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Intermediates and mechanisms of heterogeneous catalytic reactions. Oxidation reactions involving molecular oxygen and sulfur

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Abstract. The structure of the intermediate surface compounds in heterogeneous catalytic oxidation reactions involving molecular oxygen and sulfur is discussed. The degrees of reliability of the role of various proposed structures in catalysis are evaluated. The reaction mechanisms derived from information on the surface complexes are presented. The bibliography includes 141 references.

I. Introduction

In our previous review[1,2] we have discussed the intermediate surface compounds observed during spectroscopic surface studies under the conditions of various heterogeneous catalytic reactions. The present review, which concludes the series, deals with oxidation reactions involving oxygen and sulfur. These reactions differ from those previously considered[1,2] by strongly involving atoms from the catalyst lattice.

The problem of the intermediate form of both the oxygen and the substance to be oxidised, and of the mechanism of their activation, invariably arises in studies of the mechanism of oxidation reactions.

Oxygen can be incorporated in an oxide lattice, or convert a metal into an oxide. In these cases the lattice can be treated as an intermediate form. The ionic forms O_2^-, O^{2-}, and O^- were observed by EPR and Raman spectroscopy during the reduction of the O_2 molecule to the regular lattice of O^{2-}. They were treated as compounds taking part in the catalytic reaction.

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II. Oxidation of carbon monoxide

The simplest oxidation reaction is the oxidation of CO. Its mechanism has been studied by many workers both on metals and on nonmetals. In particular, detailed studies have been made of the oxidation of CO on the faces of single crystals of the metals Pt, Pd, Ir, Ru, and Rh.[3]

On Pd(111) this reaction has been studied at low pressures (1.5 Torr) by absorption-reflection IR spectroscopy combined with kinetic measurements.[4] The rate of the reaction depended on the coverage of the surface by carbon monoxide.

The adsorption of CO and O_2 was also studied by low-energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPES). It is widely thought that at temperatures close to or below that of the catalytic reaction CO is adsorbed as bridging or linear carbonyls. Oxygen is adsorbed in a molecular or an atomic form. The mechanism of their interaction can include the following steps:

$$CO \rightleftharpoons CO_{ads},$$

$$O_2 \longrightarrow 2\,O_{ads},$$

$$O_{ads} + CO_{ads} \longrightarrow CO_2,$$

$$O_{ads} + CO \longrightarrow CO_2,$$

$$O_2 + 2\,CO_{ads} \longrightarrow 2\,CO_2.$$

The last of these reactions can be ignored, because the formation of CO_2 is not observed on a surface saturated with CO and exposed to gaseous oxygen. The interaction of CO with O_{ads} can take place with CO either in the gas phase (the Eley–Rideal mechanism) or in the adsorption layer (the Langmuir–Hinshelwood mechanism).

In the various mechanisms for the interaction of CO with C_{ads} it is assumed that the reaction takes place between neighbouring O_{ads} and CO_{ads} species, between more distant species (when the reaction is made possible by surface diffusion), or on the boundary of surface islets consisting of O_{ads} and CO_{ads}.

It is not self-evident that the effects observed at very low pressures can occur also at the higher pressures more commonly used in catalysis. It has been suggested[3] that since the pressure ratio

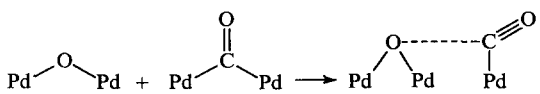
$$r = k\frac{P_{O_2}}{P_{CO}},$$

occurs in the rate equation for the reaction the rate should be independent of the total pressure, and therefore all the features of the reaction should be the same at low and at high pressures.

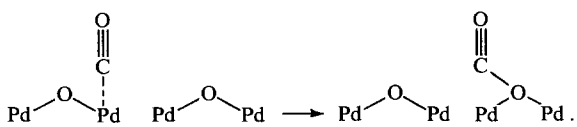
The same forms of adsorbed CO and oxygen were observed in a study by IR spectroscopy of the oxidation of CO on Pd at steady state.[5]

Bridging and linear forms of adsorbed CO, located both on terraces and on steps, were observed[6] on a Pt(335) surface by IR absorption–reflection spectroscopy. The carbon monoxide on the steps was oxidised substantially faster than the carbon monoxide on the terraces.

The oxidation of CO on Pd supported on a layer of SiO_2 deposited on a Mo(110) crystal face was studied by absorption–reflection IR spectroscopy and by temperature programmed desorption (TPD) over a wide range of pressure (10^{-9}–10^{15} Torr) and temperature (70–700 °C).[7] At low pressures the CO and the oxygen were adsorbed separately, probably as islets. In order to induce the reaction a CO molecule must diffuse into an islet of O_{ads}, surmounting the opposing barrier as a result of the exothermic reaction



At high pressures and relatively low temperatures a shift in the CO frequencies was observed in the stationary state, and attributed[7] to the simultaneous adsorption of CO and O on the same atom of Pd (O–Pd–CO), or to the formation of the weakly adsorbed precursor



The transition state is reminiscent of the CO_2 molecule. We know[8] that the vibrational excitation of the CO_2 molecule is strongest when the molecule is formed in a layer strongly covered with oxygen before being desorbed. Under certain conditions this can give rise to a 'pressure gap': a large difference between the effects observed at high and at low pressures.

A study of the EELS spectra during the oxidation of CO on Rh(111) showed[9] that the Rh–O–CO_2 complex, stabilised by OH groups, is formed on oxidised rhodium (i.e. in an excess of O_2). Carbon dioxide adsorbed on a clean Rh–O surface is desorbed at a temperature 100 K lower than from a Rh–OH surface.[9] It was concluded that the decomposition of the carbonate species could be rate-limiting.

Many studies of the oxidation mechanism of CO were carried out on supported metals,[10–21] because in these systems the specific surface of the catalyst is much greater and the intensity of the IR bands is correspondingly high.

According to Cant and Donaldson[10] the CO absorption band at 2075 cm^{-1} is unchanged during the interaction of CO with O_2 on Pt/SiO_2 at 40–50 °C. The kinetic order of the reaction (first order) with respect to the coverage of the surface with CO molecules (θ_{CO}) is attributed[10] to the location of the reaction at the boundary between CO_{ads} and O_{ads} islets.

A study of the IR spectra in the transition regime during the oxidation of CO on a 9.1% Pt/SiO_2 catalyst at 100–160 °C detected[11] a transition from the Eley–Rideal to the Langmuir–Hinshelwood mechanism as the adsorption of CO increased. However, unambiguous spectroscopic studies (i.e. studies of the kinetics of the intensity changes of the IR bands of the adsorbed species) were not attempted.

A study in which the rate of the reaction on Pt/SiO_2 was compared with the kinetics of the change in the Fourier transform IR (FTIR) spectra has been reported.[12] At 300 °C, when the rate of the reaction was high, the coverage θ_{CO} was less than 1% (i.e. below the sensitivity limit of the apparatus). Linearly bound CO was observed under conditions of low catalyst activity.

Simultaneous measurements of the band intensities in the FTIR spectra with one-second resolution and of the rate of the reaction in the transition regime were carried out[13] on Pt/Al_2O_3 at 140 °C. Self-oscillations were observed, with four linear forms of adsorbed CO and one bridging form. The linear CO–Pt form (2073 cm^{-1}) responds most rapidly to a change in composition of the gas phase. The yield of CO_2 is most accurately correlated with the intensity of the absorption band of the linear form (2092 cm^{-1}), which corresponds to the adsorption of CO on a Pt atom adjacent to a Pt–O bond. The following mechanism has been proposed for the oxidation mechanism of CO on Pt:

$$O_2 + 2\,Pt_n \overset{(1)}{\rightleftharpoons} 2\,Pt_nO,$$

$$O_2 + 2\,Pt \xrightarrow{(2)} 2\,PtO,$$

$$CO + Pt_nO^* \xrightarrow{(3)} CO^*Pt_nO^*,$$

$$CO^*Pt_nO^* \xrightarrow{(4)} Pt_n + CO_2,$$

$$CO + Pt \overset{(5)}{\rightleftharpoons} PtCO^*,$$

$$CO + 2\,Pt \overset{(6)}{\rightleftharpoons} Pt_2CO^*,$$

$$CO + PtO \overset{(7)}{\rightleftharpoons} PtOCO^*,$$

$$PtOCO^* \xrightarrow{(8)} Pt + CO_2,$$

$$PtCO^* + Pt_nO \xrightarrow{(9)} CO^*Pt_{n+1}O^*,$$

$$CO^*Pt_{n+1}O^* \xrightarrow{(10)} Pt_{n+1} + CO_2,$$

$n > 2$, surface compounds are shown by an asterisk.

Reactive oxygen is formed with the participation of at least two Pt atoms. The monoxide is easily formed, but when adsorbed on PtO it is inactive in this reaction. The reaction between O* and CO* can take place if the O* diffuses to a CO* centre or if gaseous CO interacts with PtO*. The reaction is possible also at the boundaries of the CO islets, where the linearly adsorbed CO can react, though this species has no activity when located within the islet.[14]

Also the oxidation of CO on Pt/SiO_2 and Pd/SiO_2 at 80–320 °C has been studied by FTIR spectroscopy with one-second resolution, and the kinetics of the reaction were studied with a quadrupole mass spectrometer.[15] It was found that the dissociation of O_2 is probably the rate-limiting step, and the adsorption of CO is a fast process. All three forms of CO react with O_2 at the same rate. The model proposed for the reaction assumes the presence of CO islets with very reactive boundaries.

In a study of the reaction of CO with O_2 on Ru/SiO_2, Rh/SiO_2, and Pd/SiO_2 it was found that the linear and the bridging forms of CO react faster than the dicarbonyl forms.[16] On Pt supported on graphite the bridging forms of CO have a greater reactivity than the linear forms (Pt–C≡O).[17] Conversely, it was reported[20] that on Pd–Rh/SiO_2 the linear forms of CO are more active than the bridging forms. According to Anderson[18] on Pt–Rh/Al_2O_3 only the linear forms adsorbed on the Pt can contribute to the reaction. The $Rh(CO)_2$ forms are not active in this reaction.

Six forms of surface carbonyl were detected on Rh supported on SiO_2, Al_2O_3, or La_2O_3: Rh–CO, Rh_2–CO, Rh^+–CO, $ORh^+(CO)_2$, ORh^+CO, and $Rh^+(CO)_2$.[19] The following reaction mechanism was proposed:

$$Rh^0 + CO \xrightarrow{(1)} Rh^0CO,$$

$$Rh^0 + \tfrac{1}{2}O_2 \xrightarrow{(2)} Rh^+O_l \rightleftharpoons Rh^+O_s \rightleftharpoons Rh^0O_s,$$

$$Rh^+O_s + Rh^0CO \xrightarrow{(3)} CO_2,$$

$$Rh^+O_s + CO \xrightarrow{(4)} O_sRh^+CO \xrightleftharpoons{CO} O_sRh^+(CO)_2,$$

$$Rh^+ + O_2 \xrightarrow{(5)} Rh^{n+}O_s \xrightarrow{CO} Rh^+ + CO_2,$$

$$O_sRh^+(CO)_2 \xrightarrow{(6)} Rh^0CO + CO_2,$$

$$O_sRh^+CO \xrightarrow{(6a)} Rh^0 + CO_2.$$

Here O_s is oxygen on the surface, and O_l is oxygen in the lattice.

The breakdown of the complexes with formation of CO_2 takes place at high temperatures. When transition metal oxides are added to the supported metals the lattice oxygen also contributes to the oxidation of CO. On $Pd-CeO_x/Al_2O_3$ the kinetics of the oxidation of CO have been studied by EPR.[21,22] It was found that the low-temperature (100–150 °C) reaction takes place only on catalysts which contain the reactive $O_2^- - Ce^{4+}$ ion. The kinetics of the change in concentration of the O_2^- ion at 100 °C correspond to the kinetics of the oxidation of the CO. In the high-temperature region (> 200 °C) the O_2^- form is not observed. As reported,[21] in this case the lattice oxygen $O^{\delta-}$ takes part in the reaction.

In a study by FTIR spectroscopy of the oxidation of CO on Au supported on Co_3O_4, α-Fe_2O_3, or TiO_2 carboxylate and CO_3^{2-} groups were seen on the catalyst surface, and the last names disappeared during the reaction.[23] Nevertheless a mechanism which ascribed the formation of CO_2 to the decomposition of carboxylates was proposed.

The oxidation of CO at 20 °C on Ag/Y_2O_3 and Cu/Y_2O_3 has been studied by EPR.[24] At low concentrations of Cu and Ag the reaction followed the mechanism

$$e \longrightarrow \square_O^- \xrightarrow{2\,CO} (CO)_2^- \xrightarrow[-CO_2]{O_2} O_2^- \xrightarrow[-CO_2]{2\,CO} CO_2^- \longrightarrow CO_2 + \square_O + e,$$

$$CO + 2\,O_2^- \longrightarrow CO_3^{2-} + \square_O,$$

$$e + Ag^{2+}(Cu^{2+}) \longrightarrow Ag^+(Cu^+).$$

$\square_O$ is an oxygen vacancy.

At high concentrations of Ag or Cu the reaction follows a different path:

$$Ag^+(Cu^+) + CO + 2\,O^- \longrightarrow Ag^{2+}(Cu^{2+}) + CO_3^- + 2e + \square_O,$$

$$CO_3^- \longrightarrow O^- + CO_2,$$

$$e + Ag^{2+}(Cu^{2+}) \longrightarrow Ag^+(Cu^+),$$

$$Ag^+(Cu^+) + CO \longrightarrow Ag^+(Cu^+)\text{–}CO,$$

$$\tfrac{1}{2}O_2 + 2e + \square_O \longrightarrow O^{2-}.$$

The participation of conduction electrons and of lattice oxygen is stipulated also for the oxidation of CO on oxides. The oxidation of CO on ZnO after exposure to light was studied[25] by EPR between −50 and +80 °C, and the following reactions were observed:

$$Zn\text{–}O^- + CO \longrightarrow Zn\text{–}CO_2^-,$$

$$Zn\text{–}CO_2^- \longrightarrow Zn\text{–}CO_2 + e,$$

$$Zn\text{–}CO_2^- + O_2 \longrightarrow Zn\text{–}CO_2 + O_2^-,$$

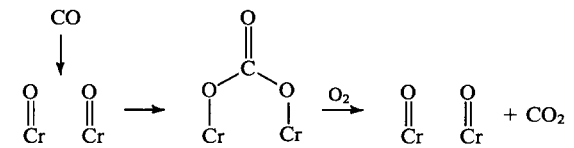
$$Zn\text{–}\square\text{–}Zn + 2e \longrightarrow Zn\text{–}O\text{–}Zn + Zn_i^0,$$

$$Zn\text{–}\square\text{–}Zn + \tfrac{1}{2}O_2 \longrightarrow Zn\text{–}O\text{–}Zn,$$

Zn_i^0 is an interstitial zinc atom.

According to data on the potentiometric monitoring of the state of an MnO_x surface[26] a metastable state of the oxide is produced under the condition of CO oxidation at 138–310 °C. The oxygen does not fill the anion vacancies on the surface but takes part in the catalytic reaction.

The mechanism of the oxidation of CO on Cr_2O_3,[27,28] ZnO,[29] and CuO,[30,31] was studied by IR spectroscopy (but not in situ). On Cr_2O_3 surface carbonates of type **1** are formed after the admission of a CO + O_2 mixture at low temperatures. At 150 °C their rate of decomposition with formation of CO_2 is quite high. In a flow of CO + O_2 the rate of decomposition of the carbonates is two orders of magnitude higher in the absence of O_2. In both cases the rate of decomposition of the carbonates is close to the rate of formation of CO_2. The following associative mechanism has been proposed[27,28] for the reaction:



1

Above 300 °C almost no carbonate groups are formed on the Cr_2O_3 surface. At this temperature the increase in the reactivity of the lattice oxygen produces a transition from an associative to a dissociative mechanism. The oxidation of CO can also take place without the participation of molecular oxygen from the gas phase. The acceleration of the decomposition of carbonates in the presence of O_2 has been observed also on ZnO.[29] According to EPR data the O_2^- ion radical contributes to this decomposition (oxidation). On the surface of CuO both carbonyl and carbonate compounds can exist.[30,31] The Cu^{2+}–CO carbonyl complexes are formed only at subzero temperatures. They are then oxidised according to the scheme:

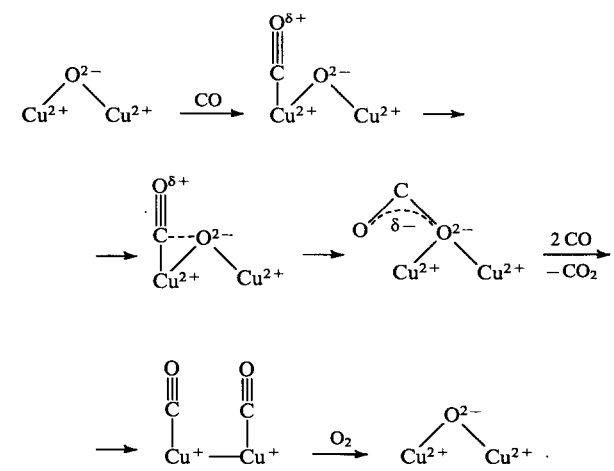
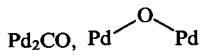
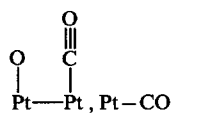
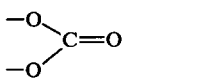
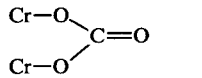
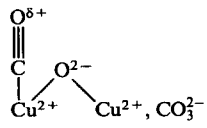
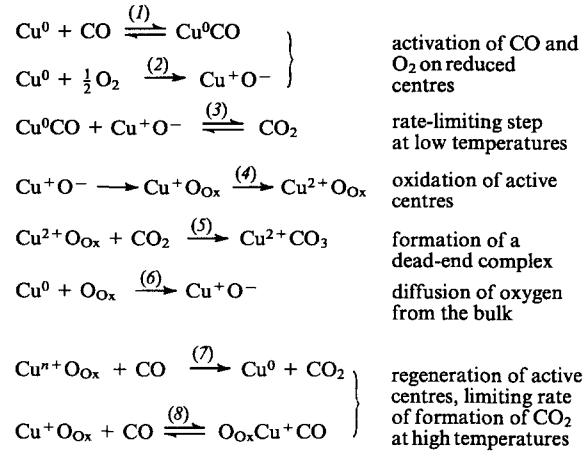


Table 1. Intermediate compounds in the oxidation of CO.

Catalyst	Intermediate complex	Reliability[a]	Ref.
Pt, Pd, Rh, Ir	M–CO, M_2CO, M–O	M	5,6
Pd/SiO_2-MoO_3	Pd–O–Pd–CO, Pd_2CO, 	H	7
Pd(111)	Pd–CO	H	4
Rh(111)	HO–Rh–O–CO_2	M	9
Pt/SiO_2	Pt–CO, Pt_2CO	H	10–12
Pt/Al_2O_3		H	13
Pt, Pd, Ru, Rh on SiO_2	M–CO, M_2CO	H	15,16
Pt/graphite	Pt_2CO	L	17
$Pd-Rh/SiO_2$	Pd–CO, Rh–CO	M	20
$Pd-Rh/SiO_2$	Pd–CO	M	18
Rh on SiO_2, Al_2O_3, La_2O_3	Rh^0CO, Rh^+CO, $ORh^+(CO)_2$, ORh^+CO, Rh_2CO, $Rh^+(CO)_2$	L	19
$Pd-CeO_2/Al_2O_3$	$Ce-O_2^-$	M	21,22
Au on Co_3O_4, Fe_2O_3, TiO_2		L	23
Cu/Y_2O_3, Ag/Y_2O_3,	O_2^-, CO_2^-	M	24
ZnO	$Zn-O^-$, $Zn-CO_2^-$	M	25,29
Cr_2O_3		M	27,28
CuO		L	30,31
CuO	Cu–CO, Cu^+-O_{ads}	H	32,33

[a] Here and elsewhere the symbol H denotes a high level of reliability, M a medium level, and L a low level.

In the presence of O_2 the surface carbonates are decomposed, possibly by a displacement mechanism (associative substitution). The overall rate of formation of CO_2 by the dissociation of all the carbonates is close to the observed rate of oxidation of CO on CuO. In spite of statements to the contrary,[30] a study by FTIR spectroscopy failed to detect surface carbonates under the conditions of the oxidation of CO on CuO.[32] It was suggested that the surface carbonates are formed by the readsorption of CO_2, i.e. they are dead-end forms. The following reaction mechanism was proposed:



A similar conclusion (that the carbonates are dead-end compounds) was reached in a study[33] of the oxidation of CO on a $CoO-Co_3O_4$ catalyst.

The intermediate compounds observed in the oxidation of CO are listed in Table 1. Thus, it has been shown fairly reliably that surface carbonyls and atomic oxygen take part in the oxidation of CO on both metals and oxides. Apparently the carbonates are dead-end compounds. At low temperatures we can observe the formation of associative complexes, in which O_{ads} and CO_{ads} are bound to the same or to neighbouring metal atoms on the surface.

III. Oxidation of ammonia

The oxidation of ammonia to NO and H_2O takes place on the platinum metals at high temperatures (800–1000 °C), when the reaction follows mainly a heterogeneous–homogeneous mechanism. Spectroscopic studies were carried out at lower temperatures. Under these conditions the reaction products include nitrogen and the nitrogen oxides N_2O and NO. On massive platinum the oxidation of ammonia was studied by emission IR spectroscopy,[34] which detected the formation of NH_2 species. The complex $Ag(NH_3)_x(NO)_y$ was observed on a silver surface, and NO_{ads} on an iron surface. On catalysts having a high activation energy for NH_3 a complex corresponding to the initial stages of the reaction is formed (in the case of Pt, the NH_2 entity). On the other hand if the catalyst has a low activation energy the species adsorbed on its surface participate in the later stages, closer to the stages which take the reaction to completion (in the case of Fe this is the adsorbed NO molecule). The formation of HNO, which apparently dissociates into OH and N_{ads}, has been observed[35] by EELS and thermal desorption methods during the oxidation of ammonia on Pt(111).

After carrying out the $NH_3 + O_2$ reaction on an MgO–CoO catalyst spectral bands corresponding to the NO_2^- and NO_3^- groups were observed[36] in the IR spectra measured at room temperature. The following mechanism for the formation of these groups was proposed:

$$Co^{2+}O^{2-} + NH_3 \longrightarrow NH_2^- Co^{2+}OH^-,$$

$$Co^{2+} + O_2 \rightleftharpoons Co^{3+}O_2^- \text{ (from EPR data)},$$

$$2\,NH_2^- + 3\,Co^{3+}O_2^- + 2\,O^{2-} \longrightarrow$$

$$\longrightarrow 2\,NO_2^- + 4\,OH^- + 3\,Co^{2+},$$

$$NH_2^- + 2\,Co^{3+}O_2^- + O^{2-} \longrightarrow$$

$$\longrightarrow NO_3^- + 2\,OH^- + 2\,Co^{2+}.$$

The following reactions are also possible:

$$2\,NH_3 + 3\,Co^{3+}O_2^- + 4\,O^{2-} \longrightarrow \longrightarrow 2\,NO_2^- + 6\,OH^- + 3\,Co^{2+},$$

$$2\,NH_3 + 4\,Co^{3+}O_2^- + 4\,O^{2-} \longrightarrow \longrightarrow 2\,NO_3^- + 6\,OH^- + 4\,Co^{2+}.$$

The formation of NO^- also cannot be excluded, but the NO^- bands in the IR spectrum are obscured by those of NO_2^- and NO_3^-.

An IR spectroscopic study[37] of the interaction of NH_3 with O_2 on MgO detected the NH_2^- complex on the surface. The $Si-NH_2$ and $Fe-NH_2$ complexes formed during the oxidation of ammonia on Fe_2O_3/SiO_2 have been described.[38] In the oxidation of NH_3 under the influence of NO on NaY zeolite Naito and Tamaru[39] observed the double complex $Ag(NH_3)_x(NO)_y$, which decomposes into N_2 and H_2O. It was shown[40-42] that the surface ammonium ion is an intermediate in the oxidation of ammonia by nitrogen oxides on V_2O_5 catalysts. We note that the information on the surface compounds given in the latter reports was obtained under conditions far removed from those of a practical catalytic reaction. Therefore it is doubtful whether or not the specified complexes have any relevance to actual reactions. The only exception is a group of papers[43-45] in which the role of the surface complexes is determined on the basis of simultaneous measurements of the reaction rate and of the rate of conversion of the surface compounds.

Table 2. Intermediate compounds in the oxidation of ammonia.

Catalyst	Intermediate complex	Reliability	Ref.
Pt	NH_2	M	34
Ag	$Ag(NH_3)_x(NO)_y$	M	34
Fe	NO_{ads}	M	34
Pt(111)	HNO	L	35
CoO–MgO	NO_2^-, NO_3^-	L	36
MoO_3	NH_4^+	H	43
ZnO	N_2O(ads)	H	44
Fe_2O_3	OH, NH_3(ads), NH_4^+, NH_2	M	45
Fe_2O_3/SiO_2	$FeNH_2$	L	38
V_2O_5	NH_4^+	L	40–42

Exposing MoO_3 to an $NH_3 + O_2$ mixture at 25–400 °C produces NH_4^+ ions on the surface.[43] A study of this catalytic reaction by the response method provide a quantitative proof that the ammonia is an intermediate compound. In the case of ZnO (see Ref. 44) N_2O(ads) is formed on the surface, and on α-Fe_2O_3 the OH group is formed (see Ref. 45) with coordinately bound ammonia, NH_4^+, and the NH_2 group. The following self-consistent chain of conversions of these complexes can be suggested:

$$NH_3 \longrightarrow NH_4^+ \longrightarrow NH_2\,(ads) \longrightarrow \longrightarrow N_2O(ads) \longrightarrow N_2 + NO.$$

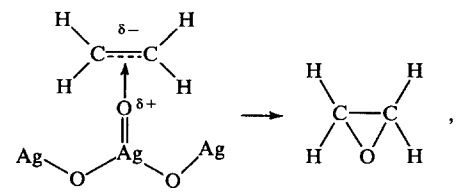
As in the case of metals the activation energy for the overall reaction (oxidation of NH_3) is lower for the catalysts on which intermediates formed in stages close to the final stage of the reaction are adsorbed.[43] Data on the intermediate compounds taking part in the oxidation of NH_3 are summarised in Table 2.

IV. Partial oxidation of olefins

The oxidation of hydrocarbons takes place by two main paths: to compounds containing oxygen (partial oxidation) and to CO_2 and H_2O (extensive oxidation). We shall first examine a partial oxidation reaction in which the main skeleton of the molecule is not broken down, and one or two oxygen atoms are added to the molecule with formation of compounds containing oxygen.

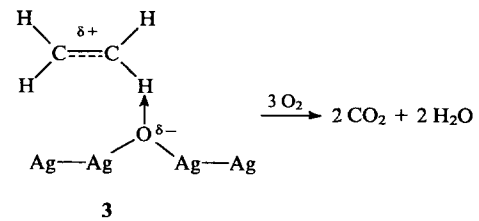
The simplest olefin (ethylene) gives ethylene oxide (C_2H_4O) after partial oxidation. Both weakly and strongly bound acetaldehyde, and also silver acetate, have been detected[46] on an Ag/α-Al_2O_3 catalyst by diffuse reflectance FTIR spectroscopy combined with kinetic measurements in the transitional regime under conditions conducive to the oxidation of C_2H_4 to C_2H_4O. An analogous study on an Ag/γ-Al_2O_3 catalyst revealed adsorbed ethylene,[47] carbonates, and Ag–CO, which are probable precursors of the extensive oxidation products.[48]

New possibilities in the study of intermediate compounds were offered by the development of the TAP (temporal analysis of products) reactor, in which the product directly desorbed from the surface can be analysed by using special attachments, thus avoiding the problem of readsorption. This development also allowed the use of millisecond (and even microsecond) measurement times, well beyond the limits of the characteristic catalysis times (10^{-2}–10^2 s) (see Gleaves et al.[49]). The application of the TAP reactor to the study of the oxidation mechanism of ethylene on powdered Ag showed[50] that the deep and the partial oxidation reactions of ethylene involve the same surface complexes of ethylene but different forms of oxygen. Carbon monoxide is formed more rapidly than ethylene oxide, mainly because of the interaction with the more weakly bound surface oxygen. Ethylene oxide is formed from both the atomic oxygen on the surface and the subsurface oxygen, which keeps the silver in an intermediate charge state Ag^{n+} (probably Ag^{3+}). Svoboda et al.[50] confirmed a scheme[51] according to which 'electrophilic' oxygen $O^{\delta+}$ forms the complex **2**, which is a precursor of ethylene oxide,



2

whereas 'nucleophilic' oxygen $O^{\delta-}$ gives the complex **3**, which is an intermediate in the deep oxidation reaction:

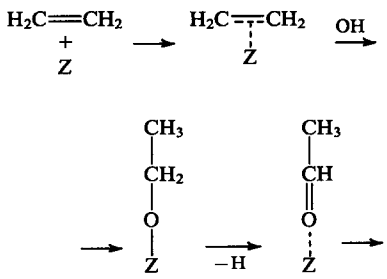


3

This mechanism is further confirmed by an analysis of the Raman spectra obtained in situ during the oxidation of ethylene on Ag(111) and Ag(110). Under the catalysis conditions three Ag–O vibration bands were observed, corresponding to $Ag-O_{ads}$, the –Ag–O–Ag– subsurface group, and dissolved oxygen. The subsurface oxygen disappears as ethylene oxide is formed.

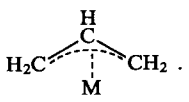
In the oxidation of ethylene to acetaldehyde on MoO_3/TiO_2 the complex π-$C_2H_4^+$ and adsorbed acetaldehyde have been observed, as well as a weak enolic complex.[52] It is assumed that

the reaction takes place with the participation of an OH surface group by a hydration–dehydrogenation mechanism:



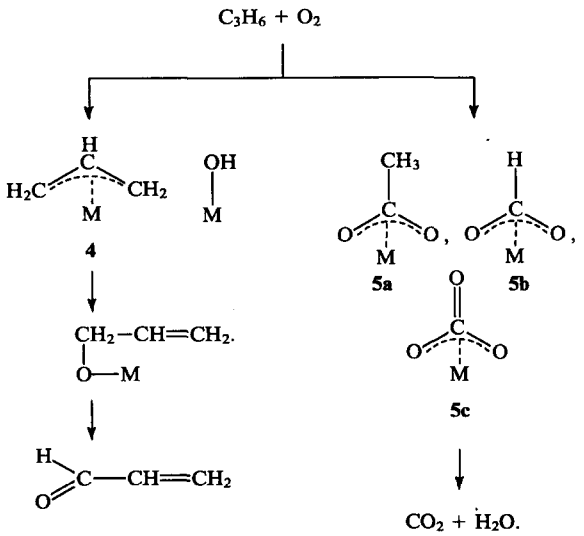
Under the conditions of the oxidation of C_3H_6 on Ag/SiO_2 a bidentate carbonate and polymeric surface formations were observed on the surface. An analysis of the in situ FTIR spectra also revealed the presence of adsorbed acrolein.[53]

The oxidation of propylene to acrolein on oxide catalysts takes place through the intermediate formation of a π-allyl complex. Many isotopic studies have established the indistinguishability of the C(1) and C(3) carbon atoms in the propylene molecule, and of the hydrogen atoms attached to them.[54] This is evidence for the symmetry of the complex:



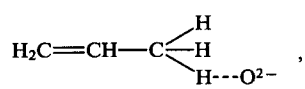
4

The precursor of the π-allyl complex is a π-olefin complex. The adsorption centres for the olefin in the form of π-complexes on the oxides can be not only the metal ions but also surface acidic centres of the Brønsted type.[55] π-Allyl complexes **4** were detected spectroscopically on $Bi_2O_3-MoO_3$,[55] Cu_2O, and Ga molybdates.[56] On the other hand the carbonate–carboxylate complexes **5a–5c** are most often observed on the deep oxidation catalysts. This suggested the following general scheme for the oxidative transformations of C_3H_6:



On ZnO acrolein is not formed, and diallyl is obtained ($CH_2=CH-CH_2-CH_2-CH=CH_2$).[57] According to IR spectral studies in this case the π-allyl is converted into σ-allyl $[CH_2=CH-CH_2]^-$, which is probably anionic. Subsequent transformations give the dimer C_6H_{10}. On Bi–Mo oxide propene oxidation catalysts the π-allyl complex was observed under the conditions of the reaction.[58] The kinetics of the processes leading to its formation and decomposition were measured by in situ IR spectroscopy. Increasing the activity of the catalyst (by increasing its molybdenum content) lowers the activation energy for the consumption of π-allyl. We note that the number of cases in which the presence of π-allyl complexes on the surface has been truly established is small, and that the catalysts on which the observations were made were not good catalysts for the oxidation of propene to acrolein. Evidently the formation of the π-allyl complex (the initial rupture of a C–H bond) is the rate-limiting step of the reaction, after which the complex rapidly undergoes further transformations. Satisfactory spectroscopic studies of this process have not yet been reported. In the oxidation of C_3H_6 to acrolein on $USb_{4.6}O_{13.2}$ bands due to adsorbed acrolein were observed[59] in the IR spectra. It was concluded from isotopic data that the π-allyl complex takes part in the reaction.

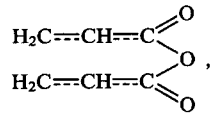
Weakly bound adsorbed forms of propene observed on Ti–Sb–O[60] and Fe–Sb–O catalysts,[61]



6

could be the precursors of acrolein. The process does not necessarily require activation of the double bond.[60,61] The acrolein can be formed immediately after the breaking of the C–H bond coordinated to O^{2-} in the complex **6** (see also Ref. 62). The participation of weakly bound forms of adsorbed propene in the oxidation to acrolein on $Bi_2O_3-MoO_3$ was detected during experiments with the TAP reactor.[63] Two forms of adsorbed oxygen were also observed: one contributes to the partial oxidation, the other does not contribute directly but exchanges readily with the oxygen from the gas phase.

A study by FTIR spectroscopy of the partial oxidation of propene and isobutene to acrolein on the industrial Co(Mg)–Mo–Bi–Fe oxide catalyst showed that under the conditions of the reaction 1% of the surface is occupied by the compound **7** of the acrylic anhydride type:

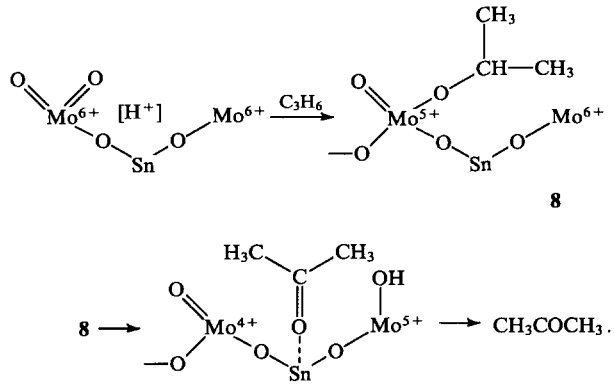


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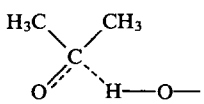
which is converted into an unsaturated aldehyde by reacting with a proton-donor reagent (i.e. with another olefin molecule, for example C_3H_6 or iso-C_4H_8).[64,65] This allows the associative substitution mechanism to take place.

The first stages of the oxidative ammonolysis of propylene with formation of acrylonitrile ($CH_2=CHCN$) are apparently similar to the first stages of the oxidation of propene to acrolein (through π-olefin and π-allyl complexes).[66] However, it was found that the rate of oxidative ammonolysis is always higher than the rate of oxidation of olefins to unsaturated aldehydes. Obviously, the ammonia gives intermediate forms which intercept (for example) the hydrogen from olefins. Bands due to NH_4^+ and to coordinatively bound ammonia have been observed in the IR spectra obtained after the oxidative ammonolysis of propene on a Co–Mo–Bi–Fe oxide catalyst.[67]

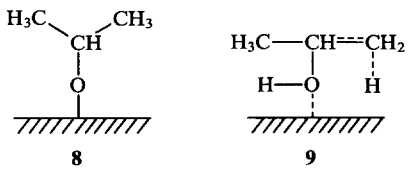
On oxide catalysts containing V and Mo propene can undergo partial oxidation to acetone but not to acrolein. A spectral study[68–71] of this reaction detected the surface isopropylates **8**. As reported,[68] the oxidative transformations of olefins on Sn–Mo–O catalysts take place by the scheme



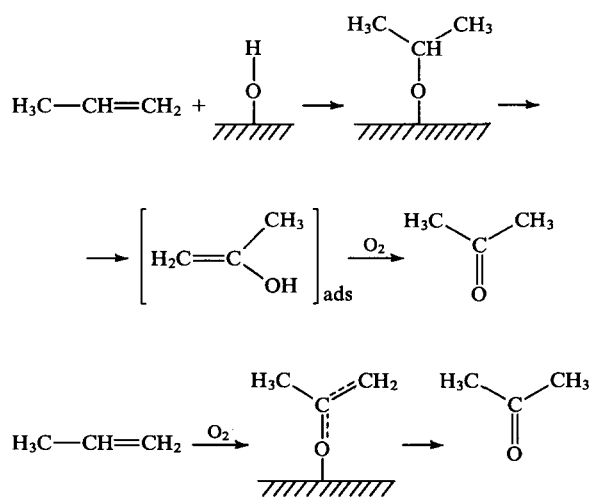
Here the rate-limiting step is the dehydrogenation of the surface isopropylates **8**, and the intermediate complex is



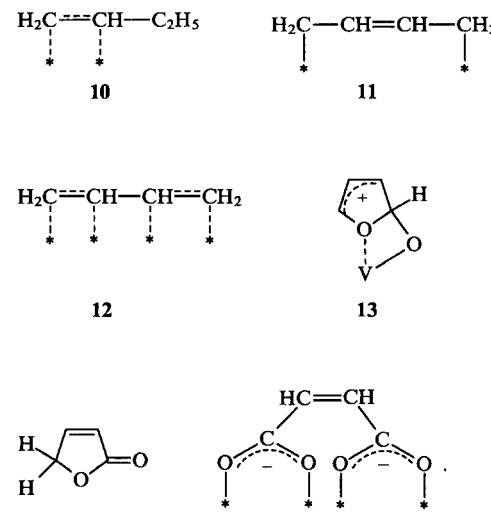
However, the reliability of these results is doubtful because the IR spectra were not measured under the conditions of the catalysis. An in situ study by IR spectroscopy on the Sn–Mo–O and Sn–V–O catalysts revealed the presence of two surface complexes:[71]



The intensity of the bands of the complex **8** on Sn–V–O increases with temperature up to 120 °C, and then decreases (while the yield of acetone increases). It was concluded that the complex **8** is an intermediate. On Sn–Mo–O the enol complex **9** contributes to the formation of some of the acetone. The following mechanism was proposed for the reaction:



In the oxidation of but-1-ene on $V_2O_5-P_2O_5/Al_2O_3$ at 100–150 °C (i.e. below the stationary reaction temperature) adsorbed 1-C_4H_8 (two π-complexes), 1,3-C_4H_6, furan, maleic anhydride, and 2,5-H-furanone were detected by IR spectroscopy.[72] Butadiene forms complexes of two types: the π-complexes **10** and **12** (interaction at the C=C bond) and the σ-complex **11** (1,4-addition). Furan is adsorbed at the C(2) atom (complex **13**), and 2,5-H-furanone forms the complex **14**. Maleic anhydride is chemisorbed as the stable complex **15**, but physisorbed maleic anhydride is also formed



The asterisks denote surface atoms.

Among the complexes which have been observed only 2,5-H-furanone (**14**) is active under the catalysis conditions.[72] Bands from π-allyl and adsorbed butadiene were observed[73] in the IR spectra during the oxidative dehydrogenation of butenes on the ferrites $MgFe_2O_4$, $CoFe_2O_4$, and $CuFe_2O_4$. The breaking of the C–H bond and the formation of the π-allyl are probably the rate-limiting step. The formates, carboxylates, and carbonates formed during the adsorption are intermediates in the deep oxidation reaction.

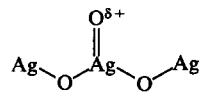
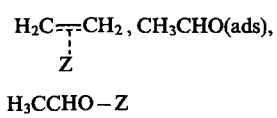
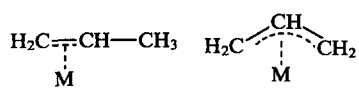
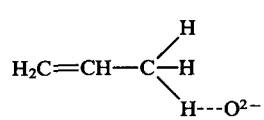
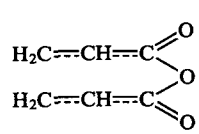
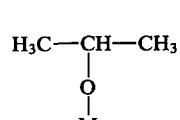
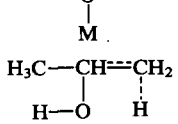
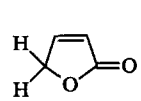
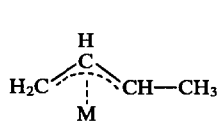
The oxidation of C_3H_6 and 1-C_4H_8 on γ-Bi_2MoO_6 was studied in the TAP reactor.[74] The reaction takes place by an oxidation–reduction mechanism. In spite of widely held views to the contrary there is no fast exchange of oxygen between the catalyst and $^{18}O_2$ from the gas phase. Therefore there can be no fast reversible chemisorption of O_2 with formation of O, O^-, or O_2^-. It is pointed out[74] that two types of centre are present on the surface: M and M′ (different oxygen vacancies). The M centres can be reoxidised by oxygen, and they can then reoxidise the M′ centres. The M′ centres are created by reduction and they cannot be directly reoxidised by oxygen. In the oxidation of C_3H_6 and iso-C_4H_8 no difference is found between the types of centre. Evidently these results can be explained in terms of our two- or three-phase catalyst model,[75] according to which the activation of olefins takes place on some centres, the activation of oxygen on others, and the diffusion of oxygen involves a third phase.

The intermediate oxygen forms produced in the oxidation of C_3H_6 on V_2O_5/SiO_2 were studied by EPR.[76] The products of the interaction of C_3H_6 with O_2^- and those of the oxidation of C_3H_6 in the stationary regime are identical, but the concentration of O_2^- under the reaction conditions is two orders of magnitude lower than the level required to achieve a stationary rate.

Table 3 summarises the data on the intermediate compounds which take part in the partial oxidation of olefins.

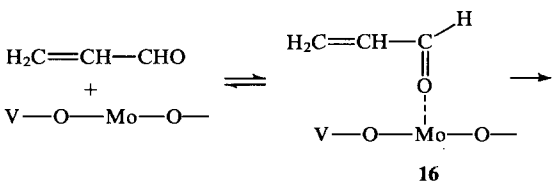
In conclusion we note that many published papers have dealt with the mechanism of the partial oxidation of olefins, and many surface forms have been observed, but so far there have been very few reports containing all the necessary spectral and kinetic data, and the existence of most of the suggested intermediates is hypothetical.

Table 3. Intermediate compounds in the partial oxidation of olefins.

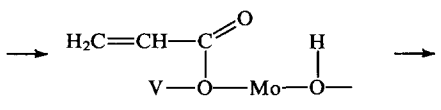
Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oxidation of ethene on Ag/Al_2O_3	CH_3CHO(ads)	L	46
Oxidation of ethene on Ag/γ-Al_2O_3	C_2H_4(ads)	L	47
Oxidation of ethene on Ag		M	50–52
Oxidation of ethene and acetaldehyde on MoO_3/TiO_2	 $H_3CCHO-Z$	M	52
Oxidation of propene and acrolein on Ag/SiO_2	$H_2C=CHCHO$(ads)	M	53
Oxidation of propene and acrolein on $Bi_2O_3-MoO_3$, Cu_2O and Ga molybdates		L	55, 56
Oxidation of propene and diallyl on ZnO and Bi_2O_3	$H_2C=CH-CH_2-O-M$	M	57, 58
Oxidation of propene and acrolein on Ti–Sb–O and Fe–Sb–O		L	60, 61, 63
Oxidation of propene and acrolein on Co–Mo–Bi–Fe–O		M	64, 65
Oxidative ammonolysis of propene on Co–Mo–Bi–Fe–O	$H_2C{=}{=}CH{=}{=}CH_2$, NH_4^+, NH_3-M	L	66, 67
Oxidation of propene to acetone on Sn–Mo–O		L	68–70
		M	71
Partial oxidation of but-1-ene on $V_2O_5-P_2O_5/Al_2O_3$		L	72
Oxidative dehydrogenation of butenes on $MgFe_2O_4$, $CoFe_2O_4$, and $CuFe_2O_4$		L	74

V. Oxidation of aldehydes to unsaturated acids

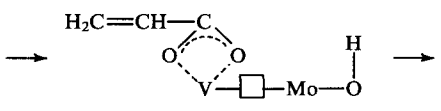
Unsaturated acids can be prepared by the further oxidation of unsaturated aldehydes produced from olefins. The reaction takes place on V–Mo oxide catalysts, including V–Mo–O heteropolycompounds and heteropolyacids. The oxidation of acrolein to acrylic acid was studied by in situ IR spectroscopy on VMo_3O_{11}[77] and on V–Mo–O/SiO_2.[78] Several complexes containing C=C bonds (complex **16**) and also COO^- (complexes **17** and **18**) and C=O (molecular adsorption of CH_2=CHCOOH, complex **19**) were seen. The rate constants for the transformations of these complexes were measured. The following reaction mechanism was proposed:



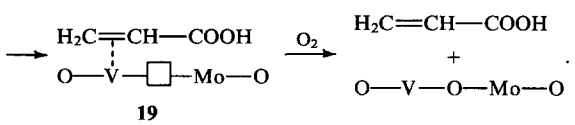
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17



18

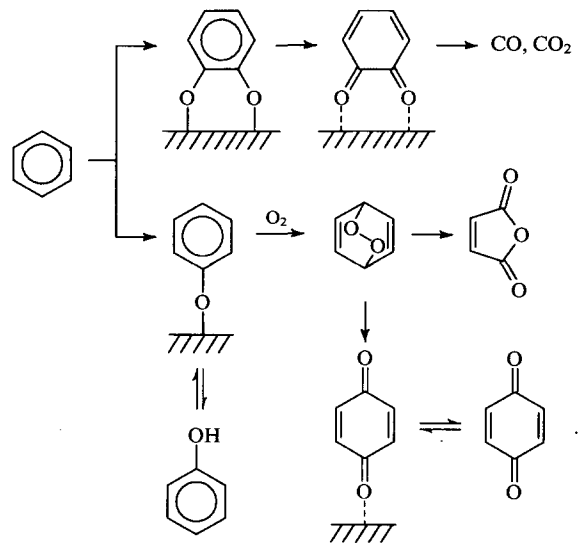


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The rate-limiting step is the conversion of the complex **17** (which is not observed in practice) into the complex **18**. The catalyst should contain Mo^{6+} (or W^{6+}) ions for the σ-bonding of the acrolein, and V^{4+} (Mo^{4+} and Ti^{4+}) ions of the weakly basic or amphoteric type for the formation of salt-like acrylates. However, the degree of correspondence between the kinetics of the change in intensity of the IR lines and the kinetic curves describing the formation of acrylic acid is not stated. The reliability of the observed intermediate complexes can be classified as high (H).

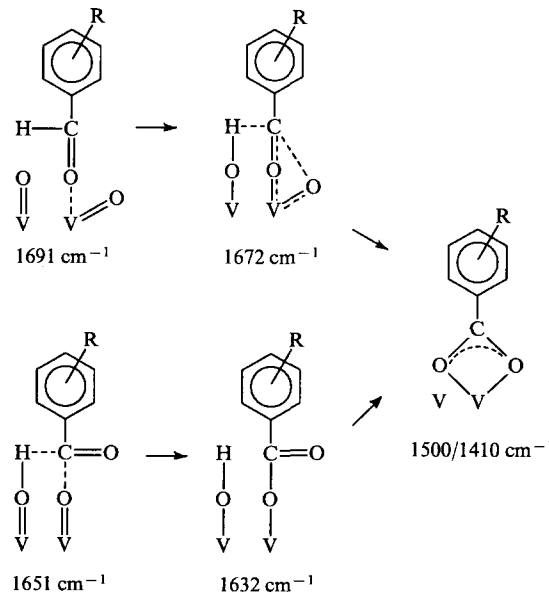
VI. Partial oxidation of aromatic hydrocarbons

Aromatic hydrocarbons undergo partial oxidation on the same catalysts as olefins. The surface compounds formed by the interaction of benzene with oxygen at 280 °C on a V_2O_5/TiO_2 catalyst have been studied by FTIR spectroscopy.[79] Adsorbed quinone, phenol, maleic anhydride, and carboxylates were detected on the surface. The following mechanism was proposed:

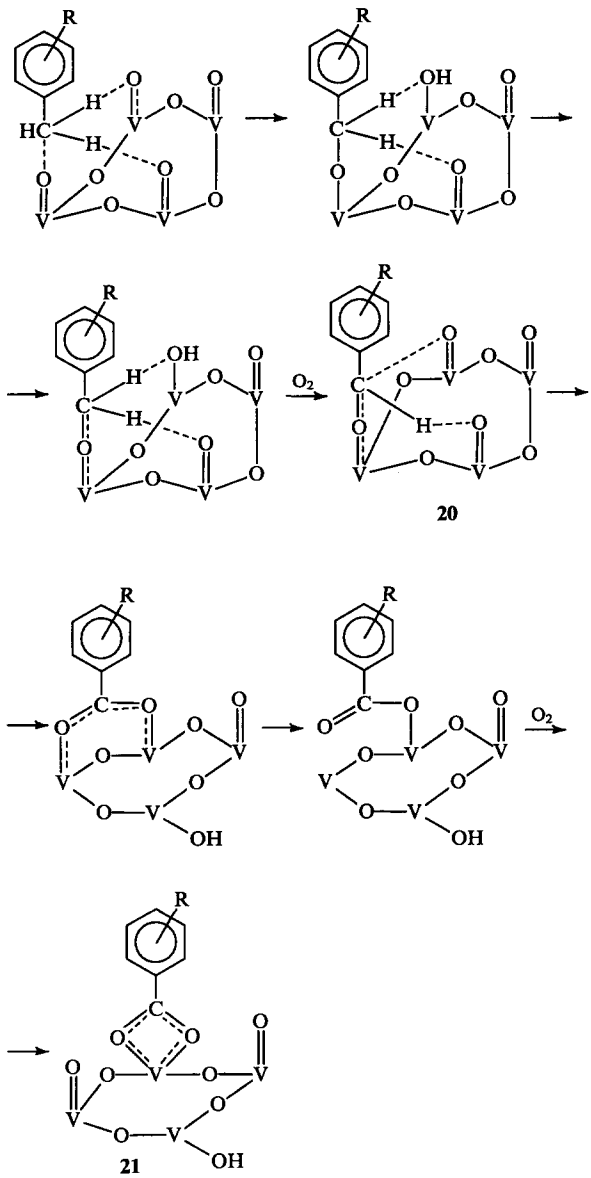


The IR spectra of the resulting surface compounds were recorded[80] at room temperature after the partial oxidation of toluene and *o*-xylene on V_2O_5/TiO_2. The $C_6H_5-CH_2-V$ and $C_6H_4(CH_3)CH_2-V$ complexes which were observed led to the conclusion that the first step of the reaction is the breaking of the C–H bond in the methyl group. In these complexes the aromatic ring is positioned parallel to the surface.

In situ FTIR spectra were obtained[81] during the selective oxidation of toluene to benzaldehyde and of *o*-xylene to α-toluyl aldehyde on V_2O_5/TiO_2. Complexes of aldehydes, carboxylates, and benzoates were observed on the surface.



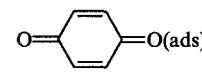
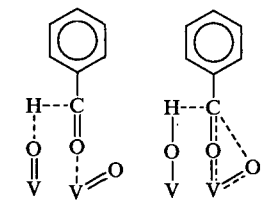
The following mechanism has been proposed for the oxidative transformations of toluene (or xylene) on the surface: it assumes that an aldehyde can be formed by the decomposition of the complex **20** without oxidation, and an acid by the decomposition of the complex **21**.



The oxidative ammonolysis of toluene on V–Sb–Bi–O/Al_2O_3 was studied by thermal desorption and IR spectroscopy.[82] NH_4^+ ions and ammonia coordinately bound to Lewis-acid centres were detected. Heating the system to 200 °C to 300 °C produced also NH_2. The adsorption of toluene leads to the formation of π-complexes and benzoate structures, and in the reaction with NH_3 benzamide and benzimide structures were also noted. The concentration of benzoate (unlike that of benzimines) is not correlated with the yield of the reaction products (nitriles). Adsorbed ammonia poisons the deep oxidation centres and thus prevents the formation of benzoates. The mechanism of the partial oxidation of benzene and phenol in the presence of N_2O has been studied on the Fe–ZSM-5 catalyst.[83] Bands of adsorbed phenol were seen in the diffuse reflectance IR spectra. Active oxygen O_{ads}, which has a very low bond energy, is formed during the decomposition of N_2O.

Table 4 shows the intermediate compounds which contribute to the partial oxidation of aromatic compounds.

Table 4. Intermediate compounds in the partial oxidation reactions of aromatic compounds.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oxidation of benzene to oxygen compounds on V_2O_5–TiO_2	M–OC_6H_5, M–OC_6H_4OH, 	L	79
Oxidation of toluene to toluic aldehyde and of *o*-xylene to benzaldehyde on V_2O_5–TiO_2	$C_6H_5CH_2$–V, $C_6H_4(CH_3)CH_2$–V 	L M	80 81
Oxidative ammonolysis of toluene on V–Sb–Bi–O/Al_2O_3	NH_4^+, NH_3–M, NH_2, π-$C_6H_5CH_3$, C_6H_5–CH=NH	L	82
Oxidation of benzene to phenol by N_2O on Fe–ZSM-5	O(ads), C_6H_5OH(ads)	M	83

VII. Partial oxidation of alkanes

Very detailed studies of the oxidation of methane with formation of C_2H_4, C_2H_6, CH_3OH, and CH_2O have recently been reported. Attempts to obtain the in situ spectra of surface compounds under the conditions of the partial oxidation of methane were unsuccessful.[84] This is evidently due to the fact that at high temperatures the reaction proceeds by a heterogeneous–homogeneous mechanism, and the lifetime of the intermediate species on the surface is very short. Under the conditions of its oxidative condensation (700–900 °C) methane interacts with the surface oxygen O_s, forming methyl radicals and OH groups on the surface.

$$CH_4 + O_s \longrightarrow CH_3^{\cdot} + OH_s,$$

$$2\,OH_s \longrightarrow H_2O + O_s.$$

The methyl radicals recombine in the gas phase, and are thus converted into ethane and (further) into ethylene.

$$2\,CH_3^{\cdot} \longrightarrow C_2H_6,$$

$$C_2H_6 + O_s \longrightarrow C_2H_4 + H_2O.$$

The interaction of methane with films of oxide catalysts under the conditions of adsorption at 300–500 °C and under the conditions of CH_4 oxidation was studied *in situ* by the new and very sensitive surface electromagnetic waves method.[85,86] Bands from OH and OCH_3 groups were detected in the IR range at 900–1100 °C. They are obviously associated with the compounds formed during the extensive oxidation of methane to CO_2 and H_2O.

$$CH_4 + O_s \longrightarrow CH_3 + OH_s,$$

$$CH_3 + O_s \longrightarrow OCH_3,$$

$$OCH_3 + O_2 \xrightarrow[-H_2O]{} \overset{O}{\overset{\|}{CH}}(O) \longrightarrow CO_2$$

Bands ascribed to OCH_3 and carbonate complexes were observed also in the FTIR spectra recorded after the oxidative condensation of methane into C_2 hydrocarbons on MgO.[87] These complexes take part in the extensive oxidation processes on the surface. Similar processes were observed by XPES during studies of the oxidation of CH_4 on NaOH/CaO and NaOH/(BaO, CaO).[88] It was found that methane interacts with surface carbonate (CO_3^{2-}) at 500–750 °C, forming a surface compound which rapidly disappears when the methane is pumped off. Possible intermediate complexes include the CH_3O and C=O groups, which are further oxidised to CO_2.

A study of the mechanism of oxidative condensation by combining the TAP reactor[89] with isotopic methods[90] showed that the methane taking part in the reaction is effectively not adsorbed on MgO and BaO/MgO surfaces. Apparently it reacts by the collision mechanism

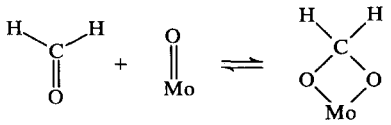
$$CH_4 + O_s \longrightarrow CH_3^{\cdot} + OH_s,$$

and initiates further oxidative processes in the gas phase.[84] On the other hand heterolytically adsorbed methane is involved in the $CH_4 + CD_4$ isotope exchange.[90] It forms complexes of the $CH_3-Mn^{n+}O^{2-}H^+$ type on the basic centres, which differ from the O^- centres involved in the homolytic breakdown of the CH_4 molecule.

The surface forms of oxygen created during the oxidative condensation of methane on BaO/MgO were studied by in situ Raman spectroscopy.[91,92] The peroxide groupings (O_2^{2-}) observed in this way at 844 cm^{-1} are stable in the presence of O_2, and at 740 °C they react with CH_4 over a period of several minutes. By using a TAP reactor it was shown that the lifetime of the adsorbed oxygen which reacts with methane on BaO/MgO is greater than 20 s. This species could also be the peroxide group. However, a longer-lived form of surface oxygen (O_s) is involved in the oxidative condensation of methane on MgO.

The oxidation of methane to formaldehyde takes place most selectively on catalysts which contain molybdenum, vanadium, or silicon oxides. A study by in situ laser-Raman spectroscopy of the partial oxidation of methane to formaldehyde on MoO_3 monocrystals led to the conclusion[93] that in this reaction the intermediate oxygen compounds are the Mo=O groups on a (100) MoO_3 face, whereas the Mo–O–Mo groups are involved in the extensive oxidation. A dispersed heteropolyacid is formed on the surface of the Mo–Si–O catalyst.[94] According to XPES and Raman spectroscopy Mo=O groups are formed as well under the catalysis conditions.

A study of the isotope exchange of O_2 under the conditions of the oxidation of methane to formaldehyde on MoO_3/SiO_2 showed[95] that not only the MoO_3 but also the SiO_2 contributes to the exchange. A very fast exchange between CH_2O and the oxygen of the catalyst was also noted: it was ascribed to the equilibrium



According to data obtained in a TAP reactor[96] a surface oxygen species with a lifetime between 5 and 60 s is responsible for the oxidation of CH_4 to CH_2O on V_2O_5/SiO_2. Compounds containing oxygen and related to the oxidative condensation or to the oxidation of methane to formaldehyde were not detected under the catalysis conditions. Intermediate compounds such as the $^{\cdot}CH_3$ and $CH_3O_2^{\cdot}$ radicals migrating from the surface into the gas phase[84,91] will not be considered here.

Dissociative forms of carbon on the surface of metals [C(ads), CH_x(ads)] are apparently intermediates in the oxidation of methane by oxygen[97] or by carbon dioxide[98] with formation of synthesis gas (CO + H_2). The vapour phase conversion of methane on Ni/NaY at 300 °C has also been studied by in situ IR spectroscopy.[99] Formate was found on the surface after the reaction. The following reaction mechanism was proposed:

$$H_2O + S \rightleftharpoons H_2O-S,$$

$$CH_4 + M \rightleftharpoons MC + 2H_2,$$

$$MC + H_2O-S \rightleftharpoons HCO-M + \tfrac{1}{2}H_2 + S,$$

$$HCO-M + H_2O-S \rightleftharpoons HCOO-M + H_2 + S,$$

$$HCOO-M \longrightarrow CO_2 + \tfrac{1}{2}H_2 + M.$$

The last step is rate-limiting.

In the oxidation of ethane on Pd/Al_2O_3 and Pd/SiO_2 in situ IR spectra obtained at 200–600 °C revealed acetate and carbonyl complexes acting as intermediates in the extensive oxidation reaction.[100] The oxidative dehydrogenation of ethane to ethylene apparently takes place by a heterogeneous–homogeneous mechanism.[101]

The oxidation of CH_4, C_2H_6, and C_2H_4 on Co_3O_4 and on Pd/TiO_2 has been studied.[102] The interaction of CH_4 with Co_3O_4 produces surface OH groups, carbonates of two types, and (apparently) Co–CH_2–Co groups. The formation of CH_3CHO and acetate adsorbed on the TiO_2 carrier has been observed in the reaction of C_2H_4 with O_2 on Pd/TiO_2. The ethane is first dehydrogenated to ethylene by an oxidation–reduction reaction, involving the $Pd^{2+}-O_2^{2-}$ ion pair, and then the C_2H_4 is rapidly oxidised to CH_3CHO, which undergoes decarbonylation with formation of Pd–CH_3 + CO. The Pd–CH_3 complex is formed also by the reaction between CH_4 and the $Pd^{2+}-O_2^{2-}$ pair. This is followed by the reactions

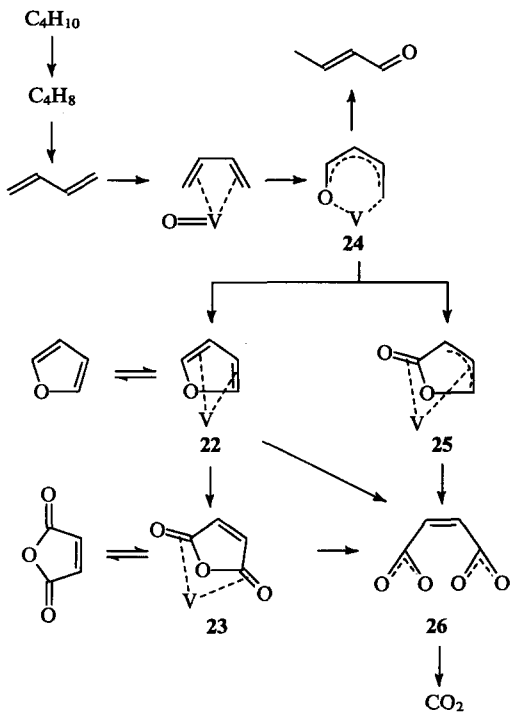
$$CH_3 \xrightarrow{O_2} CH_2 + H(OH) \xrightarrow{O_2} CH_2O \xrightarrow{O_2} CO + H_2O.$$

The final result is deep oxidation of the CH_4.

Many studies have been devoted to the partial oxidation of butane to maleic anhydride and other oxygen compounds on V–Ti and V–P oxide catalysts. The mechanism of the oxidation of butane on TiO_2 and $V_2O_5-TiO_2$ has been examined[103,104] by studying the FTIR spectra of C_4H_6, furan, and maleic anhydride on the catalysts in the presence and in the absence of O_2. The sequence of transformations on $V_2O_5-TiO_2$ shown in Scheme 1 was proposed. At room temperature the complex **22** (adsorbed furan) is first formed. At higher temperatures a strong band assigned to the complex **24** appears in the IR spectra. At 200 °C its intensity decreases, and an absorption band corresponding to the complex **26** appears. As a result of the interaction with oxygen the intensity of the band assigned to the complex **24** increases again. The absorption band which characterises the complex **24** disappears at 250–300 °C, and absorption bands due to the complexes **23** and **25** are produced. Maleic anhydride is formed only in the presence of oxygen: in the absence of oxygen the maleates **26** are obtained. Evidently, these decompose by associative interaction with O_2. On TiO_2 only the π complex of C_4H_8 (or C_4H_6) with Ti^{3+} is formed reversibly. On a V–P–O catalyst maleic anhydride is formed even in the absence of O_2, and maleates are not observed. Obviously, in this case the oxygen in the bulk of the catalyst has a higher mobility. The V–O–Ti bridging forms, which are more nucleophilic than V–O–P, may

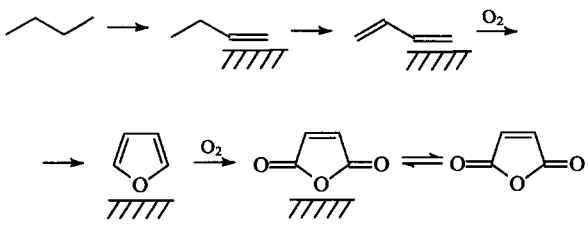
also contribute to the formation of the maleates. This leads to nonselective catalysis.

Scheme 1

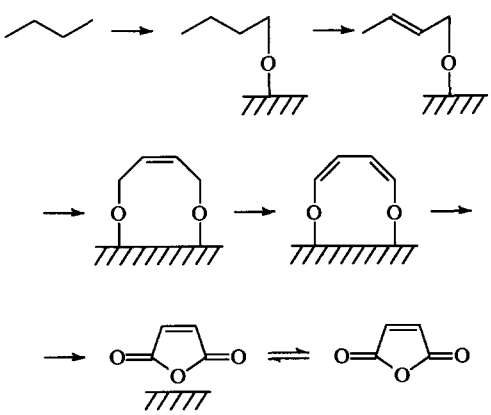


Two possible paths for the conversion of butane into maleic anhydride on a vanadium–phosphorus oxide catalyst have been considered:[105]

(a) the olefin path

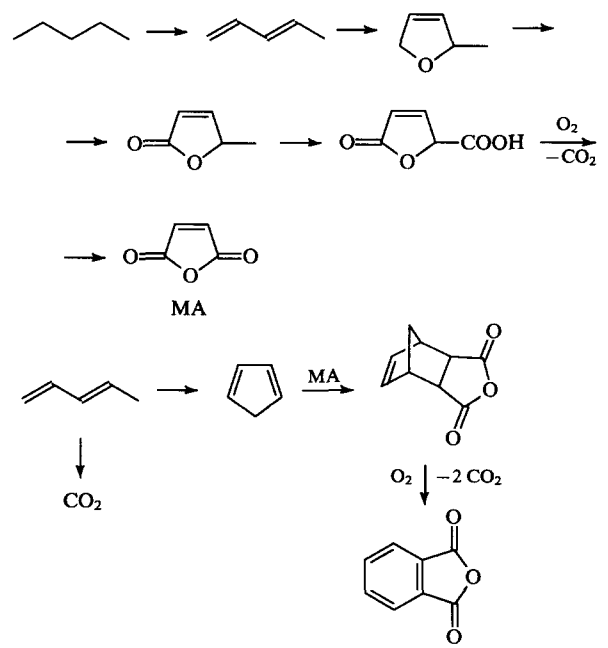


(b) the alkoxide path



The olefin path (a) has been called[105] the equilibrium path, because all the contributing intermediates are in adsorption equilibrium with the gas phase. The alkoxide path (b) is a nonequilibrium process: all the intermediates (except the last) remain on the surface, and only maleic anhydride is desorbed into the gas phase. However, the formation of the surface complexes listed above was not confirmed spectroscopically, and their structure was determined only from indirect data obtained by ^{31}P NMR and EPR methods.

The difference between the mechanisms of the partial oxidation of butane and butene (see Section IV) also suggests that the alkoxide path is preferable to the olefin path. It is assumed[106] that the oxidation of C_4H_{10} on $(VO)_2P_2O_7$ is characterised by a strong adsorption of the intermediate substances, which suppresses their desorption into the gas phase and limits their surface mobility. Under these conditions the number of free centres is also limited, leading to the geometric isolation of the active intermediates and thus suppressing the oxidation to CO and CO_2. On $(VO)_2P_2O_7$ the oxidation mechanism of butane and pentane to maleic anhydride was studied by in situ FTIR spectroscopy, and by using a TAP reactor.[106–108] Exposing the catalyst to a mixture of C_5H_{12} and O_2 produced a large number of IR spectroscopic bands for which only a tentative assignment was given.[106] The IR spectra of the sample vacuum treated at 400 °C after the adsorption of C_5H_{12} contained absorption bands from weakly adsorbed olefins, and after the adsorption of a C_5H_{12} + O_2 mixture they contained the bands from adsorbed anhydride. The intensity of the absorption band from the anhydride increases with time, and bands associated with more highly oxidised substances are produced. By using a TAP reactor it was shown that at 427 °C pentane is converted into furan (reaction time 0.2 s), which reacts further to give maleic anhydride (0.3 s) and phthalic anhydride (0.5 s). On the basis of these observations the following reaction scheme was proposed:

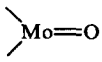
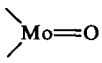
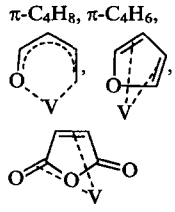
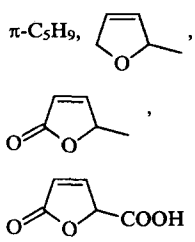


The formation of methylmaleic anhydride in the initial stages of the reaction, which confirms the proposed scheme, was observed. All the substances specified in this scheme are on the surface in an adsorbed state. A competition then takes place between the addition of atomic oxygen, which leads to the formation of maleic anhydride, and the elimination of an H atom, with formation of phthalic anhydride. To form phthalic anhydride we also require the presence on the surface of another adsorbed molecule of an unsaturated C_5 hydrocarbon. By using the TAP reactor in a study of the oxidation mechanism of butane on $(VO)_2P_2O_7$ (see Ref. 108) it was shown that this catalyst has a unique ability to retain absorbed oxygen and to transmit it effectively to a hydrocarbon. We observe the conversion of $(VO)_2P_2O_7$ into amorphous $VOPO_4$,

$$^{18}O_2 + 2\,(VO)_2P_2O_7 \rightleftharpoons 4\,VOPO_4,$$

which involves the transfer of four oxygen atoms in a single step.

Table 5. Intermediate compounds in the partial oxidation of alkanes.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oxidative condensation of methane on BaO/MgO	O_2^{2-}	H	90–92
Oxidation of methane to CH_2O on MoO_3		M	93
Oxidation of methane to CH_2O on Mo–Si–O		L	94, 95
Oxidation of methane to CO + H_2 on Mo	C(ads), H(ads)	L	97
Reaction of $CH_4 + CO_2$ on Rh/Al_2O_3, Rh/TiO_2	C(ads), H(ads), CH_x(ads)	L	98
Vapour conversion of methane on Ni/NaY	$HCOO^-$	L	99
Oxidation of ethane on Pd/TiO_2	CH_3CO-Ti, CH_3CHO(ads), C_2H_4(ads),	L	102
Oxidation of butane to maleic anhydride on V_2O_5/TiO_2	π-C_4H_8, π-C_4H_6, 	M	103, 104
Oxidation of pentane to maleic anhydride on $(VO)_2P_2O_7$	π-C_5H_9, 	H	106–108

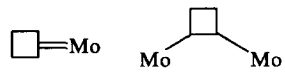
Data on the intermediate compounds which contribute to the partial oxidation of alkanes are shown in Table 5.

The oxidation reactions of alkanes can be classified into two groups: high-temperature reactions (500–600 °C, gas-phase conversion of methane and other alkanes, oxidation of alkanes to synthesis gas, and possibly also extensive oxidation), which take place by a complete dissociation mechanism with formation of H_{ads}, O_{ads}, and C_{ads}, and low-temperature reactions (oxidative dehydrogenation with formation of oxygen compounds), involving various large surface complexes. Among all the partial oxidation processes the oxidation of butane to maleic anhydride has been studied in most detail. In this stage the formation of intermediate complexes has been established with a high level of reliability.

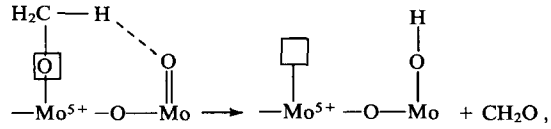
VIII. Oxidation of alcohols

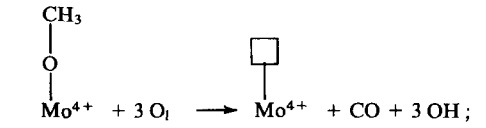
The mechanism of the oxidation of alcohols has been studied on various oxides: MoO_3,[109,110] Cr_2O_3,[111,112] TiO_2,[112] and ZnO.[113] Alkoxides, formates, and other forms resembling the complexes observed in the dehydrogenation of alcohols (see Ref. 1) were found on the surface.

The oxidation of methanol on MoO_3 at 170–440 °C was studied by in situ FTIR spectroscopy in the transition regime.[109,110] According to these data the CH_3OH is adsorbed on vacancies of two types:



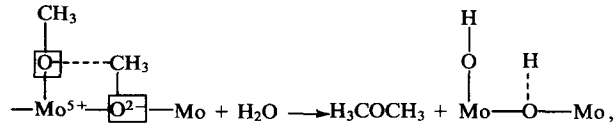
The products CH_2O and CO are formed on vacancies of the first type:

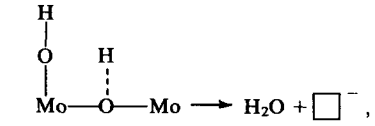


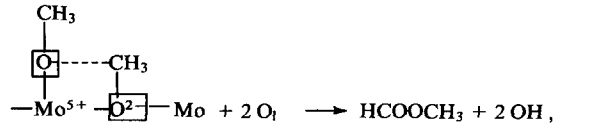


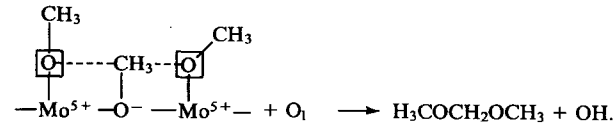
O_l is lattice oxygen.

On the vacancies of the second type the following reactions take place:









In the stationary state the MoO_3 surface is slightly reduced, and the rate-limiting step is provided by reoxidation, i.e. the filling of vacancies with oxygen.

On Cr_2O_3 the reaction was studied by in situ FTIR spectroscopy; the kinetics of the formation of the products H_2O, CO_2, and CH_2O were monitored at the same time.[112]

However, the quantity of adsorbed substances was not compared with the composition of products in the gas phase. The mechanism of the reaction is

$$CH_3OH + O^{2-} \longrightarrow CH_3O^- + OH^-,$$

$$CH_3OH + OH^- \longrightarrow CH_3O^- + H_2O,$$

$$CH_3O^- + O^{2-} \longrightarrow CH_2O + OH^- + 2e,$$

$$CH_2O + 2\,O^{2-} \longrightarrow HCOO^- + OH^- + 2e,$$

$$2\,HCOO^- \longrightarrow H_2 + 2\,CO_2 + 2e,$$

$$HCOO^- + OH^- \longrightarrow H_2O + CO + O^{2-},$$

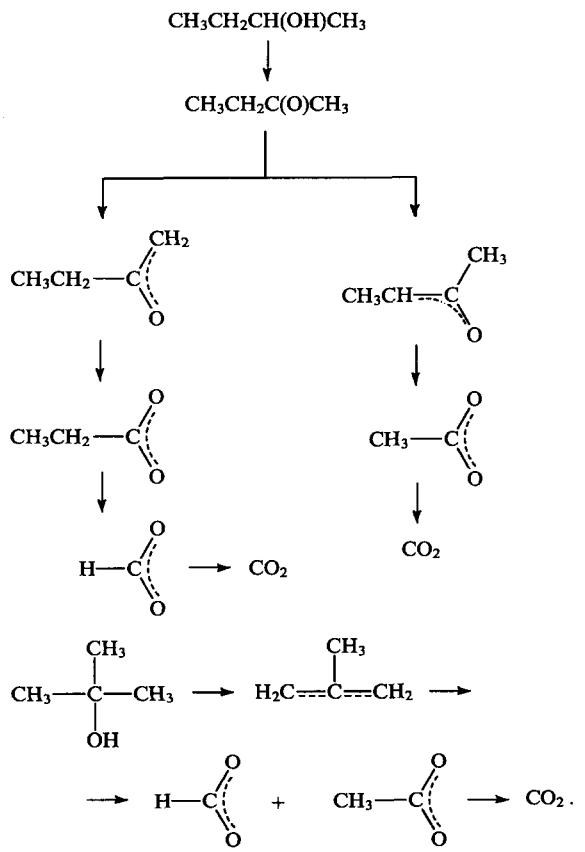
$$O_2 + 4e \longrightarrow 2\,O^{2-},$$

$$2\,OH^- \longrightarrow H_2O + O^{2-}.$$

Thus the oxidation of methanol on Cr_2O_3 takes place by the series of reactions[111]

$$CH_3O \longrightarrow CH_3O(ads) \longrightarrow HCOO(ads) \longrightarrow CO, CO_2.$$

After the oxidation of *sec*-butanol and *tert*-butanol on ZnO at 80–150 °C formates and carboxylates were detected by IR spectroscopy.[113] The same bands were found in the IR spectra after the oxidation of butan-2-one. It follows that the first step in the reaction is the conversion of butan-2-ol into butan-2-one. This is followed by the reactions



An interesting study (by in situ EXAFS spectroscopy in conjunction with UV-VIS and IR spectroscopy) of the oxidation of ethanol to acetaldehyde on dimeric Mo complexes supported on SiO_2 has been reported.[114] The EXAFS spectra were measured at 70 °C (or in some cases at −195 °C). The cooling time from the reaction temperature (150 °C) was relatively long (up to 1 h). The following oxidation–reduction mechanism was proposed on the basis of these results:

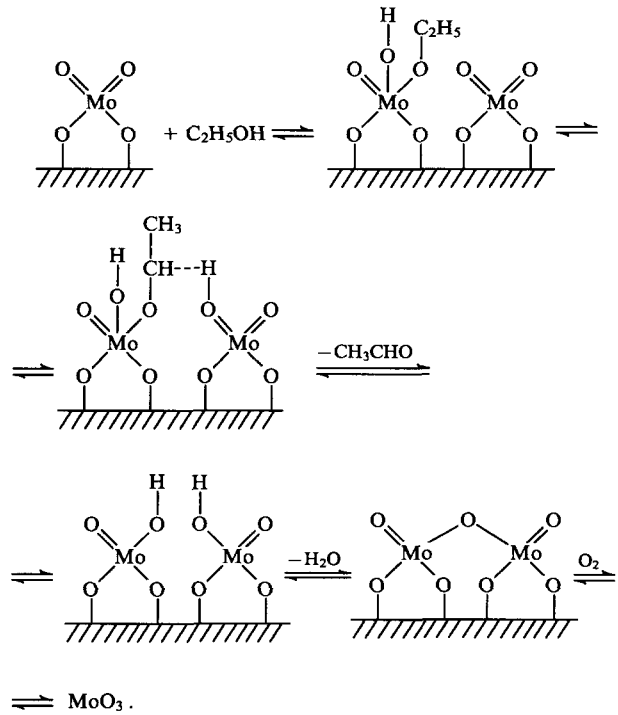


Table 6. Intermediate compounds in the oxidation of alcohols.

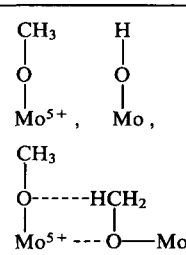
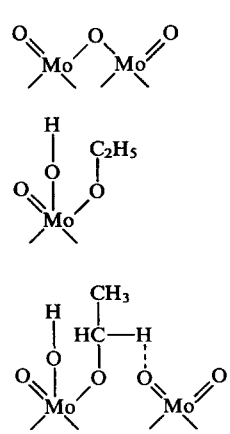
Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oxidation of methanol on MoO_3		H	109, 110
Oxidation of methanol on Cr_2O_3	CH_3O^-, OH^-, $HCOO^-$	M	111, 112
Oxidation of *sec*-butanol and *tert*-butanol on ZnO	$HCOO^-$, $RCOO^-$, $R^{\cdot}$	L	113
Oxidation of ethanol to acetaldehyde on Mo/SiO_2		L	114

Table 6 gives a summary of the data on the intermediate compounds which take part in the oxidation of alcohols.

The formation of alkoxides and carbides during the oxidation of alcohols on oxide surfaces can be taken to be established to a relatively high degree of reliability. However, their influence on the kinetics of the reaction is still uncertain.

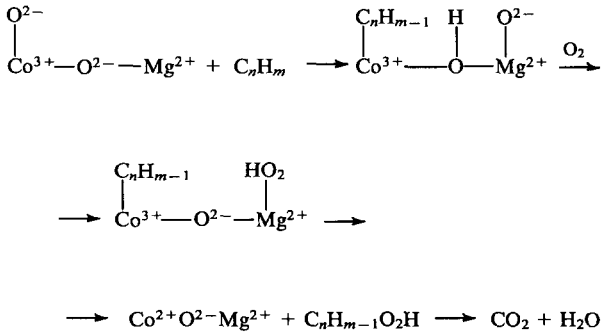
IX. Extensive oxidation of organic compounds

We have already discussed several processes which contribute to the oxidation of organic compounds and ultimately lead to the formation of CO and CO_2. It is generally thought that extensive oxidation takes place through surface carboxylates and carbonates. The formation of carboxylate structures of the $HCOO^-$ type (in some cases destructively oxidised as a C–C bond) by the interaction between hydrocarbons and surface oxygen was first reported by Kuznetsov et al.[115] However, real kinetic data on the contribution of these forms to the catalysis are still scarce.

The oxidation of CH_4, C_2H_6, and C_2H_4 on CeO_2 at 20–400 °C was studied by in situ EPR and FTIR spectroscopy methods.[116] At 200 °C the surface contains $HCOO^-$, which is converted into carbonate at 300 °C. The initiation of extensive oxidation is independent of the oxygen pressure, but it is affected by the pretreatment of the CeO_2 catalyst. The O_2^- ion is inert up to 300 °C: evidently, the O_2^{2-} ion reacts with hydrocarbons in this temperature range. In the IR spectra obtained under the conditions of oxidation of C_2H_4 and C_3H_6 at 100–300 °C on $Bi_2O_3-MoO_3$ bands from strongly bound complexes leading to the deep oxidation products were observed[48] in addition to the bands corresponding to π-allyl. On Ag/Al_2O_3 and Tl_2O_3/Al_2O_3 the precursors of the deep oxidation products were found to be surface carbonates.[48]

In the oxidation of ethane on Pd/Al_2O_3 absorption bands due to adsorbed acetates and acetaldehyde were seen in the IR spectra.[117] On Pd/SiO_2 or on pure Al_2O_3 these surface compounds are not formed: their formation requires the presence of both Pd and Al_2O_3. Probably the compounds are formed on the Pd and then migrate to the Al_2O_3 by the spillover mechanism. Under these conditions ethane is not adsorbed.

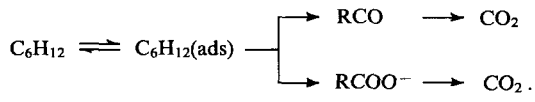
Acetates, formates, and benzoates were observed in the oxidation of C_3H_6 and $C_6H_5CH_3$ on 5% CoO–MgO.[118] The formation of O_2^- was also noted. According to these workers[118] the reaction may follow the scheme



The hydroperoxide $C_nH_{m-1}O_2R$ (for example, All–OOH) can decompose into $CH_3CHO + H_2CO$ and then be oxidised to carboxylates and finally to CO_2. We note that a similar mechanism was proposed earlier[119] for the oxidation of C_3H_6 on CoO–MgO. The oxidation of isobutene on V_2O_5/TiO_2 was studied by FTIR spectroscopy.[120] At low V_2O_5 concentrations dimerisation takes place, and at high concentrations the isobutene undergoes extensive oxidation. In the former case π-complexes of iso-C_4H_8 are observed on the surface, in the latter we find alkoxides and carboxylates. As reported,[120] acid centres of the Brønsted type and the lattice oxygen give rise to the extensive oxidation.

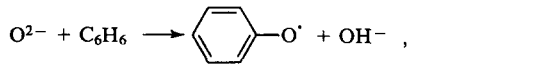
In the oxidation of butene on Mg–Fe–O and Zn–Fe–O[121] the strongly adsorbed C_4H_8 σ-complex is retained on the surface up to 500 °C, but in the presence of O_2 it is retained only up to 200 °C, i.e. up to the temperature at which CO_2 appears in the gas phase. It is suggested that the σ-complex interacts with O_2 to give the $HCOO^-$ form, which is an intermediate in the extensive oxidation reaction of C_4H_8 to CO_2. On $MgO-Al_2O_3$, $ZnO-Al_2O_3$, and Al_2O_3 the σ-complex is not oxidised to $HCOO^-$, and these catalysts do not show any activity in the extensive oxidation process. The interaction of a series of hydrocarbons (C_3H_6, C_4H_6, and C_6H_6) with oxides was studied by FTIR spectroscopy.[122] On SiO_2 only physisorbed molecules were observed. On γ-Al_2O_3 at 300 °C bicarbonates and acetates were formed from C_3H_6, whereas on γ-Fe_2O_3 carbonates were formed at room temperature, and at 150 °C formates and acetates were formed from C_3H_6, carboxylates from C_4H_6, and an oxidised product from C_6H_6. On TiO_2 bicarbonate was observed at room temperature, and at 150 °C acetone, aldol (from C_3H_6), and carboxylates (from C_4H_6) were observed. These substances may be the precursors of the extensive oxidation products.

The kinetics of the extensive oxidation of cyclohexane on NaX and KY zeolites were studied in our laboratory[123–126] in conjunction with in situ measurements of the IR spectra. The reaction can follow two paths:



The rate of the catalytic reaction is proportional to the overall concentration of the two complexes, but the carbonyl complexes decompose faster than the carboxylates (acetates and formates). Thermal desorption data confirm that the carbonyl complexes decompose at temperatures 50–100 K lower than the carboxylates, and therefore transformations through the carbonyl compounds are the main reaction path of the extensive oxidation. Self-oscillations were observed[123,125] in the oxidation of cyclohexane on KY zeolite, and oscillatory changes synchronous with those of the reaction rate were noted in the intensity of the IR bands from adsorbed carbonyl compounds. It was assumed that the carbonyl group is bound to a peroxide group.

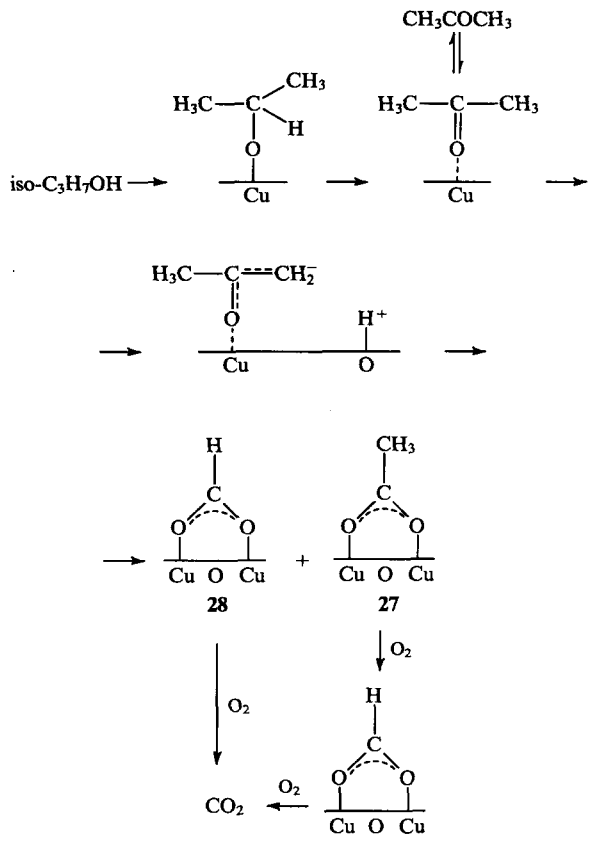
The oxidation of benzene (and also of toluene and *o*-xylene) was studied on supported vanadium oxide catalysts by the EPR method.[127] The reaction



leads to the formation of free-radical products which are ultimately oxidised to CO_2.

The mechanisms of the oxidation of alcohols on oxides have already been discussed above. Here we shall only deal briefly with some studies specially aimed at the mechanism of the extensive oxidation of alcohols. According to spectroscopic data,[128] in the oxidation of isopropanol on CuO at 20–80 °C the resulting isopropylates interact with oxygen from the gas phase. The lattice oxygen reacts in a similar way only at 120–150 °C. The formation of CO_2 is accompanied by the disappearance of the carboxylates. The kinetics of the disappearance of the carboxylates during the treatment of the surface in the iso-$C_3H_7OH + O_2$ reaction mixture at 100–200 °C were studied by in situ IR spectroscopy.

Under these conditions the concentration of isopropylates decreases, but that of formates goes through a maximum:



Under stationary conditions the concentration of formates on the surface is constant, and the time needed to establish the steady state is shorter than the time needed for the chromatographic analysis. Thus we have two extensive oxidation regimes: in the low-temperature regime the reaction proceeds through weakly bonded forms (type **27**) and through more strongly bonded forms (type **28**).

The oxidation of ethanol, n-propanol, isopropanol, n-butanol, isobutanol, and *tert*-butanol on Sn–Mo–O at 125–200 °C was studied by in situ IR spectroscopy. When the alcohol was removed from the reaction mixture the intensity of the IR bands corresponding to alcoholates and alcohols bound to the surface by a hydrogen bond and to aldehydes and acids rapidly fell to zero. The other bands remained in the IR spectrum for a much longer time. These bands are mostly due to condensation products containing carbonate and anhydride fragments. In the oxidation of butyric anhydride the same compounds are formed as in the oxidation of n-butanol, but the oxidation of the acids does not give oxidative condensation products (OCP). Under stationary conditions (in contrast to the initial period) absorption bands due to adsorbed alcohols and alcoholates are not observed. The following formal scheme has been proposed[129] for the reaction:

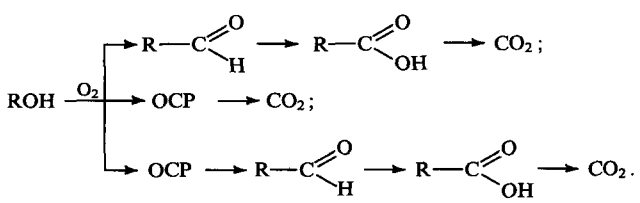
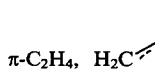
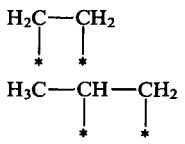
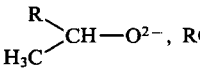
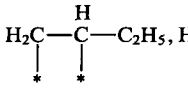
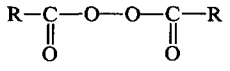
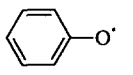
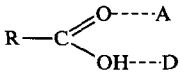
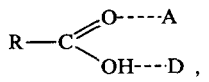


Table 7. Intermediate compounds in the deep oxidation reactions of organic compounds.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oxidation of CH_4, C_2H_6, C_2H_4 on CeO_2	$HCOO^-$, CO_3^{2-}, O_2^{2-}	M	126
Extensive oxidation of C_2H_4, C_3H_6 on $Bi_2O_3-MoO_3$	π-C_2H_4, 	L	48
Extensive oxidation of C_2H_4, C_3H_6 on Ag/Al_2O_3, Tl_2O_3/Al_2O_3		L	48
Oxidation of ethane on Pd/Al_2O_3	CH_3COO^-, CH_3CHO(ads)	M	117
Oxidation of C_3H_6, $C_6H_5CH_3$ on $CoO-MgO$	CH_3COO^-, $HCOO^-$, $C_6H_5COO^-$, O_2^-	L	118
Extensive oxidation of iso-C_4H_8 on V_2O_5/TiO_2		M	120
Oxidation of C_4H_8 on Mg–Fe–O, Zn–Fe–O		L	121
Oxidation of C_3H_6, C_4H_8, C_6H_6 on oxides	$HCOO^-$, CH_3COO^-, $RCOO^-$, CO_3^{2-}, HCO_3^-	M	122
Oxidation of cyclohexane on NaX, KY zeolites	RCO, $RCOO^-$ 	H	123–126
Oxidation of benzene on V/SiO_2, MgO, ZrO_2	O_2^-, 	M	127
Oxidation of i-C_3H_7OH on CuO	$C_3H_7O^-$, CH_3COO^-, $RCOO^-$, CO_3^{2-}, HCO_3^-	M	128
Oxidation of alcohols on Sn–Mo–O	Oxidative condensation products	M	129
Oxidation of HCOOH and CH_3COOH on Pt/Al_2O_3		L	130
Oxidation of $H_2C=CHCHO$ and CH_3CH_2CHO on Cu_2O	$RCOO^-$, $RCH=CHO^-$, C_xH_y, C_x	L	131

The oxidation of the acids HCOOH and CH_3COOH on Pt/Al_2O_3 also was studied by IR spectroscopy.[130] At low temperatures the complexes



were detected (where A is an electron acceptor and D is an electron donor).

These complexes interact with O_2 at 200–300 °C. Strongly bound acetates and formates do not react with O_2. In the HCOOH complex the C–H bond is broken during the interaction with O_2, and in the CH_3COOH complex the C–C bond is broken.

X-Ray photoelectron spectroscopy and thermal desorption methods were used to study the extensive oxidation of acrolein and propionaldehyde on a $Cu_2O(100)$ surface.[131] The products of this reaction are CO, CO_2, and H_2O. Enolate and carboxylate complexes are observed on the surface, but the latter (in general) do not take part in extensive oxidation, and only a small fraction of the products is formed from the enolate. It is suggested[131] that the main extensive oxidation path includes the deoxygenation of the adsorbate, the dehydration of C_xH_y, and the final burning of the surface carbon by oxygen from the lattice.

A list of data on the intermediate compounds which contribute to the extensive oxidation is given in Table 7.

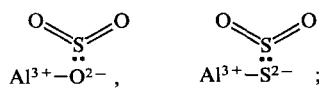
Though surface carbonates and carboxylates are very often observed in the extensive oxidation of organic compounds these complexes do not provide the main path for the formation of CO_2. At low temperatures a different path can be established, involving intermediates which are difficult to identify because of their short lifetimes. They are probably free-radical or peroxidic products. The extensive oxidation takes place by a free-radical mechanism (and in some cases by a heterogeneous–homogeneous mechanism). At high temperatures a complete decomposition of the organic molecule with oxidation of C_{ads} to CO_2 and of H_{ads} to H_2O is more probable.

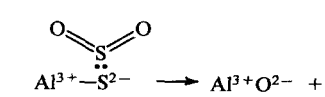
X. Reactions involving sulfur

The Klaus reaction $H_2S + SO_2 \rightarrow S_2 + H_2O$ takes place on several oxide catalysts. After the interaction of $H_2S + SO_2$ on Al_2O_3 the IR and UV spectra of the surface compounds were recorded at 20–400 °C.[132] The SH and OH groups are stable up to 150 °C.

$$H_2S + O^{2-}(surf) \longrightarrow H_2O + S^{2-}(surf)$$

At higher temperatures we find the S^{2-} form, which is stable up to 300–400 °C, with bands at 220–260 nm in the UV spectrum. The interaction of $Al^{3+}S^{2-}$ and $Al^{3+}O^{2-}$ with SO_2 at 150 °C produces sulfite–sulfate complexes:





Under the conditions of the Klaus reaction on Sn–Mo–O the reversible adsorption of SO_2 was observed by IR spectroscopy. MoS_2 is formed in the presence of H_2S. If SO_2 is adsorbed first, followed by H_2S, the absorption bands due to adsorbed SO_2 are weakened and the bands at 800–1000 cm^{-1} become stronger. This is because of the formation of S_2 molecules, with the possibility of reoxidation of the catalyst with formation of the Mo=O bond.[133] The IR and UV spectra of the adsorbed substances were recorded also after carrying out the Klaus reaction on the NaX zeolite.[134] The changes in the intensity of the bands were ascribed to the reactions

$$SO_2 + OH^- \longrightarrow HSO_3^-,$$

$$H_2S \longrightarrow HS^- + H^+,$$

$$2\,HSO_3^- + H_2S \longrightarrow S_2O_4^{2-} + S + 2\,H_2O,$$

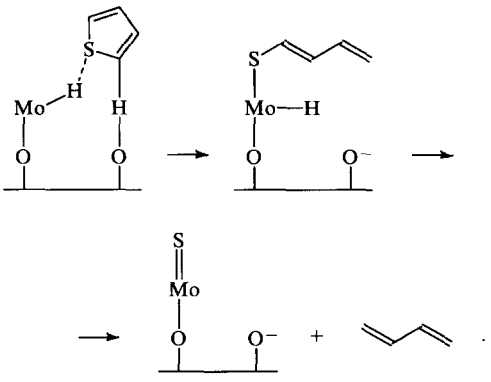
$$2\,HSO_3^- + 2\,HS^- \longrightarrow S_2O_4^{2-} + S_2^{2-} + 2\,H_2O,$$

$$S_2^{2-} + 2\,SO_2 \longrightarrow S_2O_4^{2-} + 2\,S,$$

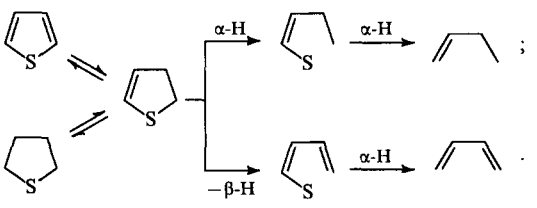
$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+.$$

Polymers of the S_8 type, which behave both as products and as intermediates, were also observed. The same products were found when the oxidiser SO_2 was replaced by oxygen.

The hydrogenation and the hydrodesulfurisation of thiophene on a 10% MoO_3/Al_2O_3 catalyst were studied by IR spectroscopy.[135,136] Thiophene weakly adsorbed on the OH groups was observed, together with carboxylates and thiocarboxylates. These may be the intermediate compounds. Thiophane is not an intermediate compound, and therefore we may assume that breaking of the C–S bond precedes the hydrogenation:



According to thermal desorption data[137,138] the key intermediate in the hydrogenation of thiophene on $Co–Mo–O/Al_2O_3$ is dihydrothiophene, which (depending on the hydrogen pressure and on the temperature) can be converted into thiophene, thiophane, and the reaction products. Butene can be formed from the dihydrothiophene intermediate by the two-stage hydrogenation of the α-carbon with simultaneous breaking of the C–S bonds, whereas β-elimination in the first stage and α-hydrogenation in the second stage give butadiene:

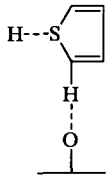
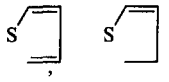


It may be assumed that the hydrogenation–dehydrogenation reactions take place on centres of one type, and the hydrodesulfurisation reactions on centres of another type. The main weakness of the published work[135–138] is the failure to allow for the contribution to the reaction from the sulfur atoms of the sulfide catalyst. It was shown[139] that under the conditions of the reaction on MoS_2/Al_2O_3 a strong exchange of sulfur takes place between H_2S and MoS_2.

The reaction of methanol with H_2S on Al_2O_3 and WO_3/Al_2O_3 was studied by NMR.[140] It follows from the analysis of the NMR spectra taken after the reaction that CH_3O and CH_2S groups are present on the surface. It is suggested that CH_3SH is formed by the interaction of the CH_3O and HS surface groups, and $(CH_3)_2S$ by the interaction of CH_3O and CH_3SH.

The data on the intermediate compounds in reactions involving sulfur are summarised in Table 8.

Table 8. Intermediate compounds in reactions involving sulfur.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Klaus reaction on Al_2O_3	SH^-, OH^-, H_2S(ads) S^{2-}, SO_3^{2-}, HSO_3^-, SSO_2^-	L	132
Klaus reaction on Sn–Mo–O	SO_2(ads), S_2(ads)	L	133
Klasu reaction on NaX	HSO_3^-, HS^-, S_2^{2-}, $S_2O_4^{2-}$, S_8	M	134
Hydro-desulfurisation of thiophene on MoO_3/Al_2O_3		L	135, 136
Hydro-desulfurisation of thiophene on Co–Mo/Al_2O_3		M	137, 138
Reaction of $CH_3OH + H_2S$ on Al_2O_3, WO_3/Al_2O_3	CH_3O, CH_3S	L	140

XI. Conclusion

In our previous reviews[1,2] an attempt was made to describe the results of studies of the surface complexes formed in heterogeneous catalysis carried out during the past 15 years using modern experimental methods. Our aim was to cover the largest possible number of investigations, but because of the rapid developments in this field of catalysis the task was not easy. Some general conclusions can be drawn from the data which have been assembled.

(1) In spite of our critical assessments of the reliability of the contributions made by various intermediate states there is little doubt that in the great majority of cases the confidence level is not high. The most convincing evidence that an observed surface compound is an intermediate in the reaction is the coincidence of the rates of transformation of the surface complex and of formation of the product. Only few studies adopting this approach have been reported, mainly because of the great experimental difficulties. The most serious of these difficulties is the need for simultaneous measurements of the spectroscopic and the catalytic characteristics of the system. Another difficulty is the need for quantitative spectroscopic measurements. This requires a knowledge of the extinction coefficients or of the scattering coefficients in the surface complexes, and information of this type is scarce. However, we should stress the fact that this approach is being strongly developed at the Institute of Chemical Physics of the Russian Academy of Sciences.

(2) Both the spectroscopic and the kinetic measurements of the consumption of reactants and of the accumulation of products in the gas phase usually have an unacceptably low time resolution. In order to create a complete picture of the mechanism we require faster measurements, at least in the millisecond range (i.e. at the lower limit of the time constants in catalysis). This calls for the development of new methods of measurement. One of the most promising of the new methods is the use of the TAP reactor.

(3) Many different surface compounds are formed when a given reaction is carried out on different catalysts. Even in the case of similar catalytic systems different workers report different surface complexes. This is usually attributed to differences in the reaction mechanism. However, another possible explanation[141] suggests that for a given mechanism the relative rates of the different stages may be different on different catalysts. As a result we may observe different surface complexes on different catalysts. Of course, in order to test this explanation we require detailed information on the intermediate compounds formed in a given reaction on different catalysts.

(4) By analogy with empirical dependences such as the Polanyi–Semenov rule, which describes the relationship between the energy of a bond and the activation energy of the reaction, it has been possible to establish general dependences relating the activation energy of a reaction to the decomposition energy of the intermediate complexes. In some cases, when the structure of the intermediates on the surface is close to the structure of the final products, we observe a lowering of the activation energy. However, data of this type are still too few to provide unambiguous conclusions.

(5) Often spectroscopic studies detect surface compounds which are formed on an active part of the catalyst but then migrate towards an inactive part. A characteristic of these compounds is their lack of sensitivity (or low sensitivity) towards changes in the reaction parameters (temperature, pressure, composition of the components). Typical of this behaviour is the accumulation of surface compounds on a carrier, on one of the phases of a mixed catalyst, or on one of the faces of a simple catalyst by the spillover mechanism. The accumulated surface compound can 'feed' the main reaction when the process conditions are changed. In complex multistage reactions this accumulation can produce the transport of molecules from some active centres towards others, spatially separated from the former.

(6) The data presented in our review show that the mechanisms proposed for heterogeneous catalytic reactions, though plausible, are largely conjectural. Obviously, this state of affairs is due to the almost total absence of reliable information on the intermediate compounds. Therefore we may finally conclude that further progress in our understanding of heterogeneous catalysis calls for a systematic study of intermediates.

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