Translated from *Uspekhi Khimii*, **43**, 1050–1073 (1974) U.D.C. 66.094.373+66.097.13

Catalysts for the Oxidative Ammoniolysis of Propene

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The effect of the electronic structure of the lattice cations, of the environment of the adsorption centres, of the relative positions of the propene and oxygen adsorption centres, of the electronic work function of the solid, and of the acidity of its surface on the activity of catalysts for the oxidative ammoniolysis of propene is examined on the basis of the literature data. The bibliography includes 185 references.

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I. INTRODUCTION

The development of the manufacture of polymeric materials, synthetic fibres, synthetic rubber, dyes, physiologically active substances, and other products of organic synthesis has led to the appearance of new effective methods for the conversion of petrochemical and coke-chemical raw materials into valuable polyfunctional organic compounds. These include oxidative ammoniolysis—an effective method for the synthesis of nitrogen-containing compounds developed recently [1-3].

The high selectivity, universality, and low cost of oxidative ammoniolysis make it one of the most promising new large-scale chemical processes. The list of nitrogen-containing substances obtained with the aid of oxidative ammoniolysis already includes several tens of names and processes such as oxidative ammoniolysis of methane [1], propene [2-4], isobutene [5], and aromatic compounds (toluene, xylene) [3,6-8] are now employed on an industrial scale.

The oxidative ammoniolysis of olefins has acquired particularly great industrial importance. It is sufficient to point out that acrylonitrile is nowadays manufactured from propene in about 30 plants with an overall output of more than 1.5 million tonnes per year in countries including the USA (in seven plants with an output of 616 000 tonnes) [8] and Japan (in nine industrial combines with an output of 670 000 tonnes per year) [9].

The studies published in recent years [1,2,10,11,12] reflect fairly completely the bulk of patent information concerning the catalysts for the oxidative ammoniolysis of propene. In Table 1 this compilation is supplemented by data from patents and the periodical literature published during 1968–1972.

Judging from the literature data, among the large number of a wide variety of compounds employed as catalysts for the synthesis of acrylonitrile only the bismuth phosphomolybdate catalyst [4,12], the uranium–antimony catalyst, (the so called catalyst-21), [52] and the iron–antimony catalyst [89] have found industrial applications. All these catalysts are made from metasilicic acid gel. The ASAHI Company improved the bismuth phosphomolybdate catalyst by incorporating iron compounds in its composition, thereby increasing the yield of acrylonitrile obtained to 72–76%. [27]

Societa Edison S.p.A. (Italy) employs the catalyst prepared from the highest oxides of tellurium, cerium, and molybdenum on silica gel [73] and SNAM Progetti S.p.A. employs vanadium and bismuth molybdates [90]. A catalyst in the presence of which the yield of acrylonitrile increases to 80–82% was developed recently by the Sohayo Company [sic], [91] but its composition was not disclosed.

Despite many studies on the preparation and properties of catalysts for the oxidative ammoniolysis of propene, the search for new effective catalysts for this process as well as for the mild selective oxidation of hydrocarbons is still continuing, largely by empirical procedures. There have been only a few studies in which relations were discovered whereby it is possible to regulate the catalytic properties of substances in these processes.

According to Lazukin et al. [92], the oxide catalyst "inherits" the activities and selectivities of its components. In order to obtain an effective catalyst, it is necessary to combine a highly active but relatively unselective metal oxide with a relatively inactive but highly selective oxide.

Alkhazov [93] believes that catalysts for the oxidative dehydrogenation of olefins can be formed only by combining in pairs oxides in the "highly isomerising and moderately oxidising" group.

According to the data of Kolovertnov and Boreskov [94], the catalytic activity of binary oxide catalysts for the oxidation of methanol to formaldehyde is a function of the amount of ionic character of the M–O bond determined from the ionisation constants of metal hydroxide compounds. The activity and selectivity of individual molybdates and vanadates are determined mainly by molybdenum and vanadium, which form part of the salt anion. The cation, stabilising the hexavalent or quinquevalent state of molybdenum or vanadium, regulates the activity.

A similar view has been expressed by Sachtler and Dorgelo [95], who investigated the oxidation of benzaldehyde to benzoic acid in the presence of the SnO_2–V_2O_5 catalyst. The authors believe that tin dioxide promotes the stability of the quinquevalent state of vanadium.

It has been suggested [96,97] that the catalytic properties of effective catalysts for the oxidation and oxidative ammoniolysis of olefins are due to the presence in their composition of doublets comprising different or identical cations. Batiste et al. [98] believe that, for mild oxidation

Table 1. Catalysts for the oxidative ammoniolysis of propene.

Catalyst	Carrier	Conditions governing the preparation of catalyst	Reaction conditions	Process parameters	References
Bismuth phosphomolybdate Bi:Mo:P = 9:1 2:1	Metasilicic acid gel	Joint precipitation and pelleting with formation of the compound $(Bi_9PMo_{12}O_{52})_x(SiO_2)_y.SiO_2$ content 50%	420-550°, $C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:1.8:3.5, fluidised bed	Conversion 80%. Selectivity 65%	12,13
Bismuth phosphomolybdate with added cobalt and nickel oxides		Mixing of solns. of bismuth and cobalt (nickel) nitrates, ammonium paramolybdate, and phosphoric acid. Heat treatment for 12 h at 550°	$C_3H_6:NH_3$:air = 10:11:110, contact time 1-20 s	Yield of acrylonitrile 62%	14-16
Bismuth phosphomolybdate	Silica gel	Impregnation of silica gel with soln. containing the active components	$C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.1:1.2-1.8:1.0-4.0, stationary bed, 480°, contact time 1.5-5.0 s	Conversion 70% Selectivity 60%	17,18
	Modified silica gel	Deposition of components from the same nitrate soln. Content of active components 12-14 wt.%	Fluidised bed, contact time 6 s	Conversion 85% Selectivity 60%	19
Bismuth phosphomolybdate	Corundum, porosity 32%	Impregnation of corundum with a soln. containing the active components	$C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:1.9:6.2, 450-500°	Conversion 60% Selectivity up to 80%	20,21,22
	Corundum	Heat treatment of alumina at 1750°. Joint pelleting with bismuth phosphomolybdate in the presence of a carrier content of 85%	Data not available		23
Iron-modified bismuth phosphomolybdate (A-112 catalyst, Japan)	Metasilicic acid gel	Joint precipitation of active compound having the atomic ratio Bi:Fe = 1:12:3:5 with metasilicic acid gel	450-500°, fluidised bed	Conversion up to 92% Selectivity 68%	23-27
Iron-modified bismuth phosphomolybdate with added lead	Metasilicic acid gel	Joint precipitation of active compound $Pb_2Bi_4Mo_{12}Fe_9P$ with metasilicic acid gel	450°, contact time 1.2 s	Yield up to 52%	28
Bismuth antimonate		Preparation of bismuth antimonate $Bi_2O_3.Sb_2O_5$	450°	Conversion 10% Selectivity 10%	29
Mixture of bismuth antimonate and molybdate		Preparation of catalyst containing 65% of bismuth molybdate and 35% of bismuth antimonate	470°	Conversion 58% Selectivity 90%	29-31
Mixture of bismuth antimonate and molybdate		Preparation of catalyst by mixing soln. of bismuth nitrate, ammonium paramolybdate, and antimony perchlorate	450-470° $C_3H_6:NH_3$:air:H_2O(vapour) = 1.0:1.0:7.0:1.0	Conversion 60% Selectivity 85%	32-36
Mixture of bismuth antimonate and molybdate	Alumina	Impregnation of carrier with soln. containing the active components. Carrier content 50-80%	Data not available		37
Mixture of bismuth antimonate and molybdate with added tin dioxide	Silica gel, 10-60%	Precipitation of bismuth antimonate on mixing $Bi(NO_3)_3$ and Sb_2O_3 solns. in HNO_3 Bismuth antimonate mixed with bismuth molybdate: SnO_2, SiO_2. $BiSbO_4:SnO_2:Bi_2(MoO_4)_3$ = 60:40:5-50	$C_3H_6:NH_3:O_2:H_2O$ = 1.0:1.0:1.4:1.0, contact time 11.2 s	Conversion 60% Selectivity 91%	38-40
Mixture of As, Mo, and W oxides		Mechanical mixture (0.1-20 wt.% As_2O_5, 1.50 wt.% WO_3, 1-50 wt.% MoO_3)	$C_3H_6:NH_3:O_2$ = 1.0:1.2:1.5-5.0, 450-500°, 480°, contact time 10-40 s, fluidised bed	Yield of acrylonitrile 58% and 60-62%	40 41-44
Mixture of As, Mo, and W oxides	Silica gel, alumina	Impregnation of carrier by aqueous soln. of Mo, As, and W compounds. Drying at 100-200° and heat treatment at 400-450°	480°, As_2O_5 introduced into gaseous mixture	Yield up to 72%	45-46
Mixture of bismuth or antimony compounds		Mixing of the compounds $Sb(VO_3)_3$ and $SbPO_4$ or $Bi(VO_3)_3$ and $BiPO_4$, treatment of mixture at 500°	450-480°	Yield 45%	47-48
Uranium-antimony catalyst		Mixing of uranyl nitrate and antimony perchlorate solns., ratio in precipitate Sb:U = 1-50:2-100	480°, contact time 5-10 s, fluidised bed	Yield 62-64%	49-51
Mixture of spent uranium oxide with antimony oxide		Catalyst 21		Yield 62%	52
Uranium-antimony catalyst	Alumina	Impregnation of carrier by soln. containing uranium and antimony salts	480°	Yield 60%	53
Antimony-tin catalysts with atomic ratio Sn:Sb = 0.1-10:1.0-20.0		Mixing of solns. of antimony and tin chloride pptn. with ammonia, heat treatment of ppt. at 500-700°	470°, contact time 4 s, $C_3H_6:NH_3:O_2:H_2O$(vapour)= 1.0:1.0:1.2:6.0	Selectivity 65% Yield 51-52%	54,55
Solid soln. of tin(IV) oxide in antimony oxide with atomic ratios Sn:Sb = 1.0:1.0 and Sn:Sb = 0.25:1.0		Mixing of solns. of antimony and tin chlorides drying at 140°, and heat treatment at 800°	480°, contact time 0.8-1.5 s, $C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:1.5:2.0	Yield 41-42%	56,57
Iron-antimony catalyst		Preparation of iron antimonate containing 55 at.% of antimony	480°, $C_3H_6:O_2$ = 1:6	Selectivity 80-82%	58,59

Table 1 (contd.)

Catalyst	Carrier	Conditions governing the preparation of catalyst	Reaction conditions	Process parameters	References
Iron-antimony catalyst		Mixing of solns. of antimony and iron chlorides. Heat treatment of ppt. for 16 h at 650°. Atomic ratio Sb:Fe from 1:50 to 99:1	480-500°, contact time 0.5-10 s, $C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.2:1.5:1.2	Conversion 74% Selectivity 70%	60,61
Iron-antimony catalyst	Metasilicic acid gel	Joint precipitation of iron nitrate and antimony chloride with silica soln. Drying at 120° and heat treatment at 750°	450-550°, $C_3H_6:NH_3:O_2$ = 1:1.2:1.2-5.0	Selectivity 70%	60-62,68
Iron-antimony catalyst	Pumice	Impregnation of pumice by solns. containing iron and antimony compounds	$C_3H_6:NH_3$:air:H_2O(vapour) = 1.0:1.1:7.5:1.0	Selectivity 80%	63
Iron-antimony catalyst with added Mo(W) and B(P)		Preparation of compound by precipitation on mixing solns. of $Fe_aSb_bMo_c.X_dO_e$, where X = P or B, a = 10, b = 5-60, c = 0.5-1, and d = 0.005-1.0	$C_3H_6:NH_3:O_2$ = 1:0.5:0.5-5.0 480°	Selectivity 80%	64-67
Iron-antimony catalyst with added vanadium		Preparation of compound with the conventional formula $Fe_aSb_bV_cX_dO_e$, where X = P or B, a = 10, b = 5-80, c = 0.01-2, and d = 0-2. Catalyst activated by heating for 2-24 h at 600° and for 20 h at 700-1000°	480-500°	Yield 60%	69-70
Tin molybdate with atomic ratio Sn:Mo = 9:1		Mixing of ammonium molybdate and tin(II) chloride soln., heat treatment of ppt. at 500°	Contact time 7 s, $C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:1.2:1.0	Conversion 75% Selectivity 65%	71
Bismuth molybdate + TeO_2	Silica gel	Joint pelleting of bismuth molybdate and tellurium oxide with silica gel	400-500°, contact time 0.5-15 s $C_3H_6:NH_3$ = 2.0-1.0:0.6-1.0	Selectivity 85%	73
Mixture of tellurium, lanthanum (cerium), and molybdenum oxides		Mixing of lanthanum nitrate with telluric acid, heat treatment at 500°		Selectivity 70%	73
Mixture of tellurium and molybdenum oxides	Silica gel	Deposition from soln. containing active components. Drying at 120° and heat treatment at 450°	$C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:2.0:2.5, contact time 6 s	Yield 32%	74-76
Mixture of tellurium and molybdenum oxides with added phosphorus		Mixing and evaporation of aqueous solns. of ammonium molybdate, phosphoric acid, and telluric acid. Heat treatment at 420°	480°, contact time 3 s	Selectivity 80% Conversion 70%	77-80
Vanadium molybdate	Metasilicic acid gel	Joint deposition of silica soln. with molybdenum and vanadium oxides. Heat treatment at 400-500°	$C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.0:1.5:1.2, fluidised bed, 400-500°	Conversion 71% Selectivity 80%	81-83
Copper phosphate	Silica gel	Impregnation of silica gel by copper pyrophosphate or triphosphate solns.	450-480°	Conversion 40%	84
Iron and bismuth phosphates			$C_3H_6:NH_3:O_2:H_2O$(vapour) = 1.0:1.2:2.0:2.0, 480°	Conversion 70% Selectivity 68%	85
Solid phosphoric acid		Mixture of titanium, molybdenum, iron, cobalt, vanadium, bismuth, etc. phosphates	500°	Conversion 30%	86
Copper phosphate	Borophosphate	Impregnation by soln. of copper nitrate and phosphoric acid		Selectivity 67%	87
Iron-containing zeolite	NaX	Ion exchange between NaX zeolite and iron thiocyanate soln.. Degree of exchange 50%	480°	Conversion 40%	88

of hydrocarbons on the surface of the catalyst, the formation of two kinds of anionic vacancies linked to the doublet centre is necessary. Unfortunately the hypothesis of the existence of doublet centres, responsible for the selective oxidation of olefins, is based only on the chemical composition and the determination of catalytic activity and requires additional evidence.

The molybdenum–oxygen plays a major role in catalytic oxidation reactions. The Mo=O bond in various metal molybdates is more reactive than other bonds [99,100]. A similar view was expressed earlier in a study of the catalytic activity of vanadium catalyst by Tarama and Teranishi [101], who observed that catalysts containing the V=O double bond exhibit the highest activity in the oxidation of benzene.

Many investigators are now seeking various correlations between particular properties of catalysts and their relative activities with respect to a specific reaction or group of reactions. Correlations have been observed between catalytic activity and properties such as the electronic work function, electrical conductivity, the width of the forbidden gap in semiconductors, etc. However, each correlation embraces a very limited range of catalysts for which the chosen property is for some reason dominant. Moreover, this property reflects only partly the characteristics of the chemical interactions of the reactant molecules with the catalyst and with one another, which determine the catalytic effect. The most reasonable are attempts to relate catalytic activity to thermodynamic characteristics—the energies of the bonds broken and formed on formation of the activated complex in the rate-determining step [102].

However, none of these hypotheses can explain fully the mechanism of the action of complex catalysts for the oxidation of hydrocarbons. From this standpoint, it is interesting to analyse the extensive literature data on catalysts for the oxidative ammoniolysis of propene in order to elucidate the nature of the active surface and its role in the selectivity of the process.

II. SOME PROBLEMS OF THE MECHANISM OF THE OXIDATIVE AMMONIOLYSIS OF PROPENE

Several communications dealing with the mechanism of the oxidation and oxidative ammoniolysis of propene in the presence of mixed catalysts were published recently[2,3,12,103,104]. According to their results, the only rigorously proved fact is that the oxidative ammoniolysis of propene as well as its oxidation proceed via the formation of an allyl complex. The constancy of the isotope effect in the formation of acrolein and acrylonitrile[105] and also the identical reaction kinetics[106] enabled many investigators[103,105,106] to suggest that the rate-limiting stages in these two processes are the same.

The discovery of the relations governing the formation of the CN group in the oxidative ammoniolysis of various compounds enabled Rafikov and Suvorov[3,107,108] to put forward the hypothesis that in the case of organic compounds of the type RCH_3 nitriles and their amide precursors are formed mainly from aldehydes. The authors believe that nitriles can be formed also via an "amine" reaction pathway. The hypothesis concerning the role of aldehydes in the oxidative ammoniolysis of hydrocarbons has found confirmation in studies by other investigators[109-112], although some of them suggest that ammonia interacts with the carbonyl group via an aldimine mechanism[111].

On the basis of kinetic data for the individual stages in the oxidative ammoniolysis of propene, Germain and coworkers[103,104] and Callahan and coworkers[4] believe that acrylonitrile is only partly formed via acrolein, while the contributions of the "amine" and "aldehyde" pathways to the formation of nitriles as well as the escape of acrolein to the gas phase apparently depend markedly on the concentration of oxygen and ammonia in the catalyst zone and on the structure of the initial hydrocarbon. On the basis of his data obtained under the condition of a low oxygen concentration and a high water concentration, Germain suggested that acrylonitrile may be formed via a stage involving the formation of an adsorbed carbene having the structure $CH_2{=}CH{-}\ddot{C}H$.

However, the mechanism proposed by the author for this reaction was not proved unambiguously and is extremely hypothetical. Gorshkov and coworkers undertook a detailed study of the mechanism of the formation and further reaction of the intermediate and side products of the joint oxidation of propene and ammonia using the kinetic isotopic method[113], with a complete computer calculation of the mechanism of the oxidation of propene[114] and the individual carbonyl compounds[115] with simultaneous evaluation of the rate constants for the individual stages. The experimental results suggested a possible process mechanism involving a number of stages[116], according to which a major role is played by the successive reaction of certain oxygen-containing compounds formed in the interaction between adsorbed oxygen and the hydrocarbon, which are desorbed from the surface in the form of aldehydes. According to a study[117] on the adsorption of propene and acrolein at 200° and 300°C on the surface of molybdenum catalysts using infrared spectroscopy, such oxygen-containing compounds are carbonyl-containing complexes coordinated to the surface via the double bond and via the carbon atom of the aldehyde group.

A significant distinctive feature of the proposed mechanism is also the demonstration of the formation of acetaldehyde and formaldehyde, like acrolein, via an allylic compound. Since it has been shown by the kinetic isotope method[113] that the intermediate in the formation of these compounds is the same, they are probably produced on the same active centres of the catalyst surface. The different modes of reaction of the intermediate are probably determined by the different energies of the bond between oxygen and the surface of the catalyst and the number of oxygen atoms involved in the formation of the surface carbonyl-containing compound. It has also been established[114-116] that carbon oxides are formed by the subsequent oxidation partly of the surface carbonyl-containing compounds and partly of the desired nitrogen-containing products via a parallel-consecutive mechanism, with the successive pathway predominating.

Infrared spectroscopic data on the oxidation of ammonia in the presence of certain metal oxides[118] and also for its adsorption on the oxidised surface of molybdenum catalysts[119] suggest that an oxygen containing complex of the type $H_2N{-}O{-}M$, adsorbed on the surface, is the most reactive. This complex probably plays a major role in the oxidation [of ammonia ?] and possibly in the oxidative ammoniolysis of propene. Similar ideas concerning the formation of NH_2 radicals bound to the surface in the presence of molecular oxygen have been put forward in other investigations[120-122].

The study of the adsorption of propene–ammonia–oxygen and acrolein–ammonia–oxygen mixtures in different sequences on the surface of molybdenum catalysts using infrared spectroscopy and a comparison of the resulting spectra with those of allylamine and acrylonitrile adsorbed under analogous conditions was undertaken[123]. The similarity of these spectra apparently confirms the hypothesis that acrylonitrile may be formed in the oxidative ammoniolysis of propene either via an intermediate surface amine compound, produced when the adsorbed propene interacts with ammonia adsorbed on top of oxygen, or via an oxygen-containing surface complex of the carbonyl type with subsequent addition to the latter of an oxygen-containing complex of ammonia and the formation of an amide.

The results are satisfactorily consistent with the calculations[124] by the LCAO-MO method of the energy scheme for the elimination of individual hydrogen atoms and the addition of oxygen and nitrogen atoms to the hydrocarbon residues in the formation of acrylonitrile on the surface of molybdenum trioxide. It was found that the pathways leading to the formation of acrylonitrile via the intermediate formation of compounds of the carbonyl or amine type are energetically equivalent.

Thus in the interaction of propene, oxygen, and ammonia with the catalyst surface dissociative adsorption of the olefin takes place with formation of an allylic surface compound[125-127] and probably of an oxygen-containing ammonia complex[119]. The allylic surface compound can be subsequently converted into an oxygen-containing surface complex of the carbonyl type, which can be desorbed into the gas phase in the form of the aldehyde or can react further with the oxygen-containing ammonia complex to form a surface amide. Moreover, the allylic surface compound can itself react with ammonia adsorbed on top of the surface oxygen with formation of an amine surface compound.

III. THE EFFECT OF THE ELECTRONIC STRUCTURE OF LATTICE CATIONS ON THE ACTIVITY OF THE CATALYSTS

It is believed[128] that the metal ions in the crystal lattice behave as hydrocarbon adsorption centres. In connection with the hypothesis that the dissociative chemisorption of propene entails the formation of a π-complex

which is subsequently converted into a π-allyl complex[125], it is necessary to examine the effect of various metal ions on the formation of complexes with olefins and to elucidate the relation between the stability of these complexes and catalytic activity.

Olefins are known to form π-complexes with vanadium, chromium, molybdenum, and cobalt[129] and π-allyl complexes with molybdenum, tungsten, cobalt, and iron[130].

Indeed, it has been shown for iron-containing zeolites[88] that iron ions can catalyse the oxidation and oxidative ammoniolysis of propene, the selectivity of these reactions depending on the distribution of the ions in the matrix and on their oxygen environment[131,132]. Presumably propene is capable of forming π-allyl complexes with iron ions like ethylene in its adsorption on silver ions in silver-zeolites[133]. If the oxygen adsorbed on the surface of the zeolite is sufficiently mobile, as happens on alumina[134], the oxidation and oxidative ammoniolysis of propene are possible.

It has been suggested[135] that the chemisorption of propene is determined by the formation of a donor-acceptor bond with a catalyst lattice cation as a result of the withdrawal of the double bond π electrons into the vacant d orbitals of the transition metal atoms. The adsorbed molecules are then positively charged.

On the other hand, the symmetry of the antibonding olefin orbital and the transition metal d orbitals promotes their interaction[136], as a result of which the positive charge produced is partly compensated by the withdrawal of the catalyst electrons into the π orbital. On this basis, it is suggested[135,136] that the electronic structure of the metal ions determines the bonding energy of the olefin in the complex.

Application of crystal field theory to the study of the catalytic activity of transition metal oxides in various reactions[136,137] led to the observation that maximum catalytic activity corresponds to the maximum stabilisation by the crystal field with increase of the coordination number, the maximum rate of catalysis corresponding to the following elements: Cr(d^3), Co(d^7), and Cu(d^9).

Data for the extensive oxidation of propene also show that metal oxides containing chromium, cobalt, and copper exhibit the highest activity[138], i.e. there is some correlation between the rate of the catalytic reaction and complex formation.

Data have been published[71,139] concerning the change of catalytic activity in the oxidative ammoniolysis of propene in relation to the formation of acrylonitrile, carbon dioxide, and the molybdates[71] and phosphates[139] of various metals in the Fourth Period as a function of the number of unfilled d levels. Fig. 1 shows that the catalytic activity of the molybdates falls on passing from the first to the last element of the Fourth Period. The maximum rates of formation of acrylonitrile and carbon dioxide are observed in the presence of iron phosphate; the activities of cobalt, nickel, and manganese phosphates are low. The data presented in Fig. 1 evidently demonstrate that there is no correlation between the catalytic activity in the oxidative ammoniolysis of propene and the maximum stabilisation of the complexes by the crystal field. The difference between the activities and selectivities of the compounds investigated in this reaction cannot be accounted for by the presence of a number of unfilled metal d orbitals.

Moreover, the experimental data obtained under analogous conditions for the catalytic activities of various mixed oxide systems showed that the compounds formed when tin ($5s^25p^2$) and lead ($6s^26p^2$) oxides are mixed with bismuth ($6s^26p^3$) oxide do not catalyse the oxidative ammoniolysis of propene[140]. It was natural to conclude that none of the above metals are active catalysts of this process, because their cations do not contain vacant d levels. However, solid solutions of tin and antimony ($5s^25p^3$) oxides proved to be extremely active and selective catalysts of the oxidative ammoniolysis although tin and antimony atoms do not contain unfilled d orbitals either.

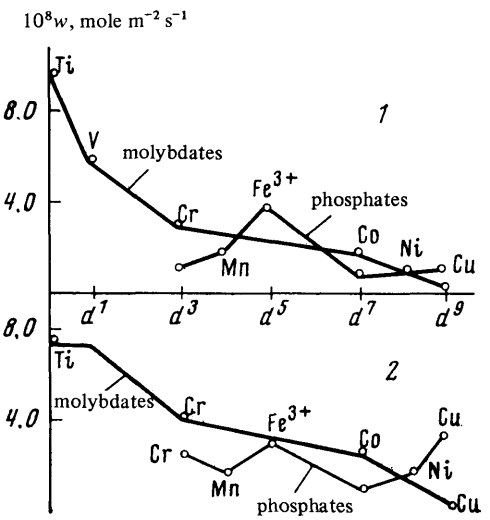


Figure 1. Dependence of the catalytic activity of molybdates[71] and phosphates[139] in the formation of acrylonitrile (1) and carbon dioxide (2) in the oxidative ammoniolysis of propene on the number of unfilled d levels in the lattice cations.

The possibility of the formation of unfilled d levels in the adsorption of oxygen on non-transition metals has been discussed in the literature[141]. For example, in the presence of oxygen silver behaves as a transition metal with this type of structure, acquiring the ability to chemisorb ethylene[142]. Oxygen binds the s electrons of silver and enables some of the d electrons to pass to the s and p levels. In this case catalysts containing, tin, antimony, and copper should be active and selective. However, it has been shown[140] that in the presence of stannates only extensive oxidation of propene takes place, while in the presence of bismuth antimonate the rate of formation of acrylonitrile is low.

Nor does the presence of cations with unfilled d levels influence the oxidation of ammonia under the conditions of the oxidative ammoniolysis of propene. The catalytic activities of various metal oxides in the oxidation of ammonia under the conditions of the oxidative ammoniolysis of hydrocarbons have been determined[143]. The maximum catalytic activity was observed in the presence of the oxides of cobalt (d^7), manganese (d^5), chromium (d^3), and copper (d^{10}), but complex catalysts containing these oxides do not exhibit an appreciable activity in the joint oxidation of propene and ammonia[140].

Thus the formation of a complex of the catalyst and the olefin requires that the catalyst contain a metal ion with a specific electronic structure. However, in the oxidative ammoniolysis of propene as well as in its oxidation[144] a correlation between the reaction rate and the stability of the metal–olefin complexes has not been observed. Such complexes are probably not the controlling intermediates in this process, oxygen being involved in its rate-limiting stage with formation of oxygen–hydrocarbon complexes.

Indeed, a Mössbauer study of the formation of a surface compound in the adsorption of propene and acrolein on the surface of an Sn–Mo–O catalyst showed[145] that the linkage between the chemisorbed organic molecule and the ion is formed via oxygen.

Moreover, as stated above, a study of the adsorption of propene on the oxidised surface of molybdenum catalysts for the oxidative ammoniolysis of propene revealed the presence of oxygen-containing complexes of the carbonyl type[117]. Oxygen also takes part in the formation of a reactive oxygen-containing ammonia surface complex.

For this reason, in the analysis of the nature of the active surface of catalysts for the oxidative ammoniolysis of propene particular attention must be paid to the type of bond between oxygen and the catalyst and to its reactivity.

IV. THE EFFECT OF THE ENVIRONMENT OF THE CATIONS IN THE CRYSTAL LATTICE ON CATALYTIC ACTIVITY

Many investigators[102,146,147] believe that the differences between the catalytic activities of oxides in oxidation reactions can be explained by the differences between the oxygen binding strengths in these oxides. The rate of oxygen isotope exchange between the gas phase and the oxide can serve as a measure of the reactivity of the oxygen in the surface layer of oxides. The mobility of oxygen in transition metal oxides frequently increases when they are mixed with oxygen derivatives of other elements. For examples, Boreskov and coworkers[148] established that potassium sulphate increases sharply the mobility of oxygen in vanadium pentoxide.

Skalkina[150] and Gel'bshtein and coworkers[151] compared the activation energies for the isotope exchange of the lattice oxygen determined for iron[149], cobalt[152], and bismuth[153] molybdates, iron and tin[154] antimonates, and molybdenum oxide[153] with the catalytic activities of these compounds in the formation of acrylonitrile by the oxidative ammoniolysis of propene. They concluded that the optimal M–O bond energy is 80–90 kcal mole^{-1}.

Such high M–O bond energies probably indicate that the lattice oxygen has a low probability of being involved in the rate-limiting reaction step, since the activation energy for the reaction does not exceed 20 kcal mole^{-1}. However, this oxygen can serve as a centre for the adsorption of the hydrogen split off in the dissociative adsorption of propene or can participate in the formation of certain other intermediates in the oxidation of propene.

Sachtler and De Boer[125] chose the rate of the partial reduction by hydrogen of various mixed catalysts as a criterion for the assessment of the lattice oxygen binding strength (ΔHM-O) in mixed oxide catalysts for the oxidation of propene, since ΔHM-O is proportional to the activation energy for the reduction reaction (Fig. 2). They estimated the rate of reduction from the quantity $10^3/T_\tau$, where T_τ is the temperature at which identical degrees of reduction are attained. Fig. 2 shows that the higher the capacity of the catalyst for reduction, i.e. the lower the metal–oxygen bond strength, the higher the degree of conversion of the hydrocarbon and the lower the process selectivity. Gel'bshtein and coworkers[155] measured the initial rate of reduction by propene of bismuth–molybdenum catalysts for the oxidative ammoniolysis of propene at 450°C and a pressure of 80 mmHg and showed that the maximum rate is observed for molybdenum oxide and the minimum for bismuth oxide. Bismuth molybdates of different compositions are reduced by the olefin at rates lower than the rate of reduction of molybdenum oxide.

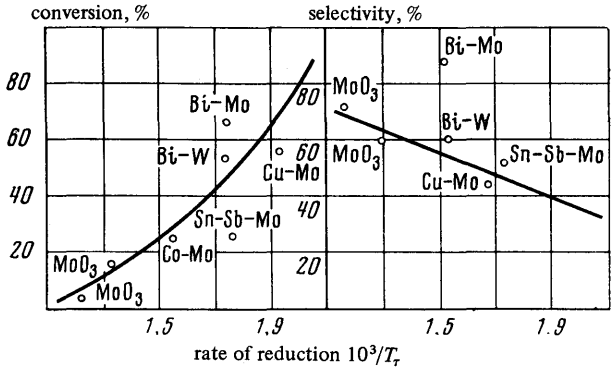


Figure 2. Dependence of the activity and selectivity of complex oxide catalysts in the oxidation of propene on their degree of reduction (T_τ is the temperature at which equal degrees of conversion are attained)[125].

Kolchin[11] also investigated this type of relation for various catalysts of the oxidative ammoniolysis of propene. Fig. 3 shows the variation of the degree of conversion and process selectivity with the rate of reduction of various complex oxide catalysts. Different relations between the rate of reduction and composition were obtained for molybdates and tungstates. Moreover, it is noteworthy that, according to Sachtler and De Boer's data[125] (Fig. 2), the activity and selectivity vary in opposition, while in another study[11] (Fig. 3) it was shown that they vary in parallel, albeit for a narrower range of catalysts. Evidently comparison of the catalytic properties of the substances for incomplete oxidation reactions with the values of ΔHM-O is possible only within the limits of fairly small groups of selective oxidation catalysts and the optimal energy of the oxygen-catalyst bond is not the only factor responsible for the high activity and selectivity of the catalyst in the oxidative ammoniolysis of propene.

The energy of the bond between the metal ions forming part of the catalyst and oxygen varies as a function of the electronic structure of the ions. Mössbauer spectroscopy has shown[157] that, when the catalyst contains atoms of two different metals, the latter interact via oxygen: M^I–O–M^{II}. The effective charge of oxygen, i.e. the real charge within the space surrounding the oxygen atom, will depend on the difference between the electronegativities of these metals[158].

The catalytic activity of various compounds in the oxidative ammoniolysis of propene is determined by active centres of the same type and consequently is influenced

not by the bulk-phase charges but by the effective surface charges of oxygen, which depend on the difference between the electronegativities of the metal ions.

It has been shown for the oxidative ammoniolysis of propene [71] that the addition to the main oxide (of tin or iron) of another oxide containing a metal having a higher electronegativity (molybdenum or antimony) than that of the cation in the basic matrix alters the reaction pathway in the oxidative ammoniolysis of propene. Only carbon dioxide is formed in the presence of iron and tin oxides, while in the presence of solid solutions based on these oxide lattices acrylonitrile is obtained and the proportion of extensive oxidation falls. The authors conclude that the environment of the metal ion and the effective charge on the oxygen both change on formation of the solid solutions.

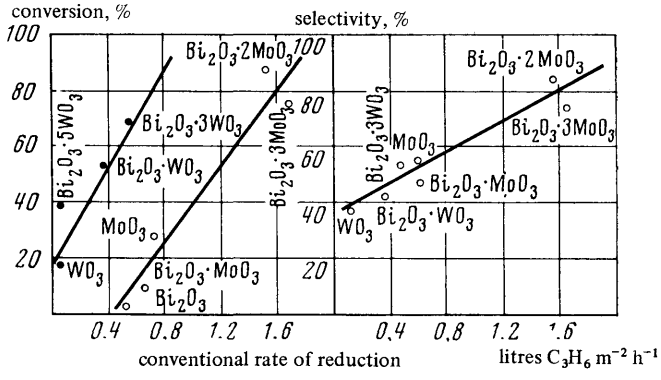


Figure 3. Dependence of the activity and selectivity of bismuth molybdates and tungstates in the oxidative ammoniolysis of propene on the rate of reduction of the catalyst [10].

In the determination of the catalytic activities of a large series of mixed oxide catalysts, Dalin et al. [159] drew attention to the fact that the highest selectivity is shown by catalysts in which there is a small difference between the ionisation potentials of the cation and the central atom of the anion. Evidently the difference between the ionisation potentials determines to some extent the amount of ionic character of the bond between the metal ion and oxygen. The isomeric shift δE of the Mössbauer spectrum, which is due to the change of the s electron density near the nucleus of the cation, can serve as a measure of the amount of ionic character of the bond.

Table 2 presents parameters of the Mössbauer spectra taken from the literature [160–162] (the isomeric shifts and the quadrupole splittings) for certain iron-containing compounds and the selectivities of the oxidative ammoniolysis of propene in the presence of such compounds. These data show that the dependence of the selectivity of the oxidative ammoniolysis on the amount of ionic character of the bond passes through a maximum. The highest selectivity is observed in the presence of iron phosphate and arsenate. A decrease and an increase of the number of s electrons in the Fe^{3+} ion both reduce the yield of acrylonitrile.

Another parameter of Mössbauer spectra, namely quadrupole splitting ΔEa, characterises the electric field gradient around the cation due to the distortion of the symmetry of the charge distribution within the crystal lattice. The electric field gradient depends on various factors, primarily on the type of bond, the crystal structure of the compound, and the electronegativity of the adjacent atoms.

Table 2. The isomeric shifts δE and the quadrupole splittings ΔEQ in the Mössbauer spectra of certain iron-containing compounds and the selectivity of oxidative ammoniolysis on their presence.

Compound	δE, mm s^{-1}	ΔE_Q, mm s^{-1}	Selectivity, %	References
$Fe_2(SO_4)_3$	1.42	0.0	9	139
Fe_2O_3	0.57	0.2	0	71
$FePO_4$	0.43	0.15	56	139
$Fe_2(CrO_4)_3$	0.34	0.38	0	71
$FeAsO_4$	0.49	0.2	50	163

Skalkina et al. [163] obtained the Mössbauer spectra of various complex oxide catalysts for the oxidative ammoniolysis of propene incorporating Fe^{3+} and Sn^{4+} ions and compared the quadrupole splitting with the activity and selectivity of the catalyst. Fig. 4 shows that the rate of extensive oxidation decreases monotonically with increase of ΔEQ, while in the mild oxidation reaction (the formation of acrylonitrile?) the rate passes through a maximum.

Since the iron(III) ion has the symmetrical electronic configuration $3d^5$, the electric field gradient at the nucleus is due solely to the external charges and is determined by the distortion of the lattice. Quadrivalent tin also has a symmetrical electronic configuration ($4d^{10}$). Thus in the given case ΔEQ characterises directly the charge distribution around the iron and tin atoms and affects the rate of reaction. For low values of ΔEQ, i.e. for slight distortions of the charge symmetry, carbon dioxide is is formed around the cation in the course of the oxidation of propene and, on further increase of ΔEQ, the formation of acrylonitrile begins. Since EM-O and qs increase with increase of ΔEQ, this can evidently be explained as follows. For low values of ΔEQ (E_{M-O} is small), a larger number of oxygen atoms enter into the reaction and extensive oxidation is observed, whereas on increase of ΔEQ a smaller number of oxygen atoms participate in the process and mild oxidation of the olefin begins. However, on further increase of ΔEQ, there is a rise in q_s also and the catalytic activity falls; the activation energy increases appreciably for these values of ΔE_q.

Evidently the differences between the ionisation potentials and quadrupole splitting both characterise the charge distribution around the cation and are probably related also to the M–O bond strength.

Apart from the oxygen adsorbed at the lattice ions, the oxygen surrounding the cation is probably also important in the oxidative ammoniolysis of propene; thus the replacement of oxygen in iron and copper oxides by sulphur and also the replacement of oxygen in vanadium pentoxide by boron, nitrogen, and carbon lead to the complete disappearance of catalytic activity in this reaction [139].

V. RELATIVE POSITIONS OF THE HYDROCARBON AND OXYGEN ADSORPTION CENTRES

According to the hypothesis of Callahan and Graselli[164], not only the electronic structure of the adsorption centres but also their number and relative positions are important for the selective oxidation of hydrocarbons. On the surfact of polycrystalline catalysts, there are planes with different indexes in which the elements entering into the composition of the catalyst are distributed with different separations.

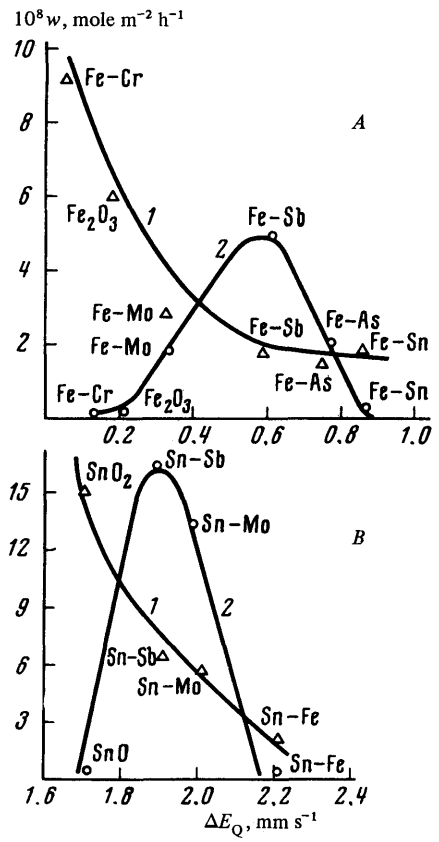


Figure 4. Dependence of the rate of formation of carbon dioxide (1) and acrylonitrile (2) in the presence of oxide catalysts containing iron (*A*) and tin (*B*) on the quadrupole splitting *E*Q (Skalkina et al.[163]).

Data are now available showing which lattice planes of the mixed oxide systems now preferentially exposed on the surface of the catalyst. These data are insufficient to analyse completely the results from the standpoint of the geometrical correspondence between the propene molecules and the atoms of the solid. However, the literature data lead to definite conclusions concerning the influence of the geometry of the active adsorption centres of the oxidative ammoniolysis of propene. Indeed, Kolchin and Gel'bshtein and coworkers showed that the most active catalysts in the Bi_2O_3–MoO_3 system usually contain compounds with the compositions $Bi_2O_3.2MoO_3$ and $Bi_2O_3.3MoO_3$ having the structures of the α- and β-phases[96,165] and that the catalytic activity of bismuth molybdate $Bi_2O_3.MoO_3$ depends on the presence of the γ''-phase structure in the crystal lattice of this catalyst[165].

It has been shown[11,165], on the basis of published data[166–168], that, on passing from molybdenum oxide to bismuth oxide and on formation of various bismuth molybdates, the distances between oxygen and bismuth and molybdenum cations are altered. For example, the distance between Mo and O in MoO_3 varies in the range 1.67–2.25 Å, depending on the position of the MoO_6 octahedra in the layer structure[167], in the bismuth molybdate $Bi_2O_3.3MoO_3$ the Mo–O distance in the tetrahedron is 1.75–1.95 Å and the Bi–O distance is 2.30–2.50 Å,[166] in the bismuth molybdate $Bi_2O_3.MoO_3$ the (Bi, Mo)–O interatomic distance is 2.35 Å, while in $2Bi_2O_3.MoO_3$ the interatomic distance is 2.45 Å.[168]

The distances between the Bi and Mo cations also change on passing from one compound to another, but in all cases are not less than the distances between the carbon atoms in the propene molecule; for this reason, the authors[11,165] conclude that the employment of a simple doublet scheme for the oxidative ammoniolysis of propene[96] on an ideal crystal is hardly valid in view of the defective structure of the catalyst surfaces.

It has been suggested[156] that the catalytic activity of compounds having the structure of the bismuth molybdates $Bi_2O_3.MoO_3$ (γ-phase) and $Bi_2O_3.2MoO_3$ (β-phase) in the oxidative dehydrogenation of n-butenes is due to the presence of Mo–O octahedra linked via their vertices within the bulk of the crystals. According to the authors, this crystal lattice structure allows the emergence onto the surface of the lateral planes of tetragonal pyramids, which leads to the occurrence of anionic vacancies associated with the molybdenum ion and these serve as the olefin adsorption centres[98].

On the other hand, in bismuth molybdates with a high bismuth content, there are vacancies on the lateral edges associated with the bismuth ion, which leads to complete oxidation. In the compound $Bi_2O_3.3MoO_3$ the Mo–O octahedra are joined via their edges and anionic vacancies associated with the molybdenum ion do not arise.

Indeed the γ-phase consists of layers of octahedra comprising molybdenum surrounded by oxygen and alternating with bismuth layers between which there is an oxygen layer[97]. Moreover, the existence of Mo–O octahedra in the structure of keochlinite has been confirmed by spectroscopic data[156].

According to crystal field theory[158], octahedral coordination leads to a greater stabilisation by the crystal field than tetrahedral coordination and for this reason compounds in which the cation is in the centre of a more or less regular octahedron catalyse many reactions.

The loss of catalytic activity by bismuth molybdates in the $\gamma \rightarrow \gamma'$ transition can be attributed to a change in the coordination polyhedron from an octahedron to a tetrahedron.

Recent structural studies[169] on individual bismuth molybdates showed that these phases are based on a face-centred pseudocubic subcell of the CaF_2 type with repeat periods of 5.4–5.8 Å, containing from MoO_2 groups, where M = W, Mo, or Bi. Since the scattering capacity of Bi and Mo atoms is much higher than that of O atoms, the above subcell should characterise primarily the distribution of the heavy atoms in the structure. Indeed, in the mineral koechlinite[167] the bismuth and molybdenum

atoms form a distorted face-centred cubic subcell in which there are four bismuth and molybdenum atoms and eight oxygen atoms.

In the range of catalyst compositions where the Bi_2O_3 content is between 0 and 50%, the subcell has vacancies corresponding to the positions of the metal atoms, when the ratio $Bi_2O_3 : MoO_3 = 1 : 1$ holds, the subcell has no vacancies, and finally in the range of compositions where the Bi_2O_3 content is between 50 and 100% the subcell has vacancies in the positions of the oxygen atoms.

Fig. 5 presents different versions of the structure, based on the data of Gal'perin and Erman [169,171], of the largest crystal faces of compounds in the Bi_2O_3–MoO_3 system. The positions of the vacancies in the distribution of bismuth atoms are indicated on the (010) face of the bismuth molybdate $Bi_2O_3.3MoO_3$ (part *a*). On the crystal faces of the compound $Bi_2O_3.MoO_3$, the vacancies are not indicated since their coordinates have not been determined. Fig. 5 shows that the structures of the largest faces of the α-, β-, and γ-phases are different and that the bismuth : molybdenum ratios also differ.

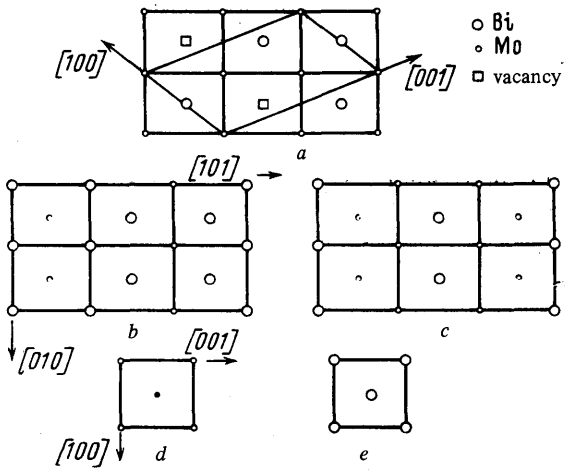


Figure 5. Distribution of metal atoms on the largest faces [144,169]: *a*) $Bi_2O_3.3MoO_3$; *b*) and *c*) $Bi_2O_3.2MoO_3$; *d*) and *e*) $Bi_2O_3.MoO_3$.

On the large (010) face of the α-phase, the presence of vacancies in the positions of the bismuth atoms increases the Bi : Mo ratio in favour of molybdenum (Mo : Bi = 1.5). On the surface of the β-phase crystals, either bismuth (1.6 : 1) or molybdenum (2.5 : 1) atoms predominate. In the γ''-phase, into which the γ-structure is converted under the conditions of the oxidative ammoniolysis of propene [11,165,170], the atoms are distributed in the same way as on the largest faces of the γ-phase (only molybdenum atoms on one face and only bismuth atoms on the other), since the expansion of the unit cell of the γ-form takes place mainly in the (100) and (001) directions, while the distances between the Bi_2O_3 and MoO_4 layers do not change significantly. Even if Bi : Mo ratios analogous to those on the faces of the α-, β-, and γ-phases hold on the surface of some of the faces of the γ'-phase, the fraction of these faces in the overall structure is small, because the γ'-phase, which exhibits the lowest catalytic activity, crystallises in the form of needles extended along the (001) axis. In the vertical band around these crystals, there are 16 faces of equal size in which both cations (Bi and Mo) are located. It is noteworthy that the presence of vacancies in the distribution of metal atoms is probably not an essential property of catalytically active phases, since they are absent from the structure of the bismuth molybdate $Bi_2O_3.MoO_3$. It is also evident that the existence of doublet centres does not play a dominant role in the activity of bismuth molybdates, because on the large faces of the catalytically active γ''-phase only Mo or Bi atoms are present.

Moreover the structural studies of Erman and Gal'perin [169,170] revealed that the length of the propene molecule and the repeat period of the sublattices of phases active in the oxidative ammoniolysis of propene are comparable. The formation of carbon–oxygen complexes probably requires the presence of a pair of identical atoms M–M with octahedral coordination and at a distance of 5.5–5.6 Å.

Comparison of the results of studies on the catalytic activities of various tin–molybdenum catalysts with the results of the phase analysis of the latter has shown [71] that, in contrast to bismuth–molybdenum catalysts, in this system catalytic activity is shown by solid solutions obtained by the substitution of both molybdenum ions in the lattice of molybdenum trioxide by tin ions and of tin ions in the lattice of tin dioxide by molybdenum ions. The solid solution based on the tin dioxide lattice with the atomic ratio Sn : Mo = 9 : 1 has the highest activity and selectivity in the oxidative ammoniolysis of propene.

Tin(IV) oxide has the rutile structure in which the cations are located at centres with octahedral coordination [172]. The replacement of a small proportion of the cations by Mo^{6+} yields a catalyst for the selective oxidation of propene. It is therefore possible that in this case, as in bismuth–molybdenum catalysts, the active centres are Mo^{6+} ions surrounded by oxygen ions with octahedral coordination.

However, in contrast to the bismuth–molybdenum catalysts, the active structure in this case is not a definite chemical compound but a solid solution obtained by the substitution of one ion by another.

In recently published detailed studies of the catalytic activity of the Fe_2O_3–Sb_2O_4 (Boreskov et al. [58]) and U_3O_8–Sb_2O_4 (Graselli and Callahan [173]) systems in the oxidative ammoniolysis of propene and the SnO_2–Sb_2O_4 system [174] in the oxidation of propene it is also emphasised that the highest catalytic activity and process selectivity are associated with the presence in the catalyst lattice of a compound having a definite structure: of iron antimonate in the Fe_2O_3–Sb_2O_4 system and of uranyl antimonate (UO_2) Sb_3O_7 in the U_3O_8–Sb_2O_4 system. In contrast to the latter, in the SnO_2–Sb_2O_4 system as for tin–molybdenum catalysts the highest activity and selectivity is shown, with a structure comprising a solid solution of antimony oxide in tin(IV) oxide. All these compounds contain Sb^{5+} ions in centres surrounded by oxygen ions with octahedral coordination [174,175].

The low activity of iron and manganese molybdates, the lattice cells of which contain, in contrast to active bismuth molybdates, MoO_4 tetrahedra between which Fe and Mn cations are distributed, can probably be explained from the same standpoint [176].

All these data show that the selectivity in the oxidative ammoniolysis of propene in the presence of various mixed oxide catalysts depends on the structure of the crystal lattice of the catalyst, which contains ions distributed at a

specific distance from one another and surrounded by oxygen ions with octahedral coordination. The accessibility of particular adsorption centres on the solid should play a major role in determining the nature of the active centres on the surface of oxidation catalysts. For example, Stone[177] believes that copper(I) oxide is more active in oxidative catalysis owing to the unusual distribution of oxygen on the faces which are preferentially exposed on the surfaces of these structures.

The low activity of iron-containing type A zeolites in relation to type X and Y zeolites, observed[131,132] in the oxidative ammoniolysis of propene, is evidently associated with the accessibility of the adsorption centres (iron ions) to the reacting molecules. In type A zeolites the size of the inlet into the large cavities is 4.2 Å, which hinders their penetration by propene molecules and hence their adsorption in the primary porous structure of this zeolite. With increase of the degree of substitution of sodium ions by iron ions, the dimensions of the octagonal oxygen inlets leading into the large cavities of the type A zeolite are somewhat altered[178] and the authors therefore believe that this makes the adsorption centre more accessible, which is probably the reason for the increased catalytic activity of the iron-containing zeolite.

VI. EFFECT OF THE ELECTRONIC WORK FUNCTION ON CATALYTIC ACTIVITY

It has been suggested[3,11,96] that in the heterogeneous oxidation of hydrocarbons the catalyst must be capable of forming a donor–acceptor bond with the organic reactant and with oxygen and also be able to transmit electrons from one molecule involved in the process to another. Depending on the mechanism of electron transfer in the solid, either the delocalised electrons of the solid or the electrons localised at the lattice cations take part in the electron exchange with the adsorbed species. As already mentioned above, in the adsorption of the reactants in the oxidative ammoniolysis of propene on the surfaces of oxide catalysts, charged oxygen-containing complexes of propene[117,135,145] and ammonia[118,119] are probably formed and therefore the rate of the process depends on their surface concentrations and the magnitude of their charges. The electron work functions of the crystals then regulate the filling of the catalyst surface by the charged intermediate species propagating the oxidation process.

It has been demonstrated in detail in a monograph[11] that, in cases where a relation is observed between the process selectivity and the electronic work function φ of the catalyst (the main characteristic of the electronic properties of the surface), it is possible to drive the oxidation of hydrocarbons in the presence of such catalysts towards partial or extensive oxidation by controlling the electronic work function of the solid. However, it has been established[179] from measurements of the conductivities of individual bismuth molybdates, which are the most active catalysts in the oxidative ammoniolysis of propene, that electrons are appreciably localised at individual lattice ions, i.e. in this case the electronic work function of the solid may play a subsidiary role in the catalytic process.

Indeed it has been shown[180,181] that, when bismuth molybdate is modified by the introduction of various additives, the electronic work functions of such catalysts hardly change. However, under these conditions their crystal lattices undergo a rearrangement, which affects the kinetic characteristics of the joint oxidation of propene and ammonia.

VII. ACIDITY OF THE CATALYST SURFACE

From an analysis of extensive experimental data for the activities of mixed oxide catalysts for partial oxidation, Roiter and Golodets[182] suggested that the stability of the activated surface complexes in the oxidation of hydrocarbons, which probably resemble salt-like formations, depends on the acid–base properties of the surface. Anphoteric properties of the catalyst surface, which ensure the ease of formation and decomposition of the salt-like complex, are particularly favourable for oxidative catalysis.

The low catalytic activity of salts of strong acids in the oxidative ammoniolysis of propene[139] compared with oxide catalysts due to the existence on their surface of mobile hydrogen atoms can probably be explained from this standpoint. The number of acid centres on the surface of these catalysts, determined by titrating them with weak bases in non-aqueous media in the presence of indicators[183,184], proved to be close to the number of acid centres on aluminosilicates (about 20 mequiv. m^{-2}, $pK \leqslant -3$).

According to Skalkina et al.[139], the presence of mobile hydrogen atoms on the surface of strong acid salts may alter the mechanism of the extensive oxidation of propene, i.e. an isopropyl carbonium ion is formed and can accelerate the subsequent conversion of the olefin molecule into final products.

In conclusion of our analysis of the published data, we may suggest that the activity and selectivity of the catalysts for the oxidative ammoniolysis of propene are determined by the structure of the oxygen-containing surface complexes of the hydrocarbon and ammonia. The active surface of the catalysts for the joint oxidation of propene and ammonia must contain active centres of the same type, the reactivity and oxygen mobility of which depend on the nature of the metal and its environment in the crystal lattice of the catalyst. Apart from the energy structure of the solid, the structure of the catalyst surface plays an important role in this reaction.

Changes in the conditions of preparation and also in the nature of the starting materials (salts, acids), which have been followed for bismuth–molybdenum[165,185], tin–molybdenum[150], and tin–antimony[174] catalysts, hardly influence the selectivity of the propene oxidation reactions.

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