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Catalytic Oxidation of Propene

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The oxidation of propene on simple and mixed oxide catalysts to form various oxygen-containing products—acrylaldehyde, acrylic acid, acetone, and acetic acid—is surveyed, and the role of individual components of the active catalysts discussed. A list of 110 references is included.

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I. INTRODUCTION

Catalytic oxidation of propene is one of the chief methods for obtaining monomers and intermediates in organic synthesis. The increasing demands made by the national economy for such important compounds as aldehydes, ketones, and carboxylic acids require the development of new, more economic methods for their production. A problem of primary importance is to choose active and highly selective catalysts. Those containing molybdenum have become the most widely used mixed oxide catalysts for the selective oxidation of propene.

A vast literature has now accumulated on the catalytic oxidation of propene to acrylaldehyde. The kinetics has been studied in detail, reliable data are available on the mechanism of the formation of acrylaldehyde on several catalysts, and highly effective industrial catalysts have been developed.

Studies of the oxidation of propene to acrylic and acetic acids, acetone, and methyloxiran have increased during recent years. The production of acrylic acid has now reached the stage of semi-industrial trials, that of acetone and acetic acid is at the level of laboratory investigation, and an active catalyst is being sought to obtain methyloxiran.

There have been hardly any reports of processes in which such oxygen-containing compounds as propionaldehyde, propionic acid, formaldehyde, formic acid, and acetaldehyde are formed as main products. These compounds are usually obtained as by-products in various processes involving the oxidation of propene.

II. OXIDATION OF PROPENE TO ACRYLALDEHYDE AND ACRYLIC ACID

Among individual oxides copper(I) oxide is the most active catalyst for the oxidation of propene to acrylaldehyde[1]. This process has been developed to an industrial level, but the use of bismuth molybdate has enabled higher indices to be achieved and also research on the preparation of mixed oxide systems containing molybdenum to be started.

In 1978 Keulks published a review[2] which touched only part of the problem, with the oxidation of propene mainly on bismuth molybdates as example. Reference 3 also reviews the physicochemical and catalytic properties of the latter products, and includes structural features and data on the kinetics and the mechanism of the oxidation of propene. The present Review attempts to summarise the disconnected data published during recent years on the oxidation of propene.

It can be accepted as established that bismuth molybdate Bi_2MoO_6 is almost inactive[4]. It comprises octahedra of oxygen atoms surrounding a molybdenum ion and alternating with layers of bismuth ions. The structures of the molybdates $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$ have been less thoroughly studied, but they definitely contain more oxygen vacancies than in Bi_2MoO_6. Among the bismuth molybdates $Bi_2Mo_3O_{12}$ possesses moderate activity, while $Bi_2Mo_2O_9$ and the two-phase catalysts (mixtures of Bi_2MoO_6 and $Bi_2Mo_3O_{12}$) have about the same high activity. X-Ray electron spectroscopy has shown that in the catalysts Bi_2MoO_6, $Bi_2Mo_2O_9$, and $Bi_2Mo_3O_{12}$ the ratios of bismuth to molybdenum are about the same on the surface and in the mass[4]. In two-phase specimens in which the mass ratio is 1–2 : 1 the surface ratio is unity; it gradually decreases with increase in the molybdenum content, and very slowly increases with increase in the bismuth content. The catalytic activity is assumed to be determined by a surface phase having the ratio Bi : Mo $\approx$ 1. One factor determining the activity and the selectivity of bismuth molybdates is the high rate of diffusion of oxygen in the crystal lattice.

Using ^{18}O and $CD_3.CD{:}CH_2$ as labelled reagents Keulks et al. have established[5] that on the bismuth molybdates $Bi_2Mo_3O_{12}$ and Bi_2MoO_6 acrylaldehyde is formed solely by a redox mechanism, and that the reaction involves oxygen from several surface layers of the lattice (respectively 13–47 and 79–280 monolayers). Oxidation of acrylaldehyde to carbon dioxide is effected also by oxygen of the crystal lattice.

The activation energy of removal of oxygen ions O^{2-} located between layers of molybdenum and bismuth atoms is much lower for those attached to molybdenum[6,7]. Hence experimental results are regarded[6,7] as indicating that on selective oxidation the adsorbed hydrocarbon interacts with an oxygen ion attached to bismuth, and are explained by the formation of oxygen vacancies in the molybdenum layer during preliminary reduction of the bismuth–molybdenum oxide catalyst; vacancies formed at bismuth(III) ions are filled by oxygen ions attached to molybdenum(VI), while oxygen from the gas phase fills vacancies at the molybdenum ions. Such a mechanism of migration of oxygen ions ensures a steady state of oxidation of the catalyst and explains the enhanced activity and the selectivity of bismuth molybdates in comparison with the individual oxides.

The structure of bismuth molybdate and the energy of bonding of oxygen in the lattice are influenced by the introduction of various additives. Heavy oxygen $^{18}O_2$ has been used as tracer to study the selectivity of the oxidation of propene to acrylaldehyde on bismuth molybdate modified with cobalt, nickel, manganese, magnesium, strontium, barium, and lead[8]. Since the acrylaldehyde and carbon

dioxide had the same oxygen-18 content, but the water a diminished content, it was supposed that two types of oxygen atoms—active towards addition to propene and active towards removal of hydrogen atoms—were present in the catalyst. After addition of cobalt, nickel, manganese, or magnesium the catalyst has the α-$MnMoO_4$ structure and the selectivity of oxidation of propene to acrylaldehyde reaches 93–97%, whereas a catalyst containing strontium, lead, or barium gives a lower selectivity (71–87%) and has the scheelite structure. The varying reactivity of oxygen in the lattice is governed by the modifying effect of the additives.

Introduction of small quantities (0.2 mass %) of phosphorus into bismuth molybdate $Bi_2Mo_3O_{12}$ transforms it into $Bi_2Mo_2O_9$. When the phosphorus content exceeds 1.3 mass %, a ternary chemical compound $2Bi_2O_3.MoO_3.P_2O_5$ is formed[1]. A ternary compound has been observed also in the bismuth–molybdenum–iron system[9–11]. Addition of iron(III) is assumed to result in filling of cationic vacancies in $Bi_2Mo_3O_{12}$ and in formation of at least two ternary compounds having the proportions Pi : Fe : Mo = 1 : 1 : 1 and 3 : 1 : 2. It appears that Bi^{3+} and Fe^{3+} ions can be interchanged in these compounds without significant structural changes. The catalytic activity of bismuth–molybdenum–phosphorus and bismuth–molybdenum–iron oxide systems is attributed to the presence of ternary compounds.

Tracer and spectroscopic methods have been widely used[12–16] to investigate the mechanism of the partial oxidation of propene on bismuth–molybdenum and copper oxide catalysts. Experiments with deuterated propene have proved that the rate-determining stage in the formation of acrylaldehyde is detachment of a hydrogen atom from the methyl group.

Considerably more by-products (e.g. carbon dioxide, acetaldehyde are formed on the interaction of allyl radicals (obtained by the thermal decomposition of azo-3,3′-propene) on the surfaces of molybdenum(VI) and bismuth(III) oxides and on bismuth molybdates than in the conversion of propene or allyl iodide under corresponding conditions[17]. The hypothesis was therefore put forward that the oxidation of propene does not involve formation of a free allyl radical. These results together with experiments on the oxidation of allyl alcohol suggested[18] a mechanism of selective oxidation of propene with transition from π-allyl to σ-allyl molybdate before detachment of the second hydrogen atom with formation of acrylaldehyde and a reduced form of the catalyst.

Comparison of the products formed in the oxidation of propene on bismuth oxide and on bismuth molybdates indicates[19–21] that dissociative adsorption of propene with detachment of the first hydrogen atom takes place on a bismuth cation, while the role of molybdenum is merely to change the energy of bonding of oxygen with the catalyst.

The opposite view is also widely represented in the literature, that an allyl complex is formed on a multivalent molybdenum ion[22–30]. The alkene interacts with an oxygen vacancy in the vicinity of a molybdenum ion and forms a π-allyl complex of molybdenum, which is then oxidised by oxygen of the catalyst to the reaction products. The role of bismuth is merely to facilitate dehydration of and to reduce the catalyst surface.

The oxidation of propene and of acrylaldehyde to acrylic acid has been studied on the tellurium–molybdenum oxide system containing various additives[31]. The sequence of the latter with respect to selectivity of such oxidation is respectively

V>Mn>Sn>Ti>W>Ni>Cr>Bi>Co>Fe>Cu,

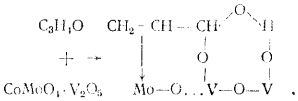
and the somewhat modified

V>Sn>Ti>Co>W>Cr>Bi>Ni>Fe>Cu>Mn.

The optimum catalyst for the oxidation of both compounds to acrylic acid is a tellurium–molybdenum oxide system containing 25 mass % of vanadium. The parallelism in the variation of catalytic properties with the vanadium content suggests that the oxidation of propene to acrylaldehyde and to acrylic acid takes place on the same active centres of the catalyst. The yield of acrylaldehyde and acrylic acid is increased significantly by the introduction of tellurium into the chromium–molybdenum oxide system[32]. Study of the acidity of the surface and of the surface complexes formed on adsorption of alkenes indicates that both carbon dioxide and acrylic acid result from the breakdown of carboxylate complexes formed on aprotic acid centres. The presence on the surface of proton-donor centres and the absence of active, weakly bound oxygen favour the formation of acids.

The catalytic properties of the cobalt–molybdenum oxide system, which is active in the oxidation of propene to acrylic acid, are significantly determined by the phase constitution. Maximum yield of the acid corresponds to the highest content of the acitve phase b-$CoMoO_4$.† Formation of the active phase is largely determined by the conditions of preparation of the specimens (pH, temperature of precipitation, concentrations of initial salt solutions, temperature of ignition).[33,34] Introduction of bismuth, chromium, and iron oxides into cobalt molybdate changes the content of the active phase and influences the selectivity of oxidation of propene to acrylaldehyde[34].

The introduction of vanadium and copper ions into cobalt molybdate increases the rate of formation of acrylic acid from acrylaldehyde by factors of 40 and 28 respectively. Nickel has the least effect[29]. It is significant that these additives lower the rate of conversion of propene into acrylaldehyde. It was suggested that they block the molybdate anions responsible for the formation of π-allyl complexes in molybdates. Electron spin resonance spectroscopy has shown that interaction of the catalyst with propene and with acrylaldehyde changes the oxidation states of the molybdenum ions and also of the additives; in particular, when the surface is modified with vanadium ions, reduced centres V^{4+} and V^{3+} are readily formed, and govern the oxidation-state transitions. Complex formation between acrylaldehyde and surface ions of the catalyst may involve interaction with both ethylenic and carbonyl bonds. Since the rate of conversion of acrylaldehyde into acrylic acid far exceeds the rate of oxidation of propene in the same direction, it was supposed[29] that in the case of acrylaldehyde interaction is effected at the carbonyl bond, with oxidation on cobalt molybdate containing added vanadium following the scheme



Catalytic activity is enhanced by the addition of tellurium and phosphorus to the cobalt–molybdenum oxide system: the conversion of propene reaches 80%, and selectivity with respect to acrylic acid and acrylaldehyde respectively 50% and 20%.[35] Investigation of the phase constitution of the cobalt–molybdenum–tellurium–phosphorus oxide catalyst has shown that it consists of a-$CoMoO_4$#, MoO_3, P_2O_5, TeO_2, and

†Here b-$CoMoO_4$ is a modification of cobalt molybdate characterised by an octahedral oxygen environment of the molybdenum.

#Here a-$CoMoO_4$ is a low-temperature modification of cobalt molybdate with four-coordinated molybdenum and six-coordinated cobalt.

a chemical compound (the x-phase§). The active component of the catalyst is molybdenum trioxide promoted with tellurium dioxide in the oxidation of propene to acrylaldehyde, but α-$CoMoO_4$ in the oxidation of acrylaldehyde to acrylic acid[35].

Several general ideas have now been formulated on the selective oxidation of alkenes and in particular of propene[36,37]. In selective oxidation activation of the propene molecule requires that the catalyst should possess certain acid–base properties in order to abstract α-hydrogen and form an allyl group. Furthermore, the catalyst should possess appropriate redox parameters in order to bind this group by electron transfer from an allyl π-orbital to a d-orbital of the cation and produce a definite charge on it, since the subsequent reaction depends on the sign of this charge.

A molecule of an oxygen-containing product is formed by nucleophilic addition of oxygen ions from the crystal lattice to the activated hydrocarbon complex. Thus oxygen ions implanted in the catalyst lattice are nucleophilic reagents devoid of oxidising properties, while lattice cations act as oxidant in selective oxidation, activating hydrocarbons and forming a hydrocarbon residue having electrophilic properties. However, what properties of a surface cation on the catalyst influence activation of the alkene remains an open question.

It has been suggested[38,39] that catalysts of partial oxidation are characterised by metal–oxygen double bonds. It has been shown for molybdates of various elements that on those containing Mo=O bonds oxidation takes place via an allyl group. Such bonds are not present in catalysts of complete oxidation, such as molybdates of Groups I and II elements having the scheelite structure. The direction of oxidation of an alkene is assumed[30] to be independent of the nature of the metal M and determined solely by the electronic structure of the bond: low polarity of the M=O bond favours selective oxidation; with a strongly polar bond electrophilic attack of π-electrons of the alkene is probable with rupture of the ethylenic bond.

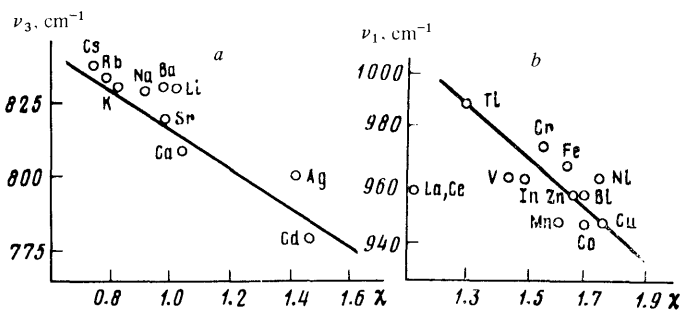


Figure 1. Comparison with the cation electronegativities χ of the wavenumbers ν of the characteristic bands in the infrared spectra of molybdates for the bonds: *a*) Mo=O, ν_3; *b*) Mo–O, ν_1.

The frequency of vibration of single and double-molybdenum–oxygen bonds depends on the nature of the cations present in molybdates[39]: the absorption bands move to lower frequencies with increase in electronegativity of the elements involved, which indicates increasing lability of these bonds (Fig.1), while the rate of allylic oxidation of propene increases (Fig.2). The formation of metal–oxygen double bonds may be promoted by oxygen vacancies appearing on the surface during the reaction, as is assumed in the mechanism of the oxidation of propene to acrylaldehyde on a uranium–antimony catalyst[40], and also by the introduction of additives, e.g. of tellurium into cadmium molybdate[41].

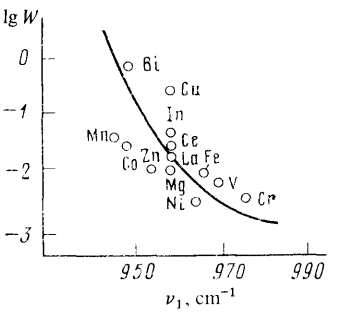


Figure 2. Specific rate of formation W of products of allylic oxidation on molybdates as function of wavenumbers of infrared absorption bands due to the Mo=O bond.

Several studies[42–50] have revealed the activating effect of excess of molybdenum trioxide on the catalytic properties of molybdates in various types of oxidation of alkenes. Such excess was assumed to be necessary to maintain the stoichiometric composition of the surface layer with loss of molybdenum during catalysis[46], to promote complete interaction of the initial salts during preparation of the normal molybdate[48], and also apparently to produce structural defects[42,43,49,50].

X-Ray diffraction, infrared spectroscopy, conductivity measurements, and density measurements on cobalt, iron, and chromium molybdates containing excess of molybdenum trioxide indicate that such excess within certain limits leads to formation of an imperfect structure, a solid solution. The defect structure produces a considerable increase in catalytic activity of the system towards the oxidation of propene[50–52] (Fig.3).

The probability of the dissolution of molybdenum trioxide in a molybdate is determined by the similarity of their structural fragments, comprising alternating oxygen octahedra and tetrahedra populated by the corresponding metal cations[53]. The degree of substitution of cations in the molybdate structure by the molybdenum ion is largely determined by the closeness of their ionic radii and also by the configuration of the electron shells. Absence of such correspondence, e.g. in indium and bismuth molybdates, leads to formation of a mechanical mixture of the molybdate with molybdenum trioxide[50].

It has been shown for isostructural cobalt and magnesium molybdates that introduction of excess of molybdenum trioxide not only increases substantially the rates of oxidation of propene to acrylaldehyde but also results in almost the same rates, evidence that active centres of closely similar composition have been formed[54].

A favourable influence of excess of one of the components on the activity and selectivity of a catalyst has been established also in other cases. Thus in the iron–antimony oxide system the selectivity of the chemical compound $FeSbO_4$

§Here the x-phase is a chemical compound formed in the tellurium–molybdenum oxide system at 425–450 °C.[35]

in allylic oxidation is considerably increased in the presence of excess of Sb_2O_4.[55] It was suggested that the latter suppresses the presence of free iron oxide, which is active in further oxidation[56,57]; formation of new chemical compounds—$FeSb_2O_4$ and $Fe_2Sb_2O_7$—may well be probable[58]. The high selectivity of the $FeSbO_4$–Sb_2O_4 system has been attributed[59] to interaction at the phase boundaries.

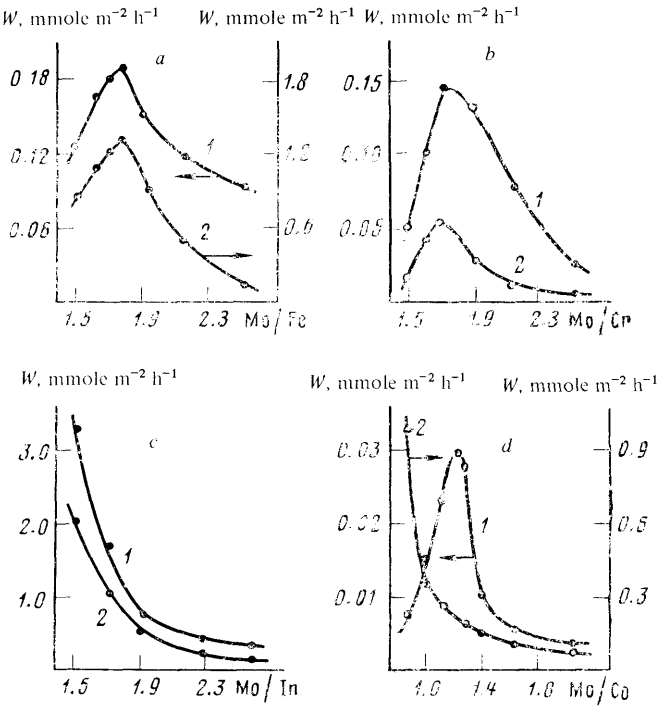


Figure 3. Variation[50] in specific rate of formation of *1*) acrylaldehyde; *2*) carbon dioxide with Mo/M ratio for M: *a*) Fe; *b*) Cr; *c*) In; *d*) Co.

Comparison of the activities of catalysts having antimony–iron ratios of 1 and 2 towards the oxidation of propene to acrylaldehyde in oxidising and reducing media indicates[55] that the decrease in the yield of carbon dioxide with simultaneous increased formation of acrylaldehyde is due to modification of the properties of oxygen on the catalyst surface: with excess of Sb_2O_4 on the surface of $FeSbO_4$ a thin (<20 Å) antimony-enriched layer is formed, responsible for the selective oxidation of propene to acrylaldehyde. Considerable enhancement of selectivity of oxidation to acrylaldehyde is possible[60] on an $FeSbO_4$ catalyst on which a small quantity (1–2 atomic layers) of Sb^{5+} ions have been deposited.

Excess of an oxide held in solid solution also enhances activity[61]. In the antimony–tin oxide system containing 5 mass % of antimony the latter is present in the SnO_2 lattice as Sb^{5+} ions, but at higher contents as a mixture of Sb^{5+} and Sb^{3+}. Calcination leads to separation of an oxide phase, identified as a two-dimensional layer of Sb_2O_4. A two-phase catalyst containing 18.7 mass % of antimony is the most selective with respect to acrylaldehyde. The effective catalyst comprises an oriented film of Sb_2O_4 deposited on an Sb^{5+}–SnO_2 solid solution[61].

The matching of activating components to simple and binary oxides with the aim of improving the effectiveness of catalysts has led to considerable complication of their composition. At the present time multicomponent systems are used in industrial production, and the majority of patents propose catalysts containing at least four different elements (Table 1). The phase composition of most mixed catalysts and the function served by their individual components have not yet been elucidated.

It is noteworthy that molybdenum predominates in almost all the catalysts listed in Table 1. Molybdenum trioxide is known as a relatively inactive but highly selective catalyst for the oxidation of propene to acrylaldehyde, and is usually employed in admixture with other oxides. Preparation of a mixed catalyst may involve various types of interaction of the trioxide with the other oxide components—formation of chemical compounds such as molybdates, solid solutions, and mechanical mixtures.

Table 1. Catalysts for the oxidation of propene to acrylaldehyde and acrylic acid.

Catalyst	Ref.
$K_{0.1}Ni_{2.5}Co_{4.5}Cr_3BiP_{0.5}Mo_{12}O_x$	[62]
$Cr_{0.5}K_{0.1}Ni_{2.5}Co_{4.5}Fe_3BiMo_{12}O_x$	[63]
$Mo_{12}Cu_{0.1-9}Te_{0.2-0.8}Sb_{0.2-15}O_{36.8-85.5}$	[64]
$W_{0.5}Cs_{0.2}Ni_{2.5}Co_{4.5}Cr_2BiMo_{12}O_x$	[65]
$K_{0.07}Mg_{4.5}Fe_4Bi_2P_{0.5}Mo_{12}O_{51}$	[66]
$Mo_{12}BiFe_{12}Co_1NiBe_2P_{0.5}KO_x$	[67]
$Mo_{12}V_{2-11}Cu_{1-6}Cr_{0-1}W_{0-12}O_x$	[68]
$Ce_3W_{1.2}V_3Mo_{12}O_x$	[69]
$Mo_{12}Cu_{0.05-3}B_{0.001-0.1}P_{0.1-5}Sb_{0.001-1}V_{0.5}K_{0.05-5}O_x$	[70]
$Mo_{8-18}V_{0.1-6}Cu_{0.1-6}Ge_{0.1-6}O_x$	[71]
$Mo_{12}P_2Cr_{0.5}Zr_{0.5}Sn_{0.5}K_2O_x$	[72]

The high activity and the selectivity of multicomponent oxide systems has been explained[54] on the assumption that most of the active centres are grouped at the boundaries between individual crystallites, where different kinds of ions differing in charge and coordination coexist, and where the diffusion of oxygen, the adsorption of reactants, and the transfer of charge are accomplished with the least consumption of energy. Examination of a catalyst of general composition $M_n^{2+}Mo_{12}Bi_{0.75}O_x$ revealed the phases $M^{2+}MoO_4$, $Bi_2(MoO_4)_3$, MoO_3, and also strongly disintegrated iron molybdate; some of the ferric ions can partly penetrate molybdenum oxide and bismuth molybdate, while some of the ferrous ions are dissolved in M^2MoO_4.[73]

Numerous examples have been published of the interpenetration of ions when molybdenum trioxide is deposited on an "inert" carrier[74–80]. Thus on silicon dioxide a limiting concentration exists (~8 mass %) above which polymolybdate particles are formed and then crystallites of molybdenum trioxide. Below this concentration the catalyst contains particles of molybdosilicic acid and dimolybdates, while Mo–O fragments appear implanted in the silica structure[74,75]. It has also been shown[76] that silicon ions incorporated into molybdenum trioxide stabilise the hexagonal structure of the latter.

Calcination of a molybdenum oxide catalyst deposited on alumina and containing <9 mass % of molybdenum results in dispersion of the molybdenum as a monolayer, but with higher contents some bulk phase is observed[77]. Ignition causes molybdenum atoms to migrate into the interior of the

γ-alumina. According to X-ray electronic spectroscopy this is accompanied by displacement of the 3*d* line in the molybdenum spectrum to higher bond energies, as a consequence of transition of molybdenum from a covalent state in surface oxy-anions to a more ionic state in cavities of the crystal lattice[78]. A low molybdenum content (1.5 mass %) is almost entirely located in tetrahedral cavities of the alumina lattice and cannot be reduced. Increase in the content is accompanied by increase in the proportion of surface molybdenum in octahedral coordination and enhancement of the reducibility of the catalyst[79].

Unlike ions deposited together interact with the substrate. In the cobalt(II)–molybdenum(VI) oxide system on alumina the molybdenum ions prevent penetration of cobalt ions into the lattice with formation of the spinel $CoAl_2O_4$ and facilitate reduction of cobalt to the metal. The appearance of metallic cobalt in turn initiates reduction of molybdenum by atomisation of hydrogen molecules and diffusion of hydrogen atoms towards the molybdenum ions, i.e. by a "spillover" effect. It is significant that surfaces differing in composition can be formed in different media: heat-treatment of the cobalt–molybdenum–aluminium oxide system in air tends to enrich its surface with molybdenum ions, but reduction of the catalyst enriches it with cobalt ions[73]. Migration of molybdenum ions takes place during heating. After γ-alumina has been impregnated successively with solutions of ammonium paramolybdate and cobalt nitrate, subsequent heating at 500 °C produces a redistribution of cobalt and molybdenum ions. As a result, a layer of molybdenum oxide is formed on the surface of the catalyst, and a layer of cobalt oxide directly covers the surface of the carrier[80].

It is now suggested that the catalytic activity and selectivity of several oxide systems based on molybdenum (the trioxide on silica and on alumina) are determined by stabilised salts of heteropoly-acids attached to the surface[81–84]. Molybdenum(VI), tungsten(VI), and vanadium(V) are known to form heteropoly-acids with heteroatoms—phosphorus, silicon, arsenic, etc.—that are strong many-electron oxidants and at the same time inorganic acids possessing high Brønsted acidity[85–87]. Heteropoly-acids are used as homogeneous catalysts for the partial oxidation of organic compounds[88], including alkenes[89]. In the Reviewer's opinion, however, further evidence is required to support the view that heteropoly-acids have a decisive role in the activity of oxide systems in heterogeneous catalysis.

Supported molybdenum catalysts containing definitely coordinated molybdenum ions have proved several times more active and more selective than corresponding catalysts prepared by impregnation[90]. The active centres are coordinatively unsaturated molybdenum ions combined with Brønsted acid centres of the carrier. Thus the construction of an active surface by attaching complexes of definite composition to a catalyst and the formation of clusters of several identical or different metal atoms may prove an effective method for enhancing the activity and the selectivity of a catalyst.

III. OXIDATION OF PROPENE TO ACETONE AND ACETIC ACID

The production of acetone and its analogues by the gas-phase catalytic oxidation of alkenes has many advantages over other methods (cheap starting materials, absence of corrosive agents, simple apparatus, etc.). Various catalysts have been proposed, including binary molybdenum-containing systems, for the single-stage oxidation of propene to acetone[91–95].

It had been shown earlier[91] that selective formation of acetone takes place on the Co_3O_4–MoO_3 system over the range of cobalt–molybdenum ratios 9–4 : 1.

This work was continued by investigating the oxidation of propene to acetone on various oxides containing 10% of molybdenum trioxide[92]. The most effective in this series was a tin–molybdenum oxide catalyst: acetone begins to be formed even at 110–120 °C, and at 170 °C the selectivity with respect to acetone is 80–85%.

The titanium–molybdenum oxide system is somewhat less effective than a tin–molybdenum oxide catalyst. It is catalytically active at 110 °C, but the rate of formation of acetone is lower than on the latter system. Isopropyl alcohol is formed on both systems at low temperatures.

The ion–molybdenum oxide system catalyses the formation of acetone above 150 °C, with a maximum rate at 200 °C (selectivity 80%). A chromium–molybdenum oxide catalyst is active above 200 °C, and approaches the cobalt–molybdenum oxide system in activity. Acetone is formed also on oxide systems of molybdenum with vanadium, nickel, copper, and zinc, but the selectivity is low.

Study of the aluminium–molybdenum oxide system[93–95] containing up to 30 mass % of molybdenum has established that water vapour increases considerably its catalytic activity and selectivity in the oxidation of propene to acetone. The active centres presumably represent a combination of reduced and oxidised forms of molybdenum(V) and (VI). Catalytic activity is determined in considerable measure by the acidity of the surface, which is governed by the presence of molybdenum(V) ions formed by reduction of the catalyst. Molybdenum(VI) ions are involved in oxidising intermediate products. The surface acidity in turn influences the mobility and the reactivity of hydroxy-groups[94].

The investigations suggested, for the oxidation of propene to acetone, the scheme

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H^+} CH_3{-}{}^+CH{-}CH_3 \xrightarrow{+OH^-} \rightarrow [CH_3{-}CHOH{-}CH_3]_{ads} \xrightarrow{O} (CH_3)_2CO + H_2O \ .$$

The intermediate complex was assumed[94] to be an isopropoxy-group.

Kinetic study of the formation of acetone by the oxidation of propene on an iron–molybdenum oxide catalyst (Mo/Fe = 1.5) showed that the quantity of acetone formed varies linearly with the partial pressures of water vapour and propene, whereas the order with respect to oxygen is zero. The reaction velocity is given by the equation

$$V = k \cdot P_{H_2O} \cdot P_{C_3H_6} \ .$$

Either acetone or acrylaldehyde can be obtained depending on the temperature and also on the presence or absence of water in the reaction zone on iron molybdate. Hence an iron–molybdenum oxide catalyst can be regarded as bifunctional. Hydroxy-groups present on the surface in the presence of water vapour are assumed to take part in the hydration of propene, whereas oxygen ions attached to molybdenum effect the formation of acetone[96]. The mechanism of the oxidation of propene to acetone on an iron–molybdenum oxide catalyst has been assumed[97] to involve a stage of hydration of propene to isopropyl alcohol followed by oxidation of the secondary alcohol to acetone.

According to some workers[98] the oxidation of propene on a tin–molybdenum oxide system yields mainly acrylaldehyde and acrylic acid, but according to others[99,100] acetone and acetic acid. Information on the phase composition of this catalytic system is also contradictory: formation of a mechanical mixture of oxides, a chemical compound, or a solid solution based on tin dioxide have been suggested[99],

but evidence has been provided[101] for the formation of a solid solution based on molybdenum trioxide. It has been established that the phase composition and the direction of the partial oxidation of propene depend significantly on the method of preparation of the catalyst—the starting materials, the temperatures of coprecipitation and ignition, etc.

Pure tin dioxide is almost completely devoid of surface acid centres[102]. As molybdenum trioxide is added, the concentration of active centres increases significantly. This is to some extent supported by experiments undertaken by Buiten[103], in which the trioxide was deposited on the dioxide at high temperatures by means of water vapour, which interacts with the former to give the volatile species $MoO_2(OH)_2$, and this migrates through the gas phase to settle on the surface of the dioxide. The activity of the specimen in the oxidation of propene to acetone and acetic acid is thus greatly enhanced.

A parallelism has been established[104] between the activity of a tin–molybdenum oxide catalyst in the isomerisation of but-1-ene and the rate of oxidation of propene to acetone. The rate of isomerisation of an oxide catalyst depends on the surface acidity[105], so that active centres formed by the combination of tin dioxide and molybdenum trioxide are probably acidic in character. The acid–base properties of specimens are in turn determined by the method of preparation. Thus at high ignition temperatures irreversible desorption of hydroxy-groups—acid centres promoting the formation of acetone—may occur on the catalyst surface, with simultaneous increase in the relative number of metal ions, which are centres for the oxidation of propene to acrylaldehyde.

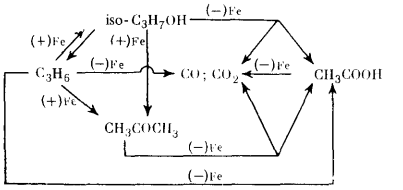
The effect of adding oxides of fourth-period transition metals to the tin–molybdenum oxide system has been investigated[106] on specimens of composition Mo : Sn : M = 3 : 1 : 0.15 (M = Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn). The catalysts were in all cases solid solutions based on molybdenum trioxide. The additives produced appreciable changes in activity and selectivity of the tin–molybdenum oxide catalyst. With the exception of cobalt and titanium they all enhanced the selectivity of formation of acetone, but the maximum yields achieved on the ternary catalysts varied: introduction of copper, zinc, manganese, and vanadium produced lower maximum yields of acetone than on the tin–molybdenum catalyst; chromium, nickel, and iron increased the maximum yield. Addition of 2 mass % of iron oxide was the most effective for the production of acetic acid (Table 2).

Table 2. Oxidation of propene on Sn–Mo and Sn–Mo–Fe oxide catalysts[106].

Catalyst	t, °C	Yields of reaction products, mass %			
		C_3H_7OH	$(CH_3)_2CO$	CH_3COOH	CO_2
Sn–Mo	175	0.1	8.2	1.9	3.7
Sn–Mo–Fe	175	3.1	11.3	0.5	0.3
Sn–Mo	200	0	9.3	5.3	9.0
Sn–Mo–Fe	200	2.1	18.5	2.0	1.9

Experimental results obtained on a tin–molybdenum oxide catalyst have shown[107] that propene is oxidised to acetone mainly via isopropyl alcohol, but acetic acid is formed both from acetone and from this alcohol.

A similar investigation has been made on a tin–molybdenum–iron oxide catalyst, with comparison of the rates of oxidation of conversion products of propene. Oxidation of isopropyl alcohol on a catalyst containing added iron ions gives a rather higher yield of acetone than on a tin–molybdenum oxide catalyst, whereas the yields of acetic acid and carbon dioxide are diminished by factors of 2 and 3.6. It is significant that the acidity of a tin–molybdenum oxide specimen is diminished by the introduction of iron. The results suggest the scheme



for the oxidation of propene on a tin–molybdenum–iron catalyst[107]. It shows the influence of positive and negative iron ions on the activity of a tin–molybdenum catalyst in various intermediate reactions in the oxidation of propene.

Table 3. Effect of potassium ions on specific rate of formation of oxidation products of propene on an Sn–Mo–Fe oxide catalyst[108].

Catalyst	t, °C	W, mmole m^{-2} h^{-1}			S*, %	K**, %
		CO_2	CH_3COCH_3	CH_3COOH		
Sn–Mo–Fe	190	0.03	0.12	0.03	83	17
Sn–Mo–Fe	230	0.15	0.15	0.08	62	29
Sn–Mo–Fe+K***	190	0.02	0.30	0.02	94	21
Sn–Mo–Fe+K	230	0.15	0.50	0.04	87	39

*S = selectivity of oxidation of propene to acetone.
**K = conversion of propene.
***Quantity of potassium introduced 0.7 mass %.

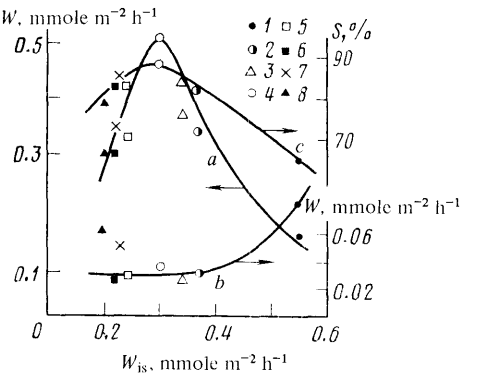


Figure 4. Variation[108] of: *a*) specific rate of formation of acetone; *b*) specific rate of formation of acetic acid; *c*) selectivity S of oxidation of propene to acetone with rate of isomerisation W_{is} of but-1-ene into but-2-ene on an Sn–Mo–Fe oxide catalyst containing added Group I elements: *1*) none; *2*) Li; *3*) Na; *4*) K; *5*) Rb; *6*) Cs; *7*) Cu; *8*) Ag.

The activity of a tin–molybdenum–iron catalyst and its selectivity of oxidation of propene to acetone are increased by the introduction of Group I elements[108]. The activity

depends on the quantity of additive, and reaches a maximum in the presence of 0.7 mass % of potassium. The yield of acetone is greatest at relatively high temperatures (Table 3).

Addition of alkali metals to a tin–molybdenum–iron oxide catalyst diminishes the surface acidity, the effect being greater the more basic the additive. Fig.4 shows the dependence of the specific rate of formation of oxidation products of propene on the acidity assessed from the rate of isomerisation W_{is} of but-1-ene into but-2-enes. With decrease in acidity the rate of formation of acetone passes through a maximum, and those of acetic acid and carbon dioxide decrease. The specific rate of formation of acetone increases more than the latter rate decreases, from which it may be concluded that the observed increase in activity is due mainly to the formation of new active centres.

The maximum specific rate of formation of acetone is achieved on catalysts containing added sodium and potassium ions[108]. The more basic the ions the higher the rate of formation of acetone and the lower the degradative oxidation of propene[108]. It can be concluded that high activity and selectivity of a catalyst in the oxidation of propene to acetone require an optimum acidity, which can be produced by introducing into a tin–molybdenum–iron oxide catalyst a definite quantity of alkali-metal ions depending on their basicity.

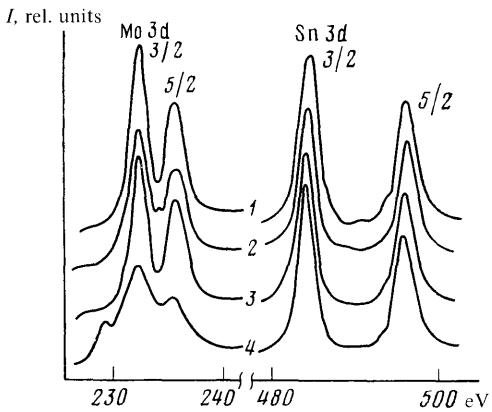
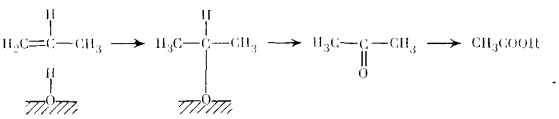


Figure 5. X-Ray electronic spectra of Sn–Mo–Fe oxide catalysts:
1) after roasting in oxygen at 250 °C;
2) after vacuum treatment at 425 °C;
3) catalyst with added potassium after roasting in oxygen at 250 °C;
4) catalyst with added potassium after vacuum treatment at 425 °C.

The incorporation of alkali metals into tin–molybdenum–iron oxide catalysts affects their X-ray electronic spectra[108]. Only tin, molybdenum, and oxygen ions are found on the surface, while iron and potassium ions are absent, which indicates that they have entered into the molybdenum trioxide structure. It is significant that reduction of a promoted catalyst affects mainly the oxidation state of the molybdenum ions, while tin ions remain almost unchanged (Fig.5). The spectrum of a reduced tin–molybdenum–iron oxide catalyst contains a weak signal due to Mo^{5+}, but in those of a promoted catalyst the signals due to reduced forms of molybdenum are considerably strengthened. The Mo^{5+}–O bond is less stable than Mo^{6+}–O, so that the introduction of potassium ions is responsible for the lability of the molybdenum–oxygen bond. The activating effect of alkali-metal ions in a tin–molybdenum–iron oxide catalyst apparently consists in changing the valency of the molybdenum, with the consequent appearance of new centres, on which alkenes undergo partial oxidation to ketones.

A mechanism of oxidation of propene to acetone on a tin–molybdenum oxide catalyst, involving formation of an alkoxy-group, was suggested by Buiten[103]. In the presence of deuterium oxide it proved difficult to exchange the hydrogen atom attached to the middle carbon atom in propene and also in isopropyl alcohol[109]. This was explained by interaction of propene with a surface hydroxyl to form an isopropyl group attached to a surface oxygen atom, and this group is an intermediate in the oxidation of propene to acetone and acetic acid:



Several results led Buiten[103] to deny intermediate formation of isopropyl alcohol in the oxidation of propene to acetone. Indeed, oxidation of the alcohol produces less acetone than expected, and furthermore the relative rates of formation of acetone and propene do not correspond to the rates of oxidation of propene to acetone and acetic acid according to the above scheme. Buiten's suggested mechanism involving detachment of the hydrogen atom from the middle carbon atom of the isopropyl group was supported by an investigation of the kinetic isotope effect of hydrogen involving comparison of the rates of oxidation of 2-deuteropropene $CH_2{:}CD.CH_3$ and non-deuterated propene[109].

Moro-Oka et al.[91,92] used a tracer method to determine the source of oxygen in the formation of acetone. In experiments on a tin–molybdenum oxide catalyst oxygen-18 was detected only in the acetone, whose content of the isotope was the same as that in the water present in the reaction system. Hence rapid exchange between adsorbed oxygen and the oxygen of the water does not take place, and oxygen-18 apparently passes into acetone by direct interaction between propene and adsorbed water[104]. Two mechanisms for the formation of acetone were suggested on the basis of these results:

$$CH_2{=}CH{-}CH_3 \xrightarrow{+OH^-} CH_2{-}CHOH{-}CH_3 \xrightarrow{\text{migration of H atom}}$$
$$\rightarrow {}^{+}CH_3{-}CHO{-}CH_3 \xrightarrow[-H^+]{} CH_3{-}CO{-}CH_3 \qquad (1)$$

$$CH_2{=}CH{-}CH_3 \xrightarrow{+H^+} CH_3{-}{}^{+}CH{-}CH_3 \xrightarrow{+OH^-}$$
$$\rightarrow CH_3{-}CHOH{-}CH_3 \xrightarrow[2H^+]{} CH_3{-}CO{-}CH_3 + H_2O \qquad (2)$$

The first mechanism involves addition of a hydroxy-group to the π-bond of the alkene with formation of a σ-complex, which is converted into the carbonyl compound with liberation of a hydrogen atom. In the second mechanism addition of a proton produces a carbonium ion, subsequent attack on which by a hydroxy-group gives the secondary alcohol, which is oxidised to acetone. Since isopropyl alcohol was detected among the reaction products, the latter mechanism was regarded[104] as the more probable.

A scheme has been suggested for the oxidation of propene on a tin–molybdenum–iron catalyst[107,110] according to which acetone is formed below 150 °C mainly from isopropyl alcohol, but above 200 °C directly from propene.

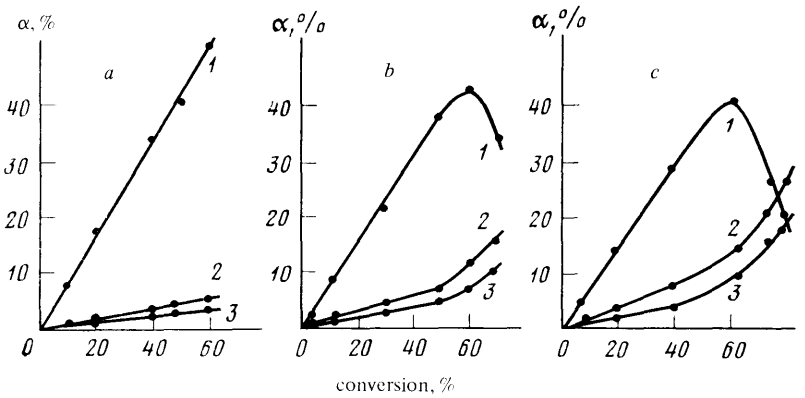


Figure 6. Degree of conversion α of propene into: *1*) acetone; *2*) carbon dioxide; *3*) acetic acid as function of total conversion[110] at various temperatures (°C): a) 190; *b*) 210; c) 230.

Formation of isopropyl alcohol was not observed[108] in the oxidation of propene on a promoted tin–molybdenum–iron catalyst at 170–210 °C. Comparison of the rates of accumulation of acetone in the oxidation of propene and of the alcohol showed that the latter is converted mainly into propene, only a small proportion being oxidised to acetone. This suggested that in the oxidation of propene the formation of acetone does not involve isopropyl alcohol:

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H_2O_{ads}} [CH_3CHOHCH_3]_{ads} \xrightarrow{+O_{ads}}$$

$$\begin{array}{ccc} CH_3COCH_3{}_{ads} & & H_2O_{ads} \\ \downarrow\uparrow & & \downarrow\uparrow \\ CH_3COCH_3 & & H_2O \end{array}$$

Propene reacts with molecularly absorbed water to form a complex of alcoholate type, whose interaction with adsorbed oxygen releases a molecule of water with the formation of acetone. The zero order with respect to oxygen indicates that the latter is not involved in the rate-determining stage of acetone formation. In the absence of oxygen, however, acetone is not formed, and adsorbed oxygen is apparently involved in oxidation of the alcoholate complex.

Mechanisms of the formation of acetic acid in the oxidation of propene on catalysts containing molybdenum have been discussed[103,104,110]. It may be formed as a result of degradation of the activated complex of propene at the double bond[104] or by the oxidation of acetone[103]. Study of the oxidation of acetone in admixture with propene[108,110] has shown that at low temperatures acetone is hardly oxidised at all, acetic acid being formed from propene, whereas at high temperatures it is formed from propene and from acetone. Discrepancies in the literature concerning the mode of formation of acetic acid are apparently due to the temperature ranges over which this reaction has been studied.

Fig.6 illustrates the dependence of the yields of acetone, acetic acid, and carbon dioxide on the conversion of propene. At 190 °C they increase linearly with the conversion: i.e. acetic acid is formed by the degradative oxidation of propene at the double bond. At 210 and 230 °C the yield of acetone passes through a maximum, while those of acetic acid and carbon dioxide increase rapidly as a consequence of subsequent oxidation of acetone.

* * *

Thus in both molybdates and solid solutions based on molybdenum trioxide partial catalytic oxidation of propene takes place on active centres containing molybdenum, but the direction of oxidation and the oxidation state of the molybdenum cation are determined also by the nature of the functional groups present in the centres.

From the totality of results obtained on the physicochemical properties of molybdenum-containing oxide systems it can be concluded that the production of practically effective catalysts requires the presence of activating additives, which dissolve in the catalyst structure, promote the appearance of additional defects, and participate in the formation of an active surface.

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[The US Patent numbers quoted in these references lack the digit 3 in front, or the patents may be from a different country (Ed.of Translation)].

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