisorption of the hydrocarbon; (2) dissociation of a C–H bond and the formation of a surface complex linked to the metal ion *via* the carbon atom; (3) abstraction of a hydrogen atom from a CH_2 group not linked to the surface.

A comparative study has been made[93] of the oxidation of toluene and xylene on the V_2O_5/TiO_2 catalyst and a possible reaction mechanism was discussed.

In a study of the oxidation of benzene to maleic anhydride on vanadium catalysts, especially on vanadium–molybdenum catalytic systems, data were obtained on the phase composition of the catalyst and the state of oxygen on their surfaces and in the bulk phase.[33] Quantum-mechanical calculation for the interaction of benzene with a vanadium catalyst (a cluster made up of vanadium ions) showed that there is a likelihood of the abstraction of a hydrogen ion from the benzene ring under the influence of the catalyst oxygen and the formation of an intermediate peroxide complex. Depending on the disposition of the benzene molecule on the surface, π- and σ-complexes may be formed.

Thus different forms of oxygen and cations having different valences participate in the activation of hydrocarbons of different classes. The acid–base centres on the catalyst surfaces exert a significant influence on these processes.

IV. The influence of the acid–base properties of catalysts on the activation of hydrocarbons

The catalysts for the partial oxidation of hydrocarbons possess acidic or basic properties. The methods for the determination of these properties, the nature of the surface acid centres, and the link between the type of such centres and the selectivities in various processes have been described in detail in a monograph.[94] Two types of acid centres are distinguished: Brønsted and Lewis (aprotic). Modern spectroscopic methods have made it possible to discover the surface compounds formed on different acid centres. It has been suggested that the Brønsted centres are bifunctional.[95–100] They are capable of being proton donors and of altering the basicity of the neighbouring oxygen atoms.

The influence of the acidity of the catalyst surfaces on the oxidation of various organic substances has been examined in a series of publications.[3,7,96,101] Acetone is formed on oxidation of propene on the Brønsted centres of the MoO_3/Al_2O_3 catalyst.[101] Intermediate forms of the type $CH_2-CH^+-CH_3$ (enolate) have been detected by IR spectroscopy on the surface of a tin–molybdenum catalyst. The Lewis centres on oxides can adsorb hydrocarbons in two ways: by abstracting a hydride ion from the alkane with formation of a carbonium ion or from the olefin with formation of a radical-cation.[102]

The interaction of hydrocarbons with Lewis and Brønsted centres has been examined, the mechanism of the activation of propene on bismuth molybdate has been discussed, and the role of the acid centres in the activation of the olefin has been demonstrated.[9,11,102,103]

The role of the acid centres in the oxidation of propene on the $MoO_3-Sb_2O_4$ system has been investigated by a spectroscopic method and by the method involving the adsorption of pyridine and ammonia.[104] The relation between the degree of conversion of propene on Brønsted centres and between the selectivity and the ratio of the concentrations of the Lewis (N_L) and Brønsted (N_B) centres has been demonstrated. The dissociation of the vinyl C–H bond leads to the formation of an intermediate oxygen-containing propene compound. The intensity of this process depends on N_L and N_B. Detailed quantitative analysis using the adsorption of pyridine and ammonia demonstrated a correlation between the ratio N_B/N_L and the selectivity of the oxidation of propane on molybdenum oxide and on the $MoO_3 + Sb_2O_4$ mixture; the greater this ratio, the higher the selectivity.

Activation in the presence of water vapour on the acid centres of V_2O_5 leads to the dehydration of propene and its dehydrogenation.[105] The activation of propene on copper molybdate results in the formation of an intermediate carbonium ion species.[103] Acidity influences also the oxidative dehydrogenation of ethane on vanadium oxide deposited on silica gel.[106] It has been shown by the method involving the adsorption of pyridine and ammonia that the higher the degree of acidity, the greater the degree of conversion of ethane.

There are strong acid centres on the $(VO)_2P_2O_4$ catalyst. They consist of V^{5+} ions involved in octahedral coordination and surrounded by the PO_4 group (tetrahedron). The acidity of the catalyst surface influences the oxidation of aromatic compounds.[107,108] The acid centres also participate in the oxidative dehydrogenation and oxidation of butane.[108–110] The properties of the acid–base centres may change significantly when additives

are introduced.[3] For example, after the addition of Group I elements (K, Na, Li) to MoO_3 deposited on TiO_2 and Al_2O_3, the rates of oxidation of propene and butene on the catalyst change; the introduction of acid (P_2O_5) and basic (Na_2O) additives into SnO_2 alters the mode of oxidation of propene: in the presence of the acid additive, propene is oxidised to acrolein, whereas modification with alkaline additives results in its dehydrogenation to benzene.

The effect of additives promotes the appearance in the vanadium catalyst of new compounds with the vanadium ion. When potassium sulfate is introduced into V_2O_5, vanadyl sulfate containing V^{4+} is formed. This is accompanied by a change in the acidity of the catalyst and in the rate of conversion of butadiene. The introduction of acid additives (tellurium and selenium ions) into bismuth molybdate accelerates the formation of acrolein. The addition of phosphorus ions to bismuth molybdate promotes the formation of π-allyl complex from butene. Thus modification of vanadium catalysts alters their acid properties and influences the activation of alkenes.

The structure of the vanadium–molybdenum catalyst for the oxidation of benzene changes when PO_4^{2-} ions are introduced into it: the lattice rearranges and the V–O and Mo–O bonds are disturbed. With increase in the PO_4^{2-} concentration, new compounds (bronzes) appear. These data indicate the influence of the modification on the structure and acidity of the catalyst and hence also on the adsorption of hydrocarbons and their activation.

The study of Blasco *et al.*[112] was devoted to the acid–base properties of vanadium catalysts deposited on various supports and to the influence of these properties on the oxidative dehydrogenation of butane. The acidity of the catalysts on different supports was determined from the degree of adsorption of pyridine and ammonia, the concentrations of the acid centres were determined, and it was shown that the selectivity in the conversion of butane depends on the acid properties of the surface. The introduction of additives also alters the acidity of the catalyst and its redox properties and it is therefore difficult to separate the influences of the nature of the support and the additives on the activation of hydrocarbons.

Lewis acid centres capable of activating butane by converting it into a radical have been identified in the V–P–O system.[8] The oxidative dehydrogenation of ethane on the V/SiO_2 catalyst has been described[10] and the redox reaction mechanism has been examined. It was shown that the activities of the catalysts depend on their acidity.

Thus the acid–base properties of oxide systems influence significantly the activation and conversion of hydrocarbons with different structures, while the alteration of these properties is accompanied by a rearrangement of the structure of the solid and the disturbance of the valence state of certain ions in the catalyst composition. It is therefore difficult to discover the influence of acidity or basicity alone on the mechanism of the activation of hydrocarbons.

V. The influence of structural defects in the catalysts on the activation of hydrocarbons

The nature of the defects in solids, especially in oxides, has been discussed in numerous communications (see, for example, Tret'yakov[113] and Tomlinson *et al.*[114]). The conditions in the preparation of the catalysts, the effect of the medium, and impurities alter the structures of solids and influence the type of defects and the distribution of additives which may interact with the basic elements. This may result in the local reconstruction of the initial oxides. Furthermore, clusters may be formed from the structural components and additives.

Defects alter the electronic characteristics of the surface and of the bulk of the solid[5,6] and thereby influence the activation of the components of the reaction mixtures.[114,115] The partial oxidation of hydrocarbons is achieved with participation of the oxygen in the oxide lattices. Oxygen vacancies are formed in the course of this process and oxygen migrates *via* the lattice and interacts with the oxygen from the gas phase.[30,32] Anionic vacancies influence the abstraction of a hydrogen atom from the propene molecule when the latter is oxidised on various spinels and solid solutions.[30,33] The structural sensitivity of oxidation reactions has been discussed.[115,116] Several types of defects in metal oxides have been examined: 'genetic' and impurity defects as well as oxygen vacancies.

Defects and vacancies may arise in complex oxide systems when additives are introduced.[117] For example, the modified Co–Mo–Bi–Fe catalyst contains the molybdate $Fe_2(MoO_4)_3$, which has a garnet-like structure with a vacant dodecahedral sublattice. When alkali elements, especially the potassium ion, the ionic radius of which is optimal for this structure, are introduced, the vacant sublattice is partly filled and the degree of defectiveness of iron molybdate increases. The latter acquires the structure of a nonstoichiometric garnet containing oxygen vacancies:

$$\square_3^0 Fe_2^{3+}(Mo^{6+}O_4^{2-})_3 \xrightarrow{K^+} K_x^+\square_x^-\square_{3-x}^0 Fe^{3+}(Mo^{6+}O_4^-)_3\,,$$

$\square^0$ — vacancy in the dodecahedral sublattice, $\square^-$ — anionic oxygen vacancy.

Such structural changes influence the mobility of oxygen in the catalyst lattice.

A process involving the appearance of defects in catalysts has been described in a review.[117] The adsorption of various substances on catalysts can also induce the appearance of defects in the lattice of the solid. Thus defects are formed after the adsorption of chloride ions on a silver single crystal,[118] oxygen from the gas phase being adsorbed on these centres. This type of centre–oxygen associated species is called a 'B defect' and serves as a kind of 'gate' for the permeation of atomic oxygen into the layers of the silver lattice. A model of the structure of silver, on the surface of which chloride ions are sorbed, has been proposed.[118]

The perovskites ABO_3 have begun to be used recently in oxidative catalysis.[119–121] Vacancies and defects are formed in the structures of these compounds owing to the nonstoichiometric amounts of the elements A and B. The same vacancies and defects appear when additives are introduced.[120,121] The properties of the lattice oxygen and adsorbed oxygen have been investigated for the pure and modified lanthanum oxides and the nature of the defects has been established.[121] A calculation has been carried out for a model of the defect and its diffusion from the bulk phase and on the surface.[122,123] The addition of strontium ions to the perovskite increases the mobility of oxygen and the number of oxygen vacancies.[124] The interaction of ethene, propene, and isobutene with a defect-containing catalyst, the composition of which is described by the formula $Bi_{1-x/3}\square_{x/3}Mo_y(V_{1-x}Mo_{x-y}Fe_x)O_y$, where $\square$ is a cationic vacancy and $x = 0.13–0.60$, has been investigated.[124–126] Schemes for the disposition of oxygen around different cations have been proposed and the view has been expressed that the coordinated cation participates in the dissociation of a C–H bond of the hydrocarbon with formation of the allyl group. The rate of oxidation depends on the number of vacancies in the catalyst. Theoretical calculations have been performed for the interaction of hydrocarbons with clusters and structural defects.

The modern experimental methods make it possible to investigate the transformations in a solid, occurring under the influence of the medium, and the structure of the surface compound *in situ*. However, the results of such studies have not been duly employed in establishing the mechanism of the activation of hydrocarbons, which is therefore purely formal.

In considering the questions concerning the influence of the chemical and structural properties of the catalyst on the activation, it is essential to take into account, apart from the factors indicated above, the electronic transitions between the solid and the hydrocarbons being adsorbed. In the electronic theory of catalysis, much attention has been devoted to the establishment of the signs of the charges of the substances adsorbed on metal oxides

and the charge on the surface of the metal.[127] As a rule, the molecular and atomic oxygen on oxides has a negative charge, while organic substances have a positive charge.[3, 28]

Adsorption on metals entails the formation of dipoles with different directions of the charge relative to the catalyst surface.[128] According to the electronic theory of catalysis, the activity of the catalyst depends on the position of the Fermi level for the lattice of the solid and electron exchange takes place between the adsorbed molecule of the given substance and the catalyst. The search for the relation between the electronic properties of a solid catalyst, on the one hand, and the charged reacting molecules, on the other, was therefore believed to be a problem of current interest. However, the electronic theory of catalysis was not developed further. The characteristics of the electron exchange process are determined from the change in the electron work function on adsorption and from the electrical conductivity. The change in the electron work function on the V_2O_5/TiO_2 catalysts, pure and modified with potassium ions, has been studied.[129] The presence of potassium facilitates electron exchange in the solid. The vacancies in oxide lattices may be charged and, when hydrocarbons are adsorbed and interact with oxygen, they may transfer electrons to the surface compounds formed.

The electron exchange between the charged forms of the hydrocarbon and the surface oxygen, observed on various oxides, has been considered in the analysis of the selectivity in the partial oxidation. The catalytic properties of many catalysts are influenced by the charge transfer between the surface and the bulk of the catalyst.[130–133] This is particularly notable on supported catalysts, the activity of which is related to the electrical conductivity.[131, 132] The electronic characteristics of the catalysts influence the rate of interaction of hydrocarbons with surface oxygen but do not alter the type of activation.

Thus analysis of the activation of hydrocarbon molecules on partial oxidation of catalysts has shown that this is a complex process which includes diverse interactions depending on the structure and energy parameters of the molecules being adsorbed and also on the characteristics of the catalyst surface (the form of oxygen, the valence state of ions, vacancies, and defects).

VI. The selectivity of the partial oxidation and activation of hydrocarbons

The principal characteristics of the partial oxidation are the rate and selectivity of the reaction.[134–138]

The partial oxidation processes are almost always accompanied by extensive oxidation. There are two mechanisms of the extensive oxidation of hydrocarbons: the consecutive mechanism, where the partial oxidation product is converted into CO_2 and water, and the parallel mechanism where CO_2 and water are formed from the hydrocarbon *via* other intermediate species (surface compounds, radicals). The selectivity of the oxidation depends on the process mechanism.[139]

The extensive oxidation of hydrocarbons of different classes on the $MgCr_2O_4$ catalyst typical for this process has been studied.[140] The spectroscopic investigation showed that hydrocarbons react with chromium ions functioning as active centres. The weakest C–H bond is then ruptured and C–O bond is formed, while further oxidation leads to the formation of carboxylates and carbonates.

The activation of hydrocarbon molecules on partial oxidation catalysts is the first and probably the rate-determining stage of the process. Further reactions of the surface forms produced with participation of oxygen determine the type and structure of the oxidation products. In the elucidation of the activation mechanism, one of the main questions is that of the role in this process of the structure and energy of the bonds in the hydrocarbon molecule and also the question of the form of oxygen capable of participating in the formation of the partial oxidation product. Comparative study of hydrocarbons of several classes makes it possible to establish the influence of their structure on the activation.

Among all the alkenes, only ethene is converted into epoxyethane on a silver catalyst. The attempt to obtain epoxypropane on this catalyst proved unsuccessful: propene is activated by involvement of the methyl group, from which a hydrogen atom is abstracted and this results in the formation of the allyl group.[140, 141] Ethene is activated as a consequence of the rupture of the double bond by oxygen, which leads to the formation of a complex preceding the formation of epoxyethane.

Aldehydes and acids or alkenes appear as a result of the activation of alkanes (oxidative dehydrogenation). For example, two hydrogen atoms may be split off from the hydrocarbon molecule on activation of butane. The products of this reaction are maleic anhydride, maleic aldehyde, or butadiene. Still more significant differences are observed in the activation of aromatic hydrocarbons. One hydrogen atom is split off in this case from the ring (benzene is formed), two hydrogen atoms are split off from the side chain (alkyl-substituted aromatic hydrocarbons are formed), or the ring is ruptured. In a study devoted to the selective oxidation of light alkanes,[142] the view has been expressed that the choice of catalytic systems for these reactions must be determined by the structure of the active centres and their redox and acid–base properties. Particular attention was devoted in this investigation to the reaction products, their stability, and the strength of the bond with the solid (ease of desorption). The adsorption mechanism and the mechanism of the insertion of oxygen in oxide catalysts were examined.

The interaction of hydrocarbons with the surface of an oxide catalyst is accompanied by its reduction, *i.e.* by a change in the valence state of the cations. This process influences the mode of activation of the hydrocarbon molecules. In a number of instances, the rate of activation and its mechanism are determined by the redox properties of the catalyst. The lack of capacity for reduction (for example, in the vanadium–phosphorus catalyst) prevents the formation of oxygen-containing products from butane and the process proceeds on other surface centres (for example, acid centres). Oxidative dehydrogenation then takes place. The rates and selectivities of the oxidation of various hydrocarbons on the same catalysts may differ as a consequence of the formation of various intermediate forms. For example, on bismuth molybdate propene gives rise to an allyl complex, whilst butene produces a π-complex with elimination of two hydrogen atoms.

The V–Mo–Ti catalytic system is the most active in the oxidation of aromatic hydrocarbons, while propene is oxidised on it with a low selectivity.[143]

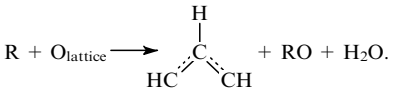
Oxidative dehydrogenation takes place preferentially on the $Mg_2(VO_4)_2$ catalyst. On other vanadium systems, the rates of partial oxidation and oxidative dehydrogenation depend on the ratio of V^{4+} and V^{5+} (see Refs 55, 64). As a consequence of the removal of oxygen from the lattice of the catalyst in the interaction of its surface with a hydrocarbon, vacancies (defects) arise and electron exchange processes take place within the lattice.

The influence of the nucleophilicity and electrophilicity of oxygen on the mechanism of the oxidation of hydrocarbons has been examined in numerous studies.[4, 33, 137–140] The abilities of Bi–Mo–O and V_2O_5 to oxidise hydrocarbons of different classes have been compared on the basis of the analysis of the interaction of electrophilic oxygen with the C–C and C–H bonds in the hydrocarbon molecule. For example, bismuth molybdate is incapable of oxidising aromatic hydrocarbons, while V_2O_5 cannot oxidise olefins. The diversity of the mechanisms of the activation of hydrocarbons on different catalytic systems is determined not only by the state of the organic molecule and oxygen but also by the properties of the catalyst surface. We have already considered the influence of the structure and redox properties of the solid on the activation of hydrocarbons. However, the characteristic features of the acid centres of the catalyst are no less important.[134, 136]

In the activation of hydrocarbons on the surfaces of catalysts, the complexes or radicals formed interact with oxygen almost simultaneously with the dissociation of the C–H bond. The lattice

oxygen of the oxide or the atomic oxygen adsorbed on the metal surface are known to participate in the partial oxidation reaction. The molecular oxygen adsorbed from the gas phase participates in the extensive oxidation. The structure of the surface and the valence state of the ions influence the bond energy of the oxygen in the lattice and its mobility. Numerous studies, in which the mechanism of the interaction of the adsorbed hydrocarbon with different forms of oxygen is discussed, have been devoted to these questions (see, for example, Refs 3, 7, and 31). In essence, the activation step involves the adsorption of a hydrocarbon molecule and its interaction with oxygen. The selectivity in the formation of the reaction products depends on the structure of the oxygen–hydrocarbon complex which has appeared and also on its mobility and reactivity.

It has been suggested that the mechanism of the partial oxidation is determined by the interaction of the mobile activated hydrocarbon complex or radical with the stationary lattice oxygen:[136]



At a low temperature there is a possibility of the formation of peroxides (as a result of the interaction with O_2^-) and their subsequent decomposition with formation of oxygen-containing products.

On extensive oxidation, the activated mobile oxygen interacts with the stationary hydrocarbon complex:

$$R + (O_2^-, O^-) \longrightarrow (H-CH=CH)_n \longrightarrow CO, CO_2.$$

The mobile oxygen may consist of an adsorbed atom or molecule. The continuation of the reaction in the gas phase is possible (a homogeneous-heterogeneous mechanism).[1]

Sokolovsky[141] carried out a kinetic analysis and proposed models for the extensive oxidation of hydrocarbons. The selectivity and the partial oxidation of hydrocarbons are determined not only by the structure of the molecules of hydrocarbons of different classes and the C–H bond energies but also by the valence state of the components of the catalyst surface. One of the stages in the activation of hydrocarbons consists of redox reactions in the catalyst. The cations in the lattice of the solid undergo a change in their valence state as a result of the adsorption of hydrocarbons. There is also a corresponding change in the mode of oxidation. For example, in vanadium catalysts, oxygen bridges may be formed on the vanadium ions. These are readily reduced when the hydrocarbon is adsorbed, as a result of which oxygen is removed and a C–O bond is formed. The reaction products contain oxygen.

The acid–base properties of the catalyst as well as the redox reactions influence the conversion of hydrocarbons and the process selectivity. When the reaction is carried out on complex oxide systems (for example, $MoO_3-Sb_2O_4$),[104] a relation is observed between the ratio of the number of Brønsted and Lewis centres and the selectivity in the conversion of propene into acrolein. On the other hand, a change in the ratio of the molybdenum and antimony oxides alters the concentration of the oxidation–reduction centres on the surface and influences the migration of oxygen *via* the lattice. The combined operation of these factors promotes the dissociation of oxygen, the enhancement of oxygen spill-over between the phases, and the adsorption of the protons split off from the propene molecule. Such is the complex mechanism of the influence on the activation of the hydrocarbon by various processes occurring on the catalyst surface.

The oxidation kinetics have been considered in a large number of publications, both review publications[138] and those devoted to the investigation of individual catalytic reactions in the extensive and partial oxidation of hydrocarbons. Apart from the dependences of the reaction rate and selectivity on the pressure, temperature, and contact time, models of the process, corresponding to the observed parameters, are presented in these communications.

In order to choose a model, it is essential to elucidate which stage of the oxidation process determines its rate. Almost all investigators believe that this stage is the activation of the hydrocarbon on the catalyst surface with formation of various surface compounds. Formal schemes, which do not always correspond to the true reaction mechanism, have been proposed in many investigations.

The foundations for the construction of a kinetic model of the methane oxidative condensation reaction on the PbO/Al_2O_3 catalyst have been described.[144] Ethene, ethane, and extensive oxidation products are formed in this process from methane. The reaction proceeds *via* a heterogeneous-homogeneous mechanism. Characteristic features of the process at different temperatures, oxygen pressures, and for other parameters have been investigated. The proposed model includes the formation of the methyl radical from methane, its dimerisation to ethane, and the reaction with oxygen to form a peroxide. The dependence of the limiting selectivity and of the rate of formation of the products on various parameters has been established on the basis of this model and it has also been shown that the process proceeds *via* a redox mechanism. It is postulated that ethane is activated and the extensive oxidation products are formed on different centres.

Albonetti *et al.*[8] investigated the kinetics of the oxidation of ethane and ethene. Kinetic analysis showed that this reaction has a redox mechanism. The rate constants for the formation of methyl radicals and the extensive oxidation products were found, equations were proposed for the rates of formation of different products, and the limiting selectivities were established.

A similar approach to the elucidation of the mechanisms of catalytic partial oxidation processes, based on a profound kinetic analysis and the establishment of a relation between the physicochemical properties of the catalysts and the selectivity of the oxidation process, has also been used in other studies.[143, 144] A two-centre model has been proposed for the oxide catalyst as well as kinetic models for the partial oxidation of olefins (propene, isobutene) and unsaturated aldehydes. It is postulated that the hydrocarbon and oxygen are adsorbed on centres of different types and that the interaction between them occurs as a result of the diffusion of oxygen from its adsorption centres to the reaction centres, which function simultaneously as the hydrocarbon adsorption centres.

Kinetic analysis of the two-centre model and the active surfaces of oxide catalysts has been carried out.[145–149] Apart from a detailed mechanism of the transfer of oxygen from its adsorption centres to the reaction centres, it proved possible to describe the principal kinetic features of the oxidation of propene, isobutene, and methacrolein to acrolein, methacrolein, and methacrylic acid respectively under stationary conditions.

VII. Conclusion

The activation of hydrocarbons on the surfaces of catalysts is the first and rate-determining stage of their partial and extensive oxidation. The hydrocarbons are converted into active radicals or complexes, which form different surface compounds, affording different oxidation products.

The way in which the hydrocarbon interacts with the surface of the solid depends on the structure of the organic molecule (bond energy) and the nature of the catalyst surface (structure, valence state of its constituent ions, and the forms of oxygen and its mobility).

In the structure of the catalyst there are defects, which can also serve as activation centres. Electron exchange takes place between the solid and the adsorbed hydrocarbon. The interaction of the hydrocarbon with oxide systems is accompanied by redox processes in the solid involving a change in the valence state of the lattice cations. Brønsted and Lewis acid centres also participate in the activation of the hydrocarbon. The mode of oxidation of

hydrocarbons, namely to oxygen-containing products or to hydrocarbons with a different structure (oxidative dehydrogenation), depends on the activation mechanism.

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