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Oxidative Dehydrodimerisation and Cyclisation Reactions of Unsaturated Hydrocarbons in the Presence of Oxide Catalysts

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The review is devoted to a comparatively new type of heterogeneous-catalytic processes—oxidative dehydrocoupling and cyclisation reactions of hydrocarbons with unsaturated bonds. The catalysts used in these processes and the rules governing their selection are examined. A systematic account is given of data on the kinetics and mechanisms of the reactions. Certain general characteristics of processes of this type are formulated and the problem of the selection of catalysts is discussed on their basis.
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I. INTRODUCTION

Oxidative dehydrodimerisation and cyclisation of unsaturated hydrocarbons constitute a comparatively new type of processes within the large class of heterogeneous catalytic reactions involving molecular oxygen. The first reports, demonstrating the possibility of these processes in principle, appeared in the patent literature in the middle 1960's and immediately attracted the attention of investigators.

The interest in the reactions under consideration is due to the possibility of processing numerous hydrocarbons with a mobile hydrogen atom in the α-position relative to the unsaturated bond. By specific catalytic synthesis, it is possible to obtain symmetrical dehydrodimers and in many instances the products of the subsequent reactions, which have practical applications. With the aid of these processes, it is possible to obtain, for example, diallyl and benzene from propene, *p*-xylene from isobutene, bibenzyl and *trans*-stilbene from toluene, and p-terphenyl from α-methylstyrene.

A number of advantages arise from the reactions being carried out in the presence of molecular oxygen compared with the familiar dehydrocyclodimerisation[1] and dehydrocyclisation[2] of paraffins and olefins. As a result of the oxidation of the eliminated hydrogen, these reactions are exothermic and the degree of conversion of the initial substance is not limited by the equilibrium conditions. The absence of carbon deposition ensures the stable operation of the catalyst and hence the continuity of the process. Finally, the oxidative version of the reaction is characterised by a narrower set of products, which greatly facilitates the isolation and purification of the required substances.

Apart from their applied importance, the oxidative dehydrodimerisation and cyclisation reactions of unsaturated hydrocarbons are of theoretical interest as an additional and convenient model for the application and refinement of the postulates of the theory of oxidative-reductive and acid–base catalysis.

Taken together, all these factors stimulated the publication during the last decade of a comparatively large number of patents and communications devoted to the above type of reactions. Among these, there have been reviews[3-5], which, however, suffer from being incomplete and one-sided. They describe mainly the compositions of catalysts found empirically and the conditions of the oxidative dehydrodimerisation and aromatisation reactions of the lower olefins. Considerably less attention has been devoted to the principles of the selection of catalysts and the problems of the reaction mechanisms, the principal data on which have been obtained very recently. Nor do they discuss the position occupied among other oxidative heterogeneous catalytic processes by dehydrocoupling reactions and the limits of the applicability to the latter of the special relations which have accumulated for total and partial oxidation reactions of hydrocarbons. The elimination of these gaps was one of the aims of the present review, which is based on studies published in the last 10–12 years.

II. OXIDATIVE DEHYDRODIMERISATION AND CYCLISATION OF OLEFINS

The principal products of the oxidative dehydrodimerisation and aromatisation of propene are hexa-1,5-diene and benzene and those obtained from isobutene are 2,5-dimethylhexa-1,5-diene and *p*-xylene. This difference from the thoroughly investigated reactions involving the partial oxidation of propene and isobutene to the corresponding unsaturated aldehydes and acids and oxidative dehydrogenation of *n*-butenes and isopentene to butadiene and isoprene is due to the differences between the compositions of the catalysts employed.

1. Process Catalysts

Table 1 presents the known catalysts of the oxidative dehydrodimerisation and cyclisation reactions of olefins. The vast majority of them consist of metal oxides. The use of noble metals, for example silver[6,7] and palladium[8], for this purpose has not developed owing to their high cost and the lack of significant advantages over oxide catalysts. For a number of technological reasons, it is difficult to carry out the process in the presence of melts of metals such as bismuth and tin[9] or salt melts of the type of lithium iodide[10].

The simple metal oxides are as a rule relatively ineffective as regards the formation of diolefinic and aromatic hydrocarbons. Among the last number of specimens investigated

Table 1. Catalysts for the oxidative dehydrodimerisation and aromatisation of olefins.

Catalyst	Method of preparation of catalyst	Reaction conditions*	Conversion of olefin, %	Selectivity, %		Refs.
				w.r.t. diolefin**	w.r.t. aromatic products	
Metallic Ag with added alkaline earth metal oxides	decomposition in a stream of air at 220 °C of silver carbonate deposited from aqueous suspension	500°; $C_3H_6 : O_2 = 39 : 1$; $t_c = 0.56$ s	1.1	61.9	—	6,7
Metallic Bi, Sn, and their alloys in the liquid state	–	593°; C_3H_6 : air = 1 : 2; t_c = 0.2—3 s	16.6	22.4	54.4	9
Fused 98% LiI + 2LiOH mixture	–	480°; iso-$C_4H_8 : O_2 = 4.2 : 10$; t_c = 0.1—5 s	36.5	—	68.8	10
Bismuth oxide	decomposition of the hydroxide at 550 °C in 24 h	575°; C_3H_6 : air : He = 2 : 5 : 10, t_c = 2.1 s	28.5	57.0	5.4	12, 13
Indium oxide	decomposition of the hydroxide at 560°	480°; $C_3H_6 : O_2 = 5 : 1$ t_c = 1.2 s	—	22.6	40	14
Thallium oxide	decomposition at 500° of the hydroxide deposited from nitrate solution by sodium hydroxide	520°; $C_3H_6 : O_2 = 10 : 1$ t_c = 4 s	—	78.0	—	14
Lead oxide deposited on Al_2O_3	repeated impregnation of the carrier *in vacuo* with a solution of the nitrate salt; heat treatment at 700°	493°; $C_3H_6 : O_2 = 15.7 : 1$; pressure —3.2 atm; t_c = 0.04 s	5.6	76	—	15, 16
Bismuth–tin oxide catalyst; Bi:Sn = (1–9):(9–1) (best 1:1)	heat treatment of a mixture of individual oxides at 540° for 16 h	470°; $C_3H_6 : O_2 = 1.4 : 1$; t_c = 3 s	24.5	—	61.5	19, 20
Bismuth–tin oxide catalyst (Bi:Sn = 2:3)	heat treatment of a mixture of bismuth nitrate and tin dioxide at 750° for 28 h	575°; C_3H_6 : air : He = 2 : 5 : 10, t_c = 1.1 s	18	24.2	27.5	22
Bismuth–phosphorus oxide catalyst (Bi:P = 2:1)	deposition from an acidified solution of bismuth nitrate and ammonium phosphates, drying, and heat treatment at 500°	500°; $C_3H_6 : O_2 = 1 : 1.6$; t_c = 1.0 g s ml^{-1}	85.8	—	44.9	25
Bismuth–phosphorus oxide catalyst (Bi:P = 2:1 with addition of 0.6% Na_2O)	joint deposition at pH 6; heat treatment of dried deposit at 600°	550°; $C_3H_6 : O_2 = 5.6 : 1$; t_c = 0.36 s	6.9	47	—	28
Bismuth–titanium oxide catalyst (Bi:Ti = 1:1)	heat treatment of a mixture of oxides	550°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = 2.0 s ml^{-1}	81.9	—	29.1	11, 30
Bismuth–titanium oxide catalyst (Bi:Ti = 4:3)	heat treatment of a mixture of bismuth nitrate and titanium oxide at 750°	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.2 s	20.2	26.8	24.6	22
Bismuth–titanium oxide catalyst (Bi:Ti = 2:1)	evaporation of a solution of bismuth nitrate and titanium dioxide in dilute nitric acid, drying, and heat treatment at 500°	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 2.1	22.0	38.4	17.5	13
Bismuth–zinc oxide catalyst [Bi:Zn = (1–3):(3–1)]	heat treatment of a mixture of bismuth nitrate and zinc acetate at 600° for 4 h	585°; $C_3H_6 : O_2 = 5.6 : 1$; t_c = 0.36 s	3.3	58.5	—	23
Mixture of bismuth and indium oxides on a carrier (Bi:In = 7:3)	–	500°; iso-$C_4H_8 : O_2 = 1 : (0.3—1)$; t_c = = 1—15 s	26.2	10.5	50.3	33
Bismuth–antimony oxide catalyst (Bi:Sb = 1:1)	heat treatment of a mixture of oxides in air at 600° for 4 h	585°; $C_3H_8 : O_2 = 5.6 : 1$; t_c = 36 s	10.0	50.0	—	23
Bismuth and antimony oxides on a carrier promoted with Na, Cu, or Zr oxides	–	420°; iso-$C_4H_8 : O_2 = 4 : 1$; t_c = = 0.45 s	32.0	65.0	—	34
Bismuth–nickel oxide catalyst (Bi:Ni = 1:1)	mixing and heat treatment of individual oxides at 540°	470°; C_3H_6 : air . $H_2O = 1 : 4 : 3$; t_c = 7.5 s	51.2	25.3	46,5	35
Bismuth–copper oxide catalyst (Bi:Cu = 1:1)	heat treatment of a moistened mixture of oxides at 540°	470°; iso-C_4H_8 . air : $H_2O = 1 : 4 : 3$; t_c = 7.5 s	51.5	30.5	45,6	35
Bismuth–iron oxide catalyst (Bi:Fe = 1:1)	decomposition of a mixture of bismuth and iron nitrates	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.1 s	16.1	20.7	14.6	22
Bismuth–iron oxide catalyst (Bi:Fe = 2:1)	heat treatment of a mixture of oxides at 600–700° for 4 h	586°; $C_3H_8 : O_2$ = 5; 7 : 1; t_c = 0.36 s	6.8	49.0	9.8	36
Bismuth–cadmium oxide catalyst (Bi:Cd = 5:3.5 with added lead and magnesium oxides)	heat treatment of a moistened and dried mixture of oxides at 540° for 16 h	500°; C_3H_8 (iso-C_4H_8) : air : H_2O = = 1 : 8 : 2; t_c = 4.3 s	20.0 (17.0)	—	55.2 (56.3)	37
Bismuth oxide deposited on alundum with added 2.8% K_2O	successive impregnation of the carrier with solutions of bismuth nitrate and potassium hydroxide, drying at 120°, and heat treatment at 550°	550°; $C_3H_6 : O_2 : N_2 = 10.8 : 1 : 71.5$	12.0	77.0	—	44
Bismuth–zirconium oxide catalyst (Bi:Zr = 2:3)	decomposition of a mixture of bismuth nitrate and zirconium oxide	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.1 s	18.0	28.0	14.8	22
Bismuth–niobium catalyst (Bi:Nb = 1:1)	heat treatment of a mixture of bismuth nitrate and niobium oxide	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 2.1 s	2.6	28.2	27.8	13
Bismuth–tungsten oxide catalyst (Bi:W = 2:1)	heat treatment of a mixture of bismuth nitrate and tungsten trioxide	575°; C_3H_6 : air : He = 2 : 5: 10; t_c = 2.1 s	14.4	6.1	19.9	13
Bismuth arsenate $BiAsO_4$ (monazite)	evaporation of a mixture of solutions of bismuth nitrate and the ammonium salt of a hydroxy acid with subsequent heat treatment	500°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = = 2 g s ml^{-1}	69	—	33.8	11, 30
Bismuthyl sulphate $(BiO)_2SO_4$	decomposition of bismuth sulphate in air at 600°	500°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = = 2 g s ml^{-1}	61	—	10.1	11, 30
Manganese and sodium oxides (Mn:Na = 1:2) on Al_2O_3, SiC, and aluminosilicate carriers	fusion of manganese dioxide with Group IA and IIA metal oxides or decomposition of a mixture of acetates, oxalates, and formates	638°; $C_3H_6 : O_2 = 1 : 1$; t_c = 0.05 s	—	54.5	—	47, 48
Mixture of manganese and sodium oxides (Mn:Na = 1:2.3) on alumina	impregnation of the carrier with solutions of manganese and sodium acetates	627°; $C_3H_6 : O_2 = 4 : 1$; t_c = 0.1—5 s HBr introduced into gas phase	9.0	7.4	46.6	49
Tin–cadmium oxide catalyst (Sn:Cd = 0.33:1)	evaporation of a mixture of cadmium oxide and a solution of metallic tin in nitric acid followed by heat treatment of the deposits at 400° for 6 h	570; iso-$C_4H_8 : O_2 = 1 : 2$; t_c = 3 s	62.5	13.4	65.5	50

Table 1 (cont'd.).

Catalyst	Method of preparation of catalyst	Reaction conditions*	Conversion of olefin, %	Selectivity, %		Refs.
				w.r.t. diolefin**	w.r.t. aromatic products	
Palladium–dimethyl sulphoxide complex deposited on rock	impregnation of the carrier with a solution of $K[Pd(DMSO)Cl_2]$ in DMSO and with an acid aqueous solution of $PdCl_2$	500°; $C_3H_6 : O_2 = 1 : 1$	58.2	75.6	11.0	51, 52

*t_c = reaction time.

**The diolefin should be understood as hexa-1,5-diene in the oxidation of propene and 2,5-dimethylhexa-1,5-diene in the oxidation of isobutene.

***The main aromatic products of the conversion of propene and isobutene are benzene and *p*-xylene respectively.

by Seiyama[11], bismuth, cadmium, zinc, and tin oxides proved to be comparatively selective in the oxidative dehydroaromatisation of propene. Analogous data have been published for bismuth oxide[12,13]. The selectivity with respect to the desired products reaches 60% in the presence of the above catalysts for a degree of conversion of the initial olefins of 28%. Indium and thallium oxides are also relatively selective[14] in the presence of a large excess of the olefin in the initial mixture. In the presence of these catalysts the overall selectivity with respect to diallyl and benzene is 60–80% for a conversion of propene less than 1%. Lead oxide has similar parameters[15–17].

Almost all the individual oxides mentioned above exhibit a low activity but a comparatively high selectivity. An additional characteristic feature of lead and thallium oxides is instability of activity due to the reduction of lead oxide to the inactive metal[17] and the volatility of thallium (I) compounds formed in the catalytic process[18]. Two-component oxide systems are more active in oxidative dehydrodimerisation and aromatisation reactions of the lower olefins. The largest group consists of catalysts based on bismuth oxide. Combinations of the latter with the oxides of tin[19–24], phosphorus[25–29], titanium[13,22,30,31], zinc[23,32], indium[33], antimony[23,24], nickel[35], copper[34,35], iron[22,35,36], cadmium[30,37], lead[37], manganese[38], and a number of other metals are effective.

The increased activity of complex oxides compared with simple oxides is apparently associated with the formation of definite catalytically active compounds. In the study of the phase compositions of bismuth–tin[39–41], bismuth–iron[36], and bismuth–titanium[42] oxide catalysts, the existence in the latter of bismuth pyrostannate ($Bi_2Sn_2O_7$), orthoferrite ($BiFeO_3$), and pyrotitanate ($Bi_2Ti_2O_7$) respectively was observed. The catalysts exhibit the maximum activity for approximately the above ratios of the elements. The data of the present author and his coworkers[41], illustrated in Fig. 1, show that the rate and selectivity of the formation of the products of the oxidative dehydrodimerisation and aromatisation of propene in the presence of bismuth–tin oxide catalysts vary in parallel with their content of the $Bi_2Sn_2O_7$ phase. A similar variation has also been established for specimens with an identical ratio of bismuth and tin obtained by different methods and differing in phase composition as a result[43].

When other metal oxides are introduced into bismuth oxide, a change in the composition of the reaction products is sometimes observed together with an increase of the overall activity. Thus, when zinc oxide[32], tin dioxide[40], and indium oxide[33] are used as the second component, the fraction of aromatic hydrocarbons increases significantly compared with pure bismuth oxide, in the presence of which the main reaction product is a diolefinic hydrocarbon.

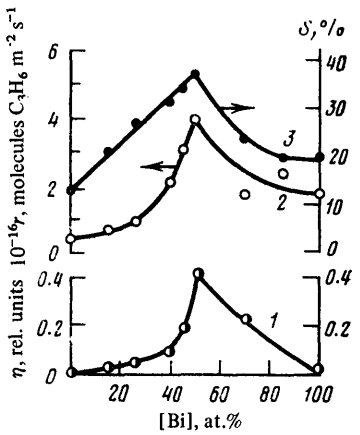


Figure 1. The influence of the composition of bismuth–tin oxide catalysts on the relative content η of the $Bi_2Sn_2O_7$ phase (curve *1*), the rate *r* (curve *2*), and the selectivity *S* (curve *3*) in the overall formation of diallyl and benzene[41].

Small amounts of added alkali metal oxides cause an appreciable increase of the selectivity of bismuth-containing catalysts in olefin dehydrodimerisation and aromatisation reactions[24,28,34,44,45]. Thus, according to a patent[44], the introduction of 2.8% of potassium oxide into deposited bismuth oxide increases the selectivity with respect to hexa-1,5-diene from 70 to 77% for the same degree of conversion of propene. Small amounts of alkali metal oxides have a similar influence on the catalytic properties of tin dioxide[11,30]. Fig. 2 shows that the maximum selectivity in the formation of benzene is observed in the presence of 5 at.% of sodium oxide in tin dioxide. These amounts of sodium oxide are uniformly dispersed on the surface of tin dioxide and do not form a chemical compound with the latter[5]. In the presence of more than 5 at.% of sodium dioxide, the uniformity of the distribution breaks down and the compound Na_2SnO_3, completely inactive in the oxidative reaction of propene, is

formed[5]. For this reason sodium bismuthate, while fairly selective, is apparently characterised by a low activity compared with bismuth oxide[46].

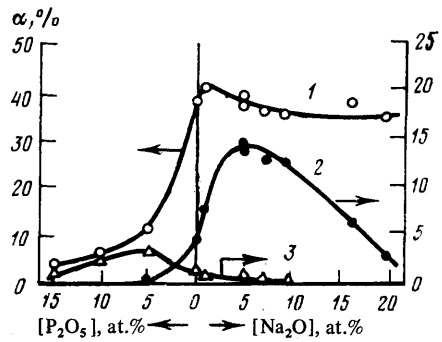


Figure 2. The promoting influence of sodium and phosphorus oxides on the catalytic properties of tin dioxide: *1*), *2*), and *3*) degrees of conversion of propene into carbon dioxide, benzene, and acrolein respectively[11].

In conclusion of the brief consideration of bismuth-containing catalysts, one must note that the introduction of zirconium[22], niobium[13], tungsten[13], arsenic[11,30], sulphur[11], and aluminium[30] compounds into bismuth oxide does not improve significantly and in some cases actually impairs its catalytic properties.

Among other oxide systems, mention should be made of the sodium–manganese oxide system[47–49]. While exhibiting a satisfactory selectivity with respect to the oxidative dehydrodimerisation and aromatisation products (50–55%), these catalysts have a low activity even at high temperatures: at 627 °C the degree of conversion of propene in their presence does not exceed 5–10%. The tin–cadmium oxide system is more active[50]. Thus, in the presence of the oxide catalyst with the composition Sn/Cd = 0.4, the degree of conversion of isobutene reaches 65–67% for a selectivity in the formation of *p*-xylene of 58–65%.

Attempts have been made to use "heterogenised" metal complex catalysts in the oxidative dehydrodimerisation of propene[51,52]. It was shown that, in the presence of palladium- and iron-containing complexes deposited on a natural silicate mineral, diallyl and benzene are formed at lower temperatures (200–300 °C) and in larger amounts than in the presence of bismuth oxide. However, here it is necessary to solve the problem associated with the stability of the activity of catalysts of this kind.

It has been suggested in a number of patents[53–56] that the reactions be carried out in the absence of gaseous oxygen and that the hydrogen split off in the dehydrodimerisation and aromatisation of the olefin be combined with the oxygen of the oxide, i.e. that the catalyst be used as an oxidant. It appears difficult to assign this version of the process to oxidative heterogeneous-catalytic reactions and to specify a clear-cut boundary between them and dehydrocyclodimerisation processes[1]. This review therefore deals only with processes carried out in the presence of molecular oxygen.

Thus the foregoing permits the conclusion that the catalysts of oxidative dehydrodimerisation and aromatisation reactions of olefins differ appreciably in their qualitative composition from the known partial oxidation catalysts containing as a rule molybdenum, tungsten, vanadium, antimony, arsenic, and tellurium oxide compounds. From this standpoint, the report[57] that the uranium–antimony catalyst, which is extremely effective in the partial oxidation and oxidative dehydrogenation reactions of olefins, is active in the dehydrodimerisation reaction appears unexpected[58,59].

2. Certain Characteristics of the Selection of Catalysts

The catalytic activities of a large number of simple and complex oxides with respect to the total oxidation of hydrocarbons are known[60–62] to be determined by the binding energy of the surface oxygen—the smaller the bond strength, the higher the rate of oxidation. The situation is more complex in partial oxidation processes whose most important characteristic is selectivity with respect to a specific substance. It has been shown for a number of reactions[60,63,64] that the selectivity with respect to mild oxidation products increases with increasing energy of the oxygen–catalyst bond.

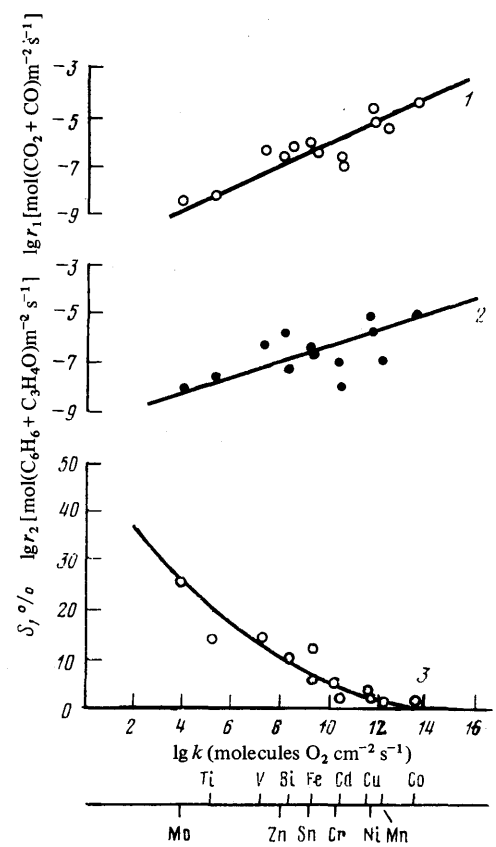


Figure 3. Dependence of the rate of total oxidation r_1 (curve *1*) and the rate r_2 (curve *2*) and selectivity S (curve *3*) in the allyl oxidation of propene[11] in the presence of simple oxides on the mobility of the surface oxygen, i.e. on the rate constant for the homomolecular exchange of oxygen k.[102]

An attempt to test the possibility of the existence of correlations of this kind for the oxidehydroaromatisation of propene was undertaken by Seiyama[11], who used the heats of formation of the individual oxides as a measure of the strength of binding of oxygen in them. When these quantities were compared with the rates of extensive and mild (acrolein + benzene) oxidative conversion of propene, it was found that the oxides can be divided into two groups, differing, according to the author, by the type of oxygen isotope exchange occurring in them. This factor as well as the considerable scatter of the points are apparently caused by the fact that the heats of formation of the oxides characterised their bulk-phase and not surface properties. It is more correct to use for this purpose the heats of desorption of the equilibrium oxygen[65] or the rates of homomolecular oxygen isotope exchange[66]. Fig. 3 shows that in the latter case the subdivision of oxides into two groups disappears and the correlation is more clear-cut.

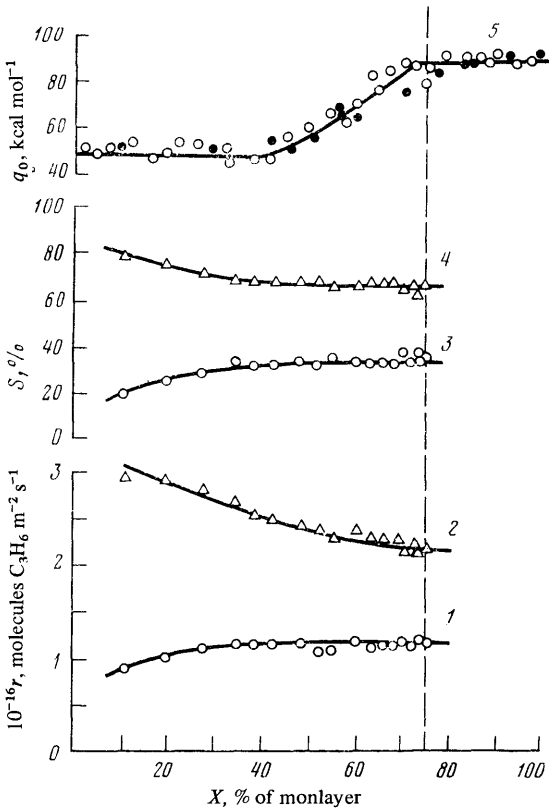


Figure 4. The influence of the degree of reduction X of the surface of the bismuth–tin oxide catalyst on the rate r and the selectivity S in the formation of diallyl (curves 1 and 3) and carbon dioxide (curves 2 and 4) and on the binding energy of oxygen q_0 (curve 5). The stationary state of the catalyst is indicated by a dashed line[69].

Fig. 3 also shows that the catalytic activity with respect to partial oxidation increases with increase of the mobility of surface oxygen to a smaller extent than in the case of total oxidation. As a result, the selectivity with respect to the overall formation of acrolein and benzene falls with decrease of the strength of binding of oxygen to the catalyst. It may be that this behaviour is caused by the fact that in the rate-limiting stage of the total oxidation reaction a larger number of oxygen–catalyst bonds are broken than in dehydroaromatisation, which is similar to the explanation used for the extensive and mild oxidation reactions of hydrocarbons[67,68].

A test of the validity of the above correlations for complex oxide catalysts of the oxidehydrodimerisation of olefins is at present difficult owing to the lack of data for the binding energies of surface oxygen in such catalysts. The possibility of the existence of correlations of this kind is supported by the results of a comparison of the relations presented in Fig. 4 between the catalytic activities and the binding energies of oxygen, on the one hand, and the degree of reduction of the bismuth–tin oxide catalyst, on the other[69]. Evidently the removal of weakly bound oxygen from the surface during the catalytic process reduces the selectivity of the total oxidation reaction and increases that with respect to diallyl - the product of the mild conversion of propene.

The problem of the way in which the strength of binding of oxygen to the catalyst influences the rate of partial oxidation of olefins to unsaturated aldehydes, on the one hand, and the rate of dehydrodimerisation, on the other, is also important. However, the relation between these quantities has not so far been discovered. One cannot rule out the possibility that different forms of surface oxygen participate in the reaction.

The dependence of the mode of oxidative transformation of olefins on the acid—base properties of the catalyst has been studied in greater detail. For many simple[11] and bismuth-,[30] zinc-,[70] cadmium-,[70] and tin-containing[71] binary oxides, it has been established that an increase of the acidity of the catalyst entails a decrease of the rate and selectivity of the formation of propene dehydrodimerisation and aromatisation products and of the increase of the yields of acrolein. The electronegativity of the metal cations[11,70], the strengths of the acid centres found by titration with *n*-butylamine[30,72], and the activity in the isomerisation involving the double bond in but-1-ene[71] are used as characteristics of the acid properties. Table 2 presents as an example, data[30] whereby one can follow the above relation between the selectivity in the oxidehydroaromatisation and partial oxidation reactions of propene and the acidity determined with the aid of Hammett indicators for bismuth-containing oxide catalysts.

Table 2. Selectivity in the allyl oxidation reactions of propene and the acid strength of bismuth-containing catalysts {500°; $[C_3H_6] = 9$ vol.%; $[O_2] = 18$ vol.%; conventional contact time 1.0 g s ml^{-1}}.[30]

Catalyst	Selectivity, %		Acid strength H_0
	benzene	acrolein	
$2Bi_2O_3 \cdot P_2O_5$	49.0	0	+7.1—+6.8
$BiAsO_4$	33.8	5.8	+6.8—+4.0
$BiPO_4$ (high-temperature form)	26.9	6.6	+6.8—+4.0
$Bi_2O_3 \cdot 2TiO_2$	18.0	0.3	+7.1—+6.8
$(BiO)_2SO_4$	10.1	4.0	+6.8—+4.0
$BiPO_4$ (monazite form)	9.1	38.6	+1.5—−3.0
$(BiO)_2MoO_4$	0	66.1	+3.3—+1.5
$Bi(BiO)(MoO_4)_2$	0	91.7	+1.5—−3.0
$Bi_2(MoO_4)_3$	0	94.9	+1.5—−3.0

This general relation makes it possible to regulate the acid–base and hence catalytic properties of the catalyst by promoting it with oxides of different kinds; this is clearly illustrated in Fig.2. The introduction of an alkali metal oxide into tin dioxide in amounts ensuring the homogeneity of the system increases the selectivity of the oxidehydrocyclisation of propene, while the addition of an oxide having acid properties (P_2O_5) suppresses this reaction and stimulates the partial oxidation of the olefin to an aldehyde.

In explaining the correlation between selectivity and acidity, it has been suggested that[5,30] the oxidehydrodimerisation of propene proceeds, like oxidation to acrolein, via an intermediate allyl compound, which either carries a weak positive charge or is neutral. As a result of the localisation on an "acid" adsorption site, regarded as a Lewis acid, of the electron of the allyl radical, the latter becomes similar to a cation and sensitive to the addition of an oxygen anion. At sites with a lower acid strength the intermediate compounds are of a more "radical type", which favours their dimerisation. Within the framework of this hypothesis, the promoting effect of basic and acid oxides on the catalytic properties of tin dioxide discussed above can be accounted for by a change in the electronic state of the centre for the adsorption of olefin (Sn^{4+}) via the $Sn^{4+}–O^{2-}–M^{n+}$ linkage in accordance with the electronegativity equalisation principle[11].

Simultaneously with the change in the electronic state of the allyl fragment, the strength of the bond between the allyl fragment and the catalyst surface can apparently also vary as a function of the electronegativity of the adsorption centre[70–72]. On specimens with a reduced acidity, a lower bond strength and an increased mobility of allyl radicals is expected, which increases the probability of their recombination. Conversely, when allyl compounds are bound strongly to the surface there is a greater number of chances of conversion into acrolein or total oxidation products.

It is suggested that the activity of the catalyst in the test reaction involving the migration of the double bond in but-1-ene can be used as a measure of the relative strength of the olefin–catalyst bond[73]. This can be done if the isomerisation is carried out with participation of aprotic centres (the ratio of the *cis*- and *trans*-isomers of but-2-ene formed should be two[74]) under conditions close to those in oxidative catalysis[75]. While maintaining these conditions, it proved possible[71] to show that, with intensification of the isomerising capacity of the catalyst and hence with the strengthening of the bond between the adsorbed olefin and the catalyst, the rate of dehydrodimerisation of propene falls and that of its partial oxidation increases; the results of this study are presented in Fig.5.

For an unambiguous test of the above relations, it is necessary to compare the selectivity not with the overall acidity, as was done in the studies mentioned above, but with acidity of a definite type, in particular with the strength and concentration of the acid Lewis centres. However, the methods for the determination of the acidity of the surface oxides available at present[76] preclude a reliable solution of this problem. Furthermore, the acidity parameters determined by the traditional titration and base adsorption methods correspond to conditions very remote from those in catalytic reactions.

Thus the features described show that catalysts of the oxidative dehydrodimerisation of olefins must have weakly basic properties ensuring a moderate strength of the binding of allyl complexes to the centre of the catalyst and their adequate mobility. Furthermore, the catalysts should not contain components causing the oxidation of the above complexes to unsaturated aldehydes. It has been shown[77] that highly charged ions of electronegative elements such as molybdenum, tungsten, vanadium, tellurium, antimony, etc. play the role of such components.

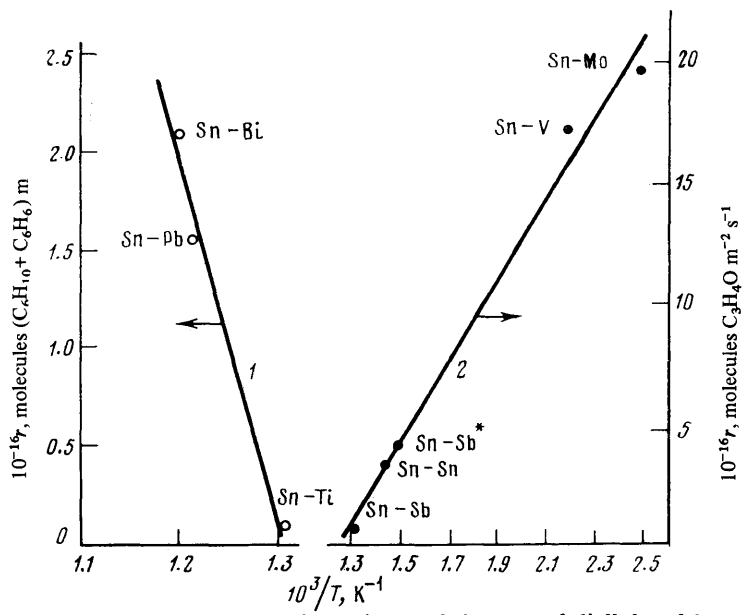


Figure 5. Dependence of the rates of formation r of the sum of diallyl and benzene (line *1*) and acrolein (line *2*) on the isomerising capacity of tin-containing oxide catalysts (on the reciprocal of the temperature $1/T$ corresponding to the attainment of the specified rate of isomerisation of but-1-ene)[71].

These two requirements are satisfied by the oxides of non-transition elements located in the lower left-hand section of the Periodic System. These include zinc, gallium, cadmium, indium, tin, thallium, lead, bismuth, etc. (zinc and cadmium are usually regarded as non-transition elements, because they do not in fact exhibit a variable valence and do not form compounds in which the *d* shell is unfilled[78]). The oxides of all these elements exhibit weakly basic or amphoteric properties and are active to different extents in the oxidative dehydrodimerisation and aromatisation reactions of lower olefins. A considerable proportion of them is also characterised, according to Sokolovskii and Bulgakov[79], by nearly optimum nucleophilic properties of oxygen required to abstract the proton from the olefin and form an allyl complex. The boundary of elements potentially active in the above processes runs along the diagonal drawn through aluminium, germanium, antimony, and polonium. The main product of the oxidative transformation of propene on pure antimony tetroxide[80] and certain antimony-containing oxide catalysts[57,81] is acrolein, while diallyl and benzene are formed in smaller amounts.

Alkali and alkaline earth metal oxides exert a positive influence on the selectivity of the processes when they are introduced in small amounts into the catalyst.

A considerable proportion of the oxides of the elements enumerated above are also incorporated in the set of catalysts recommended by Trimm[82,83]. The author assumes that diallyl is formed by the dimerisation of two allyl radicals linked to the same metal ion whose characteristic valence states differ by two charge units.

3. Kinetics and Mechanisms of the Reactions

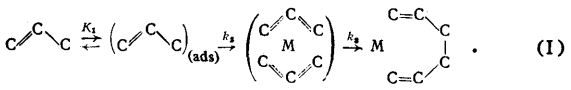
A relatively small number of studies devoted to the kinetics and certain problems of the mechanism of the oxidation of lower olefins to diolefinic and aromatic hydrocarbons are described in the literature. Kinetic studies have been made on the oxydehydrodimerisation of propene on individual thallium[18] and indium[84] oxides. For low degrees of conversion of the hydrocarbon, the main products are hexa-1,5-diene and carbon dioxide, while in the presence of indium oxide acrolein is also formed. Under these conditions, the rates of formation of diallyl and CO_2 are proportional to the concentrations of propene and oxygen raised to a power of 0.4–0.5 and the reactions are inhibited by diallyl and acrolein.

The author described the kinetic data[18,84] by the Langmuir–Hinshelwood equation. According to the model which they adopted, the rate-limiting stage in the process is the formation of hexadiene by the interaction of two molecules of propene and the dissociated oxygen, all adsorbed on the surface. Propene, diallyl, and acrolein are adsorbed competitively at the same sites, while oxygen is adsorbed at other sites. The catalytic centres are tervalent thallium or indium ions, capable of forming π-complexes with the olefin.

In the oxidation of isobutene to 2,5-dimethylhexa-1,5-diene on the same indium oxide, it was shown that the reaction is of first order with respect to the olefin and has a fractional order (0.8) with respect to oxygen[85,86]. This result, as well as the weak adsorption of isobutene on the catalyst, forced the authors to postulate that in the case of isobutene two gas-phase molecules of the latter interact with the dissociatively adsorbed oxygen. In other respects the reaction mechanism does not differ from that adopted for reaction with propene.

The individual kinetic parameters of the reactions under consideration have been determined for a number of bismuth-containing catalysts. Thus, on simple bismuth oxide, the state of dehydrodimerisation of propene is directly proportional to the partial pressure of the hydrocarbon and is independent of the oxygen concentration[12]. It has also been shown that the reactions on the bismuth–iron[87] and bismuth–tin[39] oxide catalysts are of first order with respect to the propene. For the latter catalyst, the reaction was found to be of first order also with respect to oxygen.

The kinetics of the process in the presence of the bismuth–tin catalyst were investigated in greater detail by Seiyama et al.[88], who studied the oxidative dehydrodimerisation of C_3–C_4 olefins under conditions where the products are dehydrodimers and carbon dioxide formed simultaneously. It was found that the rate of dimerisation is proportional to the partial pressure of the hydrocarbon raised to a power of 1.5–2.0 and is independent of the oxygen content in the mixture. The order of the extensive oxidation reaction was found to be close to unity with respect to the olefin and to have a fractional value (~0.5) with respect to oxygen. The authors interpreted[88] the results of the kinetic measurements within the framework of the Langmuir–Hinshelwood scheme for an ideal adsorbed layer, as in the study of Trimm and Doerr[84]. It was assumed that the adsorption of the olefin involves the formation of a π-complex which interacts weakly with the hydrogen atom in the α-position relative to the unsaturated bond and in the vicinity of an oxygen atom on the catalyst surface. Next, the above hydrogen atom is abstracted and a complex of the metal ion with two allyl radicals is formed via the mechanism



(I)

Since the reaction order is nearly two with respect to the olefin and the reaction rate constant varies in opposition to the dissociation energy of the olefin C–H bond in the allyl position (Fig.6), the authors had to assume that the rate-limiting stage is surface dimerisation (k_2). The equation

$$r_{C_6H_{10}} = k_2\left(\frac{K_1 p_{C_3H_6}}{1 + K_1 p_{C_3H_6}}\right)^2 \qquad (1)$$

which follows from this mechanism describes satisfactorily the experimental data obtained on two specimens of the bismuth–tin catalyst. The activation energy for the process on a highly selective specimen is lower by 20 kcal mol^{-1} than on a specimen with a low selectivity, which has been attributed to the presence on the surface of the former of more active centres for the allyl–hydrogen cleavage of propene[5].

Appreciably different kinetic characteristics of the oxidative dehydrodimerisation of propene have been obtained recently in the presence of a bismuth–tin oxide catalyst[89]. These are in the first place a negative variation of the rate of formation of diallyl with the partial pressure of oxygen in the reaction mixture, illustrated in Fig.7*b*, and in the second place the observation that an increase of temperature entails an appreciable decrease of the reaction order with respect to the olefin (from 2.0 at 450 °C to 1.2 at 530 °C). It may be that the discrepancies with the data of Seiyama et al.[88] are caused by the significant differences between the methods of preparation of the specimens, which frequently determine the phase composition and surface properties of the catalyst.

The observed relations can be accounted for by the following scheme[89]

$$\begin{gathered} Z + O_2 \xrightarrow{k_1} ZO_2 \,, \\ Z + ZO_2 \underset{}{\overset{K_2}{\rightleftarrows}} 2ZO \,, \\ ZO + C_3H_6 \xrightarrow{k_3} C_3H_5ZOH \,, \\ C_3H_5ZOH + C_3H_6 \xrightarrow{k_4} C_6H_{10} + H_2O + Z \end{gathered} \qquad (II)$$

(here Z denotes a reduced site on the catalyst surface). Under the conditions investigated, the following kinetic equation of the fractional-rational type corresponds to this scheme:

$$r_{C_6H_{10}} = \frac{k'k''p^2_{C_3H_6}}{k'p_{C_3H_6} + k''p_{O_2}}, \qquad (2)$$

where $k' = K_2k_3^2/2k_1$ and $k'' = k_3k_4/(k_3 + k_4)$. Eqn.(2) describes the experimental data satisfactorily (Fig.7). Other forms of kinetic equations, particularly those of the Langmuir–Hinshelwood type, give a poorer agreement with experiment[90].

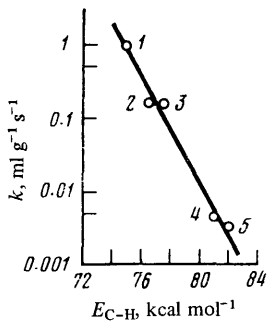


Figure 6. Dependence of the rate constant for the oxide-hydrodimerisation of olefins k on the dissociation energy E of the C–H bond in the methyl group: *1*) but-1-ene; *2*) *cis*-but-2-ene; *3*) *trans*-but-2-ene; *4*) isobutene; *5*) propene[88].

Scheme (II) presupposes that diallyl is formed by the interaction of a gas-phase propene molecule with a surface compound of the allyl type. This mechanism, which may be referred to as of the "impact" type, does not rule out the possibility of the operation of mechanism (I), which involves the stage of the surface dimerisation of allyl radicals. Furthermore, the two mechanisms can coexist. The contribution of mechanism (I) to the overall rate of the process will be evidently determined by the mobility of the allyl compound on the surface, which can depend on the reaction conditions and on the nature of the catalyst. In particular, the acid–base properties of the catalyst can play a significant role in this process[30,71].

In the interpretation of kinetic data in terms of the above mechanism, it is assumed that the oxidative dehydrodimerisation of the olefin proceeds via the formation of a π-allyl complex. This hypothesis is based on the following facts. In the presence of certain oxide catalysts[25,84], the oxide-hydrodimerisation of propene is accompanied by the formation of acrolein, which is known to proceed via an intermediate allyl compound[91]. On the bismuth–tin oxide catalyst, allyl chloride and bromide are converted into benzene in the presence of oxygen, while 2-bromopropene undergoes total oxidation[92]. Finally, the composition and structure of the diolefinic and aromatic hydrocarbons formed are not inconsistent with the allyl mechanism[93].

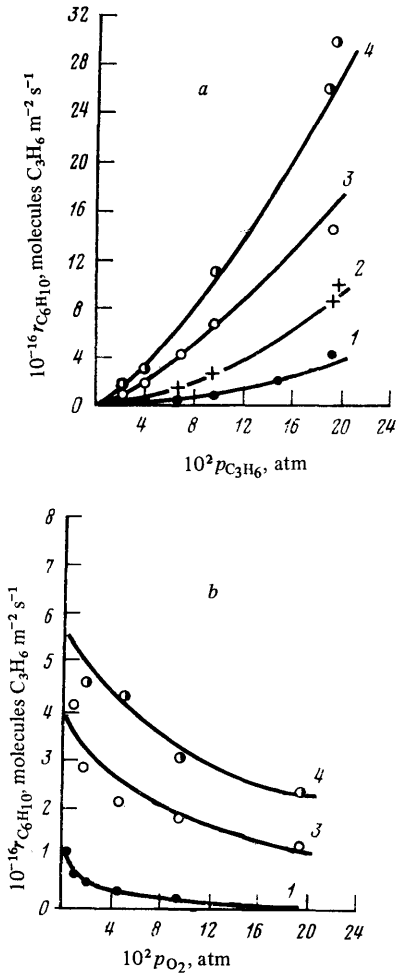


Figure 7. Dependence of the rate of formation of diallyl r on the partial pressures p of propene (*a*) and oxygen (*b*) at different temperatures (°C): *1*) 450; *2*) 485; *3*) 500; *4*) 530. The continuous curves were calculated by Eqn.(2) and the circles represent experimental data[89].

Attempts to demonstrate directly the existence of π-allyl complexes on the surface of the oxidative dehydroaromatisation catalysts have been made. Two forms of propene adsorbed on zinc oxide have been found[94–96] by infrared spectroscopy. At room temperature mainly a π-complex is formed, which is converted at higher temperatures (70 to 125 °C) into a π-allyl surface compound. The ability of zinc oxide to form allyl surface compounds of the radical-like type in the adsorption of propene has been confirmed by EPR[97].

The presence of allyl radicals has been detected also in the gas phase over manganese oxide[47,98,99] and zinc oxide[99] catalysts. It has been established by mass spectrometry that the radical concentration increases with temperature. On the other hand, the latter does not affect the significantly smaller content of free radicals over bismuth molybdate, which is a typical catalyst of the partial oxidation of olefins. These results have been explained[99] in terms of the ideas, described above, concerning the influence of the acid–base properties of the surface of the solid on the electronic structure of the adsorbed compound[11]. It is assumed that the allyl compound on a surface with acid properties (bismuth molybdate) is cationic and readily combines with the surface oxygen to form an unsaturated aldehyde. On the other hand, basic surfaces (manganese and zinc oxides) lead to the formation of free radicals.

On the basis of the results of the oxidation of propene labelled with radioactive carbon in the methylene group, it has been concluded[100] that hexa-1,5-diene is formed in the presence of a silver catalyst via an intermediate compound of the allyl type. However, the lack of data for the isomerisation of propene, the rates and mechanism of which depend on the type of catalyst[101], casts doubt on the validity of the above conclusion. In the case of rapid isomerisation, the mechanism presupposing the formation of a π-complex operates. A choice can apparently be made between these mechanisms on the basis of the results of the oxidative dehydrodimerisation of propene labelled with radioactive carbon and deuterium in different positions.

Another important factor in the mechanism of oxidative reactions involves the question of which forms of oxygen are responsible for the conversion of the hydrocarbon via a particular pathway. In the presence of many oxide catalysts the oxidative dehydrogenation[103,104] and partial oxidation[105,106] reactions of lower olefins, for example, proceed via an oxidation-reduction mechanism involving the oxygen of the surface layer of the catalyst. On the other hand, in the complete oxidation of the same hydrocarbons, the associative mechanism, which does not rule out the involvement in the reaction of forms of oxygen different from that of the oxide, makes an appreciable contribution.

Table 3. Comparison of the rates of the catalytic reaction and of the reduction and oxidation of the bismuth–tin oxide catalyst in the stationary state[107].

Reaction	Temp., °C	Mixt. compn., vol.%		$10^{-16}r$, molecules $m^2 s^{-1}$			
		C_3H_6	O_2	C_3H_6	O_2	C_6H_{10}	CO_2
Catalysis	450	0.67	0.38	1.8	5.16	0.29	4.05
Reduction	450	0.70	—	1.49	—	0.40	2.01
Oxidation	450	—	0.40	—	3.59	—	—
Catalysis	500	0.66	0.40	3.25	8.45	0.62	6.09
Reduction	500	0.67	—	2.45	—	0.65	3.52
Oxidation	500	—	0.38	—	3.69	—	—

Using the data of Gamid-zade et al.[107], the rates of the oxidative dehydrodimerisation and extensive oxidation of propene under the conditions of simultaneous and separate interactions of propene and oxygen with the bismuth–tin oxide catalyst are compared in Table 3. The satisfactory agreement between the rates of formation of diallyl in the catalytic and reduction processes shows that the oxide-hydrodimerisation proceeds via a multistage mechanism involving the separate interaction of the reactants with the catalyst surface. The main bulk of carbon dioxide is also formed from the catalyst oxygen. At the same time, the significantly higher rates of the total oxidation of propene in the catalytic process compared with the rates in the reduction process show that, under the conditions investigated, there is a considerable contribution of the combined mechanism, which diminishes with increase of temperature. It is important to note that the rates of the catalytic reaction and its individual stages have been compared for a catalyst in the stationary state. Under the conditions investigated, the stationary surface area was reduced by 70–80% and was characterised by the absence of weakly bound oxygen (Fig. 4).

The oxygen in the surface of the bismuth–tin oxide catalyst is apparently also involved in the oxidative dehydroaromatisation of propene to benzene. This was shown in a study by a pulsed method of the interaction of propene with the catalyst in the absence of gaseous oxygen[40,108].

The operation of the oxidation-reduction mechanism may be expected on the bismuth–phosphorus[109] and bismuth–titanium[110] oxide catalysts, for which a qualitative correspondence between the catalytic and reduction processes has been established. In the interaction of propene with the individual oxides of bismuth[12,111–113], tin[40,80,113], zinc[113], and indium[113] the same products are obtained (diallyl, benzene, and carbon dioxide) as under the conditions of the catalytic reaction. These findings show that a definite proportion of the products of the oxidative dehydrodimerisation and total oxidation of propene are formed with direct participation of the oxygen of the above catalysts. However, the final conclusion concerning the validity of the oxidation-reduction mechanism or lack of it could be arrived at only on the basis of a comparison of the rates of the catalytic reaction and the separate interactions of the components of the reaction mixture with the catalyst having the stationary composition, as has been done for the bismuth–tin oxide catalyst[107]. Furthermore, this procedure would permit a test, to some extent, of the possibility of the occurrence of the reaction via a heterogeneous-homogeneous mechanism.

It is known[114] that many catalytic reactions, initiated on the surfaces of solids and then transferred to the gas phase, proceed via a radical-chain mechanism. In particular, it has been suggested[115] that both reactions occur simultaneously in the oxidation of propene on certain oxide catalysts. One of these leads to the formation of acrolein via a purely heterogeneous mechanism. The second, homogeneous reaction is initiated by a surface hydroperoxide, formed via the addition of molecular oxygen to the allyl compound.

On this basis, one can assume that hexa-1,5-diene is formed via the gas-phase dimerisation of intermediate radical species (for example, allyl radicals) generated by the catalyst surface. The occurrence of oxidative dimerisation and aromatisation of propene becomes appreciable at high temperatures in excess of 450 °C. Under these conditions, there is a possibility of a weakening of the allyl–catalyst bond and of an increase of the probability of the transfer of allyl to the gas phase. This is supported by the detection of the allyl radical in the gas phase over zinc oxide and manganese oxide catalysts[98,99], which was mentioned above. However, data concerning the involvement of the allyl radical in the formation of diallyl have not so far been obtained. Furthermore, the allyl radicals generated by a pyrolytic procedure exhibit an absolute indifference to the

nature of the catalyst. When they interact with catalysts of the oxidehydrodimerisation and partial and extensive oxidation of olefins, only acrolein is formed[116]. The equality of the rates of the catalytic and reduction processes established for the bismuth–tin oxide catalyst also constitutes evidence against the heterogeneous-homogeneous mechanism, because the surface reduction of oxides usually proceeds via a heterogeneous mechanism[117].

Together with diolefins, aromatic hydrocarbons are formed on many of the known catalysts: benzene is formed from propene and xylenes are formed from butenes[25,93]. The relative content of aromatic hydrocarbons in the reaction products depends both on the chemical nature of the catalyst and on the reaction conditions. It has been noted that, on individual bismuth[12,13], thallium[18], and lead[15–17] oxides, hexa-1,5-diene is formed preferentially, whereas on catalysts of the type of zinc oxide[11], tin dioxide[11,40], and bismuth phosphate[25], the formation of aromatic hydrocarbons is more appreciable. An increase of the yield of the latter with a simultaneous decrease of selectivity with respect to diolefins is also promoted by an increase of contact time[45,84], which shows that hexa-1,5-diene is converted into aromatic hydrocarbons in successive stages.

It has been suggested[45,93] that benzene is formed via the oxidative dehydrogenation of hexa-1,5-diene to hexatrienes, the conversion of hexatrienes into cyclohexa-1,3-diene, and oxidative dehydrogenation of the latter to the aromatic compound. This mechanism is supported by the results of the oxidation of hexa-1,5-diene and cyclohexa-1,3-diene, which are converted respectively into a mixture of benzene with hexa-1,3,5-triene and benzene[93]. Furthermore, in the presence of many catalysts[12,13,22], the products include, together with diallyl and benzene, also cyclohexa-1,3-diene, which is the only cyclic diolefin detected.

Trimm and coworkers[84,85] put forward a somewhat simplified mechanism for the aromatisation of hexadienes having excluded from consideration the hexatriene formation stage. Having failed to detect hexatrienes among the reaction products, the authors suggest that the hexadiene localised on the catalyst surface is converted into cyclohexa-1,3-diene, which can then migrate to the catalytic centre, ensuring the formation of benzene. However, the absence of trienes from the reaction products cannot serve as an adequate justification for their exclusion from the formal reaction mechanism. One can assume that, by virtue of their high reactivity, the hexatrienes formed undergo readily and rapidly thermal "cycloisomerisation" to cyclohexadienes[118], as happens in the C_6-dehydrocyclisation of paraffinic hydrocarbons[2].

Indeed, Vaabel' et al.[119,120], who studied in detail the reactions of hexa-1,5-diene, cyclohexene, cyclohexa-1,3-diene, and benzene in the presence of the bismuth–tin oxide catalyst, showed that the hexatriene formed under the conditions of the oxidative dehydrodimerisation of propene cyclises and aromatises at a high rate. They also established that the pathway followed in the cyclisation of hexa-1,5-diene via cyclohexene cannot be the main one.

The facts described suggest that the oxidative dehydroaromatisation of olefins is a complex consecutive reaction, whose mechanism can be represented as follows in the case of propene:

$$\text{propene} \xrightarrow{1} \text{hexa-1,5-diene} \xrightarrow{2} \text{hexa-1,3,5-triene} \xrightarrow{3}$$

$$\text{cyclohexa-1,3-diene} \xrightarrow{4} \text{benzene.}$$

All the oxidative dehydrogenation stages (*1*, *2*, and *4*) are catalytic, while the cyclisation stage (*3*) is thermal, by analogy with the dehydrocyclisation process[2].

III. OXIDATIVE DEHYDRODIMERISATION OF OTHER HYDROCARBONS WITH MULTIPLE BONDS

The oxidative dehydrodimerisation and aromatisation of lower olefins is a special case of the more general type of reactions, which apparently extend to a wide range of compounds containing multiple bonds.

Reports of the vapour-phase heterogeneous-catalytic dehydrodimerisation of a number of compounds have been published mainly in the patent literature. Thus American investigators have patented[44,121,122] a procedure, which is feasible in principle, for the oxidative dehydrodimerisation of substances having the general formula YCRR'H to compounds of the type $(YCRR')_2$, where $Y = CH_2=CH$, Ph, CN, COOH, COOR, CO, or $CH_2=CX$ (X = halogen, alkyl, or allyl) and R and R' = hydrogen, C_1–C_6 alkyl groups, or aryl groups. The oxides of bismuth, chromium, iron, and a number of other elements, promoted by alkali metal compounds, have been suggested as catalysts. However, specific example of the processes described in the patents are confined to propene.

Among the substances enumerated above, alkyl derivatives of aromatic compounds have been studied in greatest detail. In particular, a relatively large number of patents are devoted to the selection of catalysts and the development of methods for the oxidative dehydrodimerisation of toluene to bibenzyl and stilbene.

Catalysts which are effective in the oxidehydrodimerisation reactions of lower olefins are also active in the oxidative dehydrocoupling of mono- and di-substituted benzenes. These include catalysts based on bismuth and antimony oxides with promoting additives[34,123], lead oxide on a carrier[15,16], the bismuth–tin oxide catalyst[124,125], the bismuth–iron oxide catalyst[125], and a number of others. The activity of noble metals and their oxides, hydroxides, and halides deposited on a zeolite or an aluminosilicate in these processes has also been reported[126].

The catalytic properties of the bismuth–tin oxide system have been studied in greatest detail. It has been shown[127] that the $Bi_2Sn_2O_7$ phase is formed in the course of the preparation of the catalyst, its content increasing with increasing heat-treatment temperature. At the same time the activity of the catalyst in the oxidative dehydrodimerisation of toluenes is found to increase. However, the bismuth pyrostannate phase is unstable in the atmosphere of the reaction medium at high temperatures. At 600 °C it is converted into the α-Bi_2O_3, γ-Bi_2O_3, and $Bi_{12}SnO_{20}$ phases. The bismuth–tin oxide catalysts retain a constant activity only in the course of the first three hours of operation, after which the activity and selectivity of the catalyst decrease slowly owing to coke deposition. After regeneration with air, the catalysts fully recover their properties[128].

The maximum selectivity in the formation of bibenzyl and stilbene (45%) is observed at 500 °C. With increase of temperature, the selectivity falls due to the oxidative dealkylation of toluene to benzene. With increase of the conventional contact time and the oxygen/toluene ratio in the mixture, the selectivity with respect to stilbene increases and that with respect to bibenzyl falls. These results show that stilbene is formed from bibenzyl via its oxidative dehydrogenation[128].

Oxidative dehydrodimerisation reactions of alkyl derivatives of aromatic hydrocarbons proceed much more selectively in the presence of molecular iodine. The latter arrives on the catalyst layer together with oxygen as part of the initial mixture[129–131] or is formed directly in the reaction zone as a result of the action on the catalyst by the components of the

reaction mixture, as happens in the familiar catalyst of the Shell Company (a mixture of LiI, LiOH, and Li_2SO_4 melts)[132]. For example, when melts of lithium and lead iodides are used, it is possible to achieve the dehydrocoupling of toluene to stilbene, of toluene and propene to naphthalene, and of isopropylbenzene to *p*-terphenyl[133].

It has been suggested in a number of patents[16,122,134,135] that hydrogen split off in the dehydrodimerisation of alkyl derivatives of aromatic hydrocarbons be combined with the oxygen of the metal oxides. Among the latter, mention is made of the individual and deposited oxides of bismuth, cadmium, lead, and arsenic. During the reaction, the oxides are reduced and periodic reoxidation is necessary.

Benzene apparently undergoes vapour-phase oxidative dehydrodimerisation with much more difficulty. There has been only one report of a study[126] in which noble metals were used as catalysts for this purpose. There is absolutely no information about the ability of oxides to catalyse the oxidative conversion of benzene into biphenyl. This may be explained by the fact that the dissociation energy of the C–H bond in the benzene ring (102 kcal mol^{-1}) is significantly higher than in the methyl groups of toluene and propene (83 kcal mol^{-1}).[136] In other words, the formation of phenyl radicals $C_6H_5^{\bullet}$ is energetically less favourable than that of benzyl radicals $C_6H_5CH_2^{\bullet}$, which are believed[137] to behave as intermediates in the oxide-hydrodimerisation of toluene. Furtherfore, as a consequence of the delocalisation of the π-electronic charge of the ring or the C=C bond with participation of a partially vacant orbital, the benzyl and allyl radicals exhibit an increased stability[138], which should also favour their dimerisation. The formation of the benzyl radical on the surface of zinc oxide in the adsorption of toluene has been demonstrated spectroscopically[139].

The high reactivity of lower olefins and toluenes in oxidative dehydrocoupling reactions compared with benzene indicates the possibility of the involvement in such reactions of a large number of hydrocarbons having a mobile hydrogen atom in the α-position relative to the unsaturated bond. Here one should expect the occurrence of the following consecutive stages: the abstraction of the above hydrogen atom following the adsorption of the hydrocarbon on the surface of the appropriate catalyst, dimerisation of the molecular fragments, oxidative dehydrogenation of the dimer, and, its subsequent cyclisation and aromatisation, provided that this is allowed by the structure of the compound formed.

IV. CONCLUSION

The study of heterogeneous-catalytic dehydrodimerisation and cyclisation reactions in the presence of molecular oxygen was begun comparatively recently and so far embraces a limited number of catalysts and a narrow range of hydrocarbons. Certain aspects of the conversion of substances on the surface of catalysts and the mechanisms of the action of the latter remain unelucidated. Nevertheless, the results obtained show that these reactions are fairly complex and represent a set of consecutive stages.

Oxidative dehydrodimerisation reactions of hydrocarbons are accompanied by a number of side reactions involving total and partial oxidation. The discovery of the principal features of reactions of the above type is therefore of interest for the theory of oxidative catalysis as a whole.

By virtue of the involvement of oxygen, oxidative dehydrodimerisation processes differ from the dehydrocyclodimerisation reactions of lower paraffins and olefins[1], which have been thoroughly investigated and have much in common with oxidative heterogeneous catalytic processes. In the first place the common features of their mechanisms should be noted. As shown in this review, the oxidative dehydrodimerisation of lower olefins on oxide catalysts proceeds via a mechanism involving the separate interaction of the reactants with the surface of the catalyst. A considerable proportion of the total oxidation products are formed via a combined mechanism, whose contribution to the overall rate of reaction diminishes with increase of temperature. The conversion of olefins on many oxide catalysts of the partial oxidation reaction proceeds similarly[103–106].

The similarity of the mechanisms is also manifested in the reaction kinetics. Both in the partial oxidation[91] and oxidative dehydrodimerisation[88] of lower olefins, the rate-limiting stage involves the dissociation of the C–H bond in the allyl position. Furthermore, with increase of the oxygen content in the reaction mixture, the selectivity with respect to the mild reaction product (diallyl) increases and that with respect to the extensive oxidation products increases[89], as has been observed in the oxidation of ammonia and a number of organic substances[140,141].

An increase of the binding energy of the surface oxygen on oxide catalysts leads to a decrease of the rate and an increase of the selectivity of the partial oxidation[60,61]. Similar relations have been established for the oxidehydroaromatisation of propene on simple oxides[11]. As a consequence of this, the mode and rate of conversion of olefins on dehydrodimerisation catalysts depend on the strength of binding of oxygen and the degree of surface coverage by the latter. The features observed for the bismuth–tin oxide catalyst show consistently[69,107] that a necessary condition for the selective action of the catalyst is the absence of weakly bound oxygen from its surface. In the stationary state the surface of the catalyst is characterised by a high degree of reduction and the presence of energetically homogeneous oxygen with a relatively high binding energy (90 kcal mol^{-1}). It is of interest to note that this quantity is close to the binding energy of oxygen in the stationary state on a number of selective partial oxidation catalysts[142,143].

Finally, one can postulate that the binding energy of oxygen is not the only factor determining the selectivity of oxide catalysts in oxidative dehydrodimerisation of olefins. In order to obtain a high selectivity in the presence of strongly bound oxygen, specific activation of the hydrocarbon molecule is apparently necessary, as in the mild oxidation processes[106]. It is not fortuitous that the bismuth–tin oxide catalyst, which consists of a combination of metal cations on which highly reactive allyl compounds are formed and stabilised, catalyses effectively the oxidehydrodimerisation of propene. The extension of the range of catalysts investigated will permit a comparison of the selectivities with the binding energies of oxygen and will provide a more unambiguous answer to this question.

The factors enumerated permit the conclusion that the oxidative dehydrodimerisation of unsaturated hydrocarbons is a typical example of the large class of heterogeneous-catalytic reactions with participation of molecular oxygen and that the principal relations determined previously for partial and total oxidation reactions of hydrocarbons are applicable to this process. This must be taken into account in selecting catalysts.

At the same time there is a considerable difference in the approaches to the solution of the problem of the selection of catalysts for the oxidative dehydrodimerisation and partial oxidation of olefins. This follows from the opposite variation of the activities of the oxide catalysts in these reactions with

their acid–base properties[30,70–72] and is associated with the type of conversion of the allyl type intermediates. The oxidation of the latter to unsaturated aldehydes requires the presence on the catalyst surface of Lewis acid centres with an enhanced strength and of electrophilic oxygen, which is achieved by combining amphoteric and acid oxides[79]. On the other hand, effective dimerisation requires weak acid centres and the absence of electrophilic oxygen. Such properties are characteristic of the oxides of weakly basic and amphoteric elements, combinations of which should apparently be sought as a basis for catalysts of the oxidative dehydrodimerisation of unsaturated hydrocarbons. The majority of the catalysts discussed in this review are consistent with this postulate.

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