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On the Mechanism of Catalytic Oxidation of Hydrocarbons

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Contribution from complexes to olefin oxidation is considered. The routes of conversion of oxygenated products are determined from isotope data. The effect of catalyst-ion valencies on formation of oxygen-hydrocarbon complexes is investigated making use of adsorption, electric, and γ-resonance techniques. A step-wise mechanism of propene oxidation over a tin-molybdenum catalyst is proposed.

The use of diverse kinetic, adsorption, electric and isotope techniques permitted proposing a stepwise scheme for oxidation of olefins over various catalysts (*1*). Propene may form π-complexes on the surface, or π-allyl complexes after dissociation. Both forms convert to various charged oxygen–hydrocarbon complexes by interaction with oxygen (Fig. 1).

The chemisorption of reactants under precatalysis conditions, i.e., at a temperature lower than that of the reaction onset, and the behavior of oxygenated products over a catalyst were studied by the kinetic and isotope techniques.

Sachtler (*2*) and others (*3*) have found that propene oxidation over bismuth molybdate and cuprous oxide involves only end groups of hydrocarbon molecules, allyl being probably the intermediate in acrolein formation. Catalytic oxidation of olefins yielded both unsaturated and saturated aldehydes, acetaldehyde, formaldehyde, a small amount of propionic aldehyde, etc. It was of interest to find out what were the intermediates through which the oxygenated compounds were formed.

The oxidation of differently labelled propene, acrolein and acetaldehyde over a bismuth-molybdenum catalyst was investigated (Table 1).

It was assumed earlier (*1*) that acetaldehyde and formaldehyde were formed by local oxidation of propene at the double bond to form π-complexes by olefin adsorption. On the other hand, these aldehydes could have been formed via the π-allyl complex, in the same way acrolein is formed. In the first

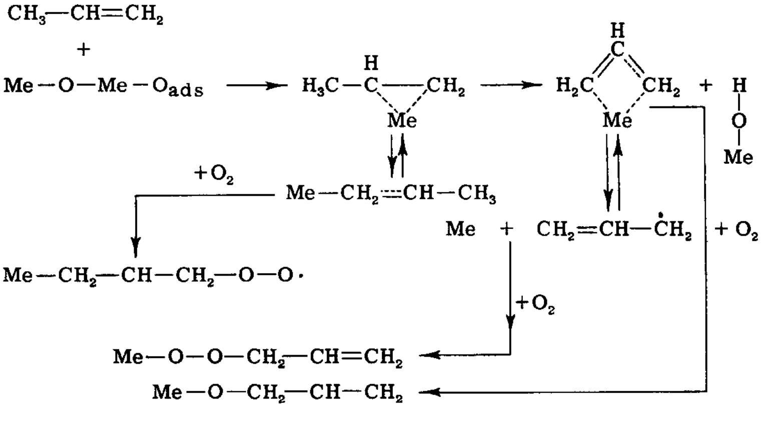


FIG. 1. Scheme of propene oxidation on an oxide catalyst.

TABLE 1
DISTRIBUTION OF RADIOACTIVITY OF PROPENE-1-^{14}C AND -2-^{14}C OXIDATION AT 460°C

Initial compounds	Time of contact (sec^{-1})	Molar radioactivity α				
		Acrolein	Acetaldehyde	Formaldehyde	CO	CO_2
$CH_2{=}^{14}CH{-}CH_3$	1.0	100	89	17	58	68
	2.0	100	83	10	42	65
	3.5	100	87	8	51	57
$^{14}CH_2{=}CH{-}CH_3$	0.5	100	52	59	56	53
	1.0	100	54	56	65	47

case, oxidation of propene-1-^{14}C would produce nonradioactive acetaldehyde, and formaldehyde would contain all the initial radioactivity (α). The molar radioactivity of formaldehyde and acetaldehyde was found to be close to 50% (*4*) (Table 1). This points to an equal contribution from the end carbon atoms of propene, and consequently the reaction seems to proceed via a surface compound of the allyl type. In experiments using propene-2-^{14}C the acetaldehyde reactivity was higher than that of formaldehyde. Thus the reaction scheme would be:

$$CH_2{=}CH{-}CH_2 \rightarrow CH{=}CH_2{=}CH_2 \rightarrow CH_3{-}CHO + HCHO.$$

Various oxygenated compounds were also found to react, along with olefins, at the catalyst surface.

The kinetics of oxidation of various aldehydes and acids over a bismuth-molybdenum catalyst was studied in detail (*5*). Table 2 shows the reaction rate coefficients.

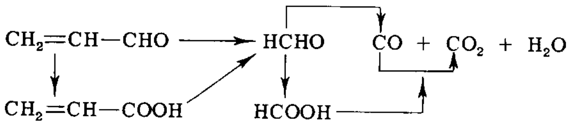
The schemes of acrolein and acetaldehyde oxidation are given as examples.

Dissociation of acetaldehyde molecules by oxidation gives formaldehyde and products of complete oxidation (CO and CO_2).

Acrolein oxidizes mostly at the double bond, and the presence of the latter in unsaturated, aldehyde molecules makes aldehyde more stable towards oxidation. For instance, the rate coefficient of acrolein oxidation is 20 times less than that of acetaldehyde (Table 2). This difference is probably due to the nature of aldehyde adsorption by the catalyst. The saturated aldehyde seems to form a complex at the carbonyl group, whereas acrolein is bound with the surface also by the double bond to form π-complexes.

The molar radioactivity of formaldehyde was only 5% of the initial acrolein-2-^{14}C activity (Table 3) so that its contribution to the formation of the central carbon atom of acrolein seems to be immaterial. The relatively low value of α for formaldehyde in experiments using acrolein-2,3-^{14}C and its almost 50% amount with acrolein-1-3-^{14}C seems to show that formaldehyde is formed mainly from the car-

Acrolein oxidation



Acetaldehyde oxidation

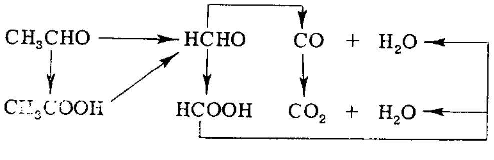


TABLE 2

RATE COEFFICIENTS FOR OXIDATION OF ALDEHYDES AND ACIDS ON A BISMUTH-MOLYBDENUM CATALYST

Compound	Rate coefficients ($sec^{-1}mole^{-2}$) CO	CO_2	Formaldehyde
Aldehydes			
Formaldehyde	0.1	0.15	—
Acetaldehyde	2.0	1.30	1.8
Acrolein	0.08	0.13	0.05
Acids			
Formic	0.4	11.8	—
Acetic	2.6	7.4	6.8
Acrylic	0.1	0.5	—

bonyl group. Carbon oxides are formed essentially from the vinyl group of acrolein molecules; the carbon atoms in positions 2 and 3 are of equal importance, both for CO and CO_2 formation. This is confirmed by the equal α values for CO and CO_2 in experiments using acrolein-2-^{14}C and -2,3-^{14}C. However, in an ideal case oxidation of acrolein-2-^{14}C would yield nonradioactive formaldehyde, and CO and CO_2 would display an about 50% radioactivity. Deviation of experimental results from ideal values seems to be due to side reactions, for instance, to further the conversion of formaldehyde, nonselective oxidation of acrolein, etc.

Acetaldehyde oxidation has shown that formaldehyde and carbon oxides were formed from the methyl and carbonyl groups, respectively.

Comparison of the acrolein and acetaldehyde behavior over bismuth molybdate has shown that formaldehyde and products of complete oxidation are formed from different molecular fractions, and the sites of oxidation are not the same for aldehydes of different structure. This is another evidence that adsorption is of a different nature for saturated and unsaturated-oxygenated products of propene oxidation.

Thus, the reaction route seems to depend on the type of the intermediate surface complex, both for the initial hydrocarbon and for reaction products.

Detailed investigation of chemisorption of reactants' mixtures on characteristic oxidation catalysts: SnO_2–Sb_2O_4 bismuth molybdate and tin molybdate, under precatalysis conditions (*6*) was undertaken. When oxygen was preadsorbed on a catalyst for partial propene oxidation, coverage with the hydrocarbon was greater. With catalysts for complete oxidation, preadsorption of olefin resulted in a greater coverage with oxygen. Determination of the electron work function has shown that the surface complexes formed are of a different composition and are charged. Table 4 lists the ratios of carbon to oxygen atoms in complexes, the charges, and the rates of complex formation by chemisorption of mixtures. The rate of partial-propene oxidation is shown for comparison.

The complexes in partial-oxidation catalysts contain more carbon than oxygen atoms, are of a positive charge, and their desorption yields mainly partial-oxidation products. The reverse is observed for complexes on catalysts for complete oxidation. The number of oxygen atoms is higher, the charge is negative, and the products they yield by decomposition are CO_2, CO, and H_2O.

Since, according to kinetic results, the interaction of hydrocarbons at the catalyst

TABLE 3

DISTRIBUTION OF RADIOACTIVITY IN THE OXIDATION PRODUCTS OF ACROLEIN LABELED IN VARIOUS POSITIONS (460°C, CONTACT TIME 2 SEC)

Reaction products	Molar radioactivity, α $CH_2{=}^{14}CH{-}CHO$	$^{14}CH_2{=}^{14}CH{-}CHO$	$^{14}CH_2{=}CH{-}^{14}CHO$
Formaldehyde	5	15	46
CO	40	37	46
CO_2	38	40	44

TABLE 4
CHARACTERISTICS OF OXYGEN-HYDROCARBON COMPLEXES ON THE SURFACE OF OXIDATION CATALYSTS (PRESSURE 0.7 TORR)

	Partial oxidation		Complete oxidation
	$SnO_2 \cdot Sb_2O_4$ Sn:Sb = 3:1	$Bi_2O_3 \cdot 2MoO_3$	SnO_2
Complex composition C:O	4	1.5	0.5
Charge sign	+	+	—
Rate of the complex formation (150–200°C) $w \times 10^9$ g-mole/m²sec	0.01	0.03	0.1
Reaction rate $w \times 10^9$ g-mole/m²sec 400–450°C[a]	0.3	20	0.6

[a] The rate of reaction on SnO_2–Sb_2O_4 at 200°C obtained by extrapolation is 0.6×10^9 g-mole/m²sec.

surface is the rate-limiting step, it was of interest to compare the rates of complex formation with those of catalysis under resembling conditions. Indeed, the rate of complex formation calculated from the kinetic isotherm seemed to show that adsorption of gas mixtures (Table 1) may be the rate-limiting step of oxidation. Unfortunately, the attempts to estimate the decomposition rate failed, and thus it was impossible to decide whether formation or decomposition represented the rate-limiting step.

Almost all oxidation catalysts contain various metals and nonmetals, with individual oxides taking a considerably lesser part in oxidation. It was of interest to find out the cause that made the catalyst more complicated, as well as its effect on the complex formation at the catalyst surface. Molybdenum ions are known to be present in most active and selective catalysts. They can form π- and π-allyl complexes with olefins. Information on the valence state of molybdenum ions on the surface and on their coordination is still insufficient.

The part played by the second metal or nonmetal ion in the catalyst composition is still less clear. It is suggested either to be the center of oxygen adsorption (*1*) or to favor vacancies in the catalyst lattice around the molybdenum ion (*7*), thus inducing the formation of an active center of partial hydrocarbon oxidation.

It follows from uv-spectra of cobalt molybdate on aluminium oxide that the coordination of both ions is tetrahedric at a low molybdate concentration and becomes octahedric with increase in molybdate (*8*).

The effect of coordination of molybdenum ions contained in bismuth molybdate and in other molybdates on the rate of propene conversion was investigated (*9*). It was suggested that a catalyst containing molybdenum is more active in the tetrahedric or in a strongly distorted octahedric form.

Investigation of the $Bi_2O_3 + MoO_3$ and $Bi_2O_3 + WO_3$ structures (*10*) has shown that the presence of vacancies in the bulk of the crystal is not indispensable for catalytic activity.

The valence of metal ions on the catalyst surface is of greater importance. Both the ion valence and the nature of its surroundings in the catalyst lattice have been determined by the Mössbauer technique for a solid solution of molybdenum oxide in tin oxide in an atomic ratio of 1:1 (*11*).

Propene and oxygen were preadsorbed on a tin-molybdenum catalyst at the reaction temperature. By analysis of the spectrum of a pure catalyst with the complex formed (Fig. 2), it was found that the organic molecule is bound to the tin ion via the oxygen atom. It will be noted that formation of a surface compound decreases the tin valence from 4 to 2. Such a change in ion charge is observed for tin-molyb-

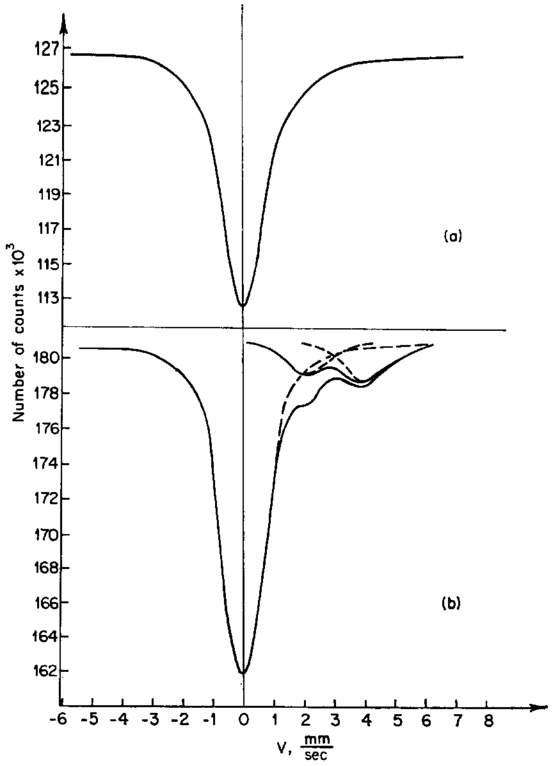


FIG. 2. γ-resonance spectra of a tin-molybdenum catalyst. (a) Initial sample. (b) After adsorption of oxygen and propene at 200°C where *v* is the relative velocity of the source motion.

denum catalysts only. Chemisorption of olefins and oxygen on pure tin dioxide brings about no change in the spectrum. Transfer of electrons from molybdenum to tin Sn seems to occur in the presence of molybdenum ions only. It may occur either through the solid lattice, or inside the complex sphere. The former is more probable. It will be noted that the $Mo_2O_2(SnCl_3)_2$ dimer, containing pentavalent molybdenum and bivalent tin, is the active complex responsible for ethylene hydrogenation (*12*).

ESR investigation of oxygen adsorption on molybdenum oxide supported by aluminium (*13*) has shown that aluminium radicals appear in the presence of molybdenum ions, due to electron transfer through the solid lattice.

The observed electron transfer from molybdenum to aluminium points to the probability of electron transfer in systems containing ions capable of existing in different valence states. When such transfer is slow, there must be a relation between olefin oxidation and electronic properties of cations in molybdates. The rate of acrylic-acid nitrile formation as a function of the number of electrons, d, in cations of the IVth Mendeleev group is given in Fig. 3. Maximum activity is observed first for titanium molybdate, then vanadium. Iron and copper-chromium salts show weak activity. The two-peak Dowden function, usually observed for complete oxidation over simple oxides, is not obtained for partial oxidation. Such a change in the reaction rate is probably due to different coordination capacities of surface ions of different electronic structure and different bond energies of the surface compounds formed.

It follows from Mössbauer spectra of various oxide catalysts (*14*), that optimal deviation from charge symmetry of tin or iron ions is needed for maximum selectivity in propene ammonolysis (Fig. 4, Table 5).

Complete oxidation usually occurs with low quadrupole splitting (with a constant

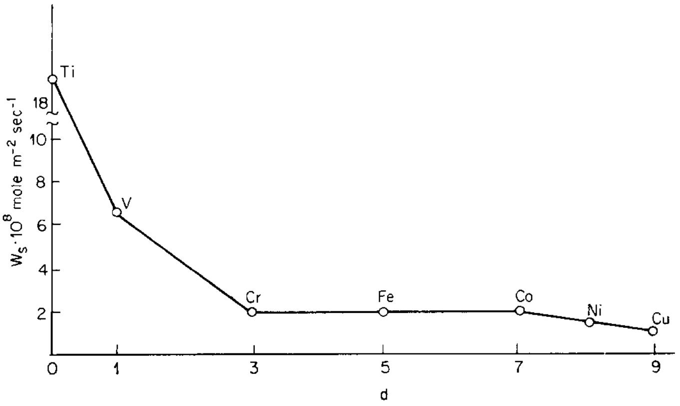
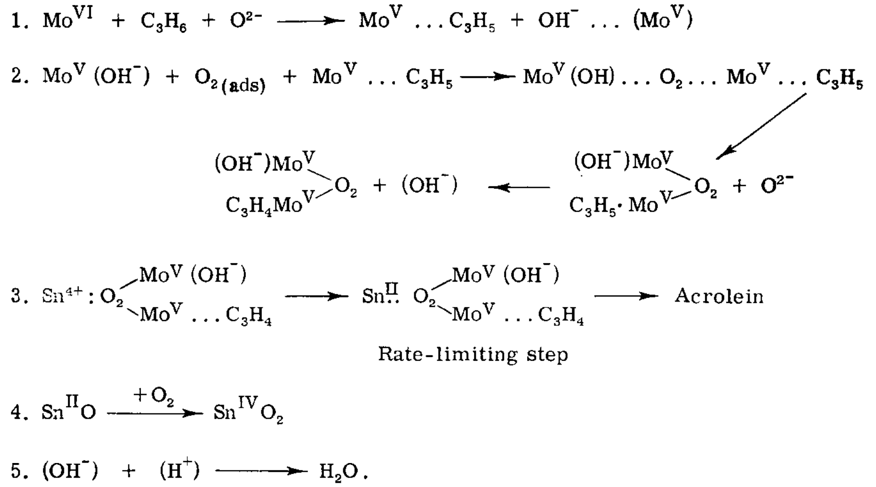


FIG. 3. The rate W_s of acrylic-acid nitrile formation as a function of the number of electrons, d, in cations of various molybdates.

chemical shift) corresponding to indifferent deviation from charge symmetry around the cations.

Oxidation of hydrocarbons seems to necessitate electron interaction between ions following scheme M–M, or M–O–M for oxide systems. A more complicated composition of the system and a greater number of diverse components would make such interaction more ready.

The scheme of propene oxidation on a tin-molybdenum catalyst for example, may be conceived as:



$$1.\ \mathrm{Mo^{VI}} + \mathrm{C_3H_6} + \mathrm{O^{2-}} \longrightarrow \mathrm{Mo^{V}} \ldots \mathrm{C_3H_5} + \mathrm{OH^-} \ldots (\mathrm{Mo^{V}})$$

$$2.\ \mathrm{Mo^{V}(OH^-)} + \mathrm{O_{2(ads)}} + \mathrm{Mo^{V}} \ldots \mathrm{C_3H_5} \longrightarrow \mathrm{Mo^{V}(OH)} \ldots \mathrm{O_2} \ldots \mathrm{Mo^{V}} \ldots \mathrm{C_3H_5}$$

$$\left.\begin{matrix}\mathrm{(OH^-)Mo^{V}}\\ \mathrm{C_3H_4Mo^{V}}\end{matrix}\right\rangle \mathrm{O_2} + \mathrm{(OH^-)} \longleftarrow \left.\begin{matrix}\mathrm{(OH^-)Mo^{V}}\\ \mathrm{C_3H_5 \cdot Mo^{V}}\end{matrix}\right\rangle \mathrm{O_2} + \mathrm{O^{2-}}$$

$$3.\ \mathrm{Sn^{4+}} : \mathrm{O_2}\left\langle\begin{matrix}\mathrm{Mo^{V}(OH^-)}\\ \mathrm{Mo^{V}} \ldots \mathrm{C_3H_4}\end{matrix}\right. \longrightarrow \mathrm{Sn^{II}} \ldots \mathrm{O_2}\left\langle\begin{matrix}\mathrm{Mo^{V}(OH^-)}\\ \mathrm{Mo^{V}} \ldots \mathrm{C_3H_4}\end{matrix}\right. \longrightarrow \text{Acrolein}$$

Rate-limiting step

$$4.\ \mathrm{Sn^{II}O} \xrightarrow{+\mathrm{O_2}} \mathrm{Sn^{IV}O_2}$$

$$5.\ \mathrm{(OH^-)} + \mathrm{(H^+)} \longrightarrow \mathrm{H_2O}.$$

According to isotope data (*2*, *3*), a π-allyl complex and a hydroxyl group, probably bound with pentavalent molybdenum, are formed by propene adsorption on ions of sextivalent molybdenum on the surface of a tin-molybdenum catalyst. The suggestion about the hydroxyl group-pentavalent molybdenum bond is based on investigation of tungsten which is a molybdenum analog (*15*). The second hydrogen atom is detached from the allyl intermediate by interaction with oxygen. The oxygen–hydrocarbon complex bound with $\mathrm{Mo^V}$ reacts with tetravalent tin ions to form an intermediate binuclear complex. The tin ion chargeschange from 4 to 2 as previously mentioned (data obtained from γ-resonance spectra). Decomposition of the complex results in acrolein desorption, restoration of initial charges of molybdenum, and tin ions i.e., of the adsorption centers,

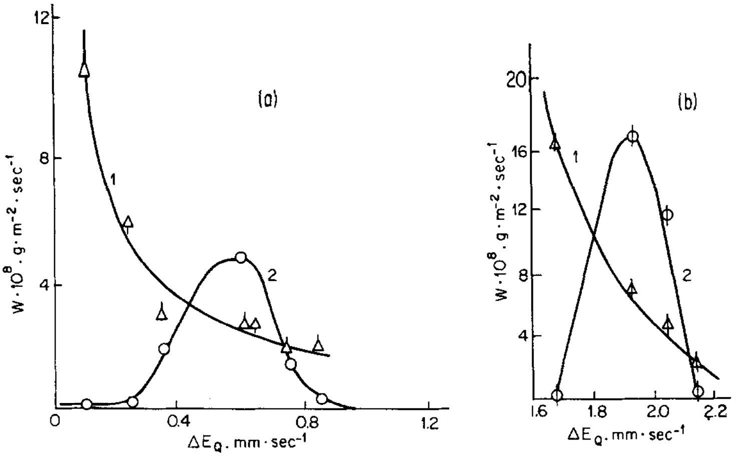


FIG. 4. The rates W of CO_2 (1) and acrylic-acid nitrile (2) formation on oxide catalysts containing iron (a) and tin (b) as a function of quadrupole splitting (ΔE_Q).

and in reaction of the hydroxyl group with protons to form water.

Since the proposed scheme involves participation of the lattice oxygen in detachment of hydrogen atoms from propene molecules, as well as contribution from the Mo^V (OH^-) center to formation of the oxygen–hydrocarbon complex, the dependence of selectivity on propene oxidation, and of the catalyst activity on the reduction capacity of oxide catalysts becomes clear (*16*). These functions may be accounted for by electron transfer between ions.

It was found for bismuth molybdate that saturated aldehydes are formed also through the intermediate allyl complex. Consequently, it may be suggested that the route of the oxygen–hydrocarbon complex decomposition is responsible for the difference in formation of acrolein and other aldehydes.

Addition of electronegative species, such as sulfur, phosphorous, selenium, and tel-

TABLE 5

QUADRUPOLE SPLITTING, E_Q, ACTIVATION ENERGY, E, AND THE RATE OF PROPENE AMMONOLYSIS, W, OVER VARIOUS IRON AND TIN-CONTAINING CATALYSTS

		$W_{aan} \times 10^8$	$W_{CO_2} \times 10^8$	E_{aan}	E_{CO_2}
Catalysts	E_Q(mm/sec)	(g/m² sec)		(kcal/mole)	(kcal/mole)
Fe_2O_3	0.2 ± 0.02	0.0	6.3	—	8.0
$Fe_2O_3\cdot Cr_2O_3$	0.1	0.02	9.2		9.0
$Fe_2O_3\cdot MoO_3$	0.33	1.9	2.7	17.0	14.0
$Fe_2O_3\cdot Sb_2O_4$	0.60	5.0	2.0	14.0	15.0
$Fe_2O_3\cdot As_2O_4$	0.75	2.0	1.9	—	—
$Fe_2O_3\cdot SnO_2$	0.84	0.4	2.0	21.0	18.0
$Ee_2O_3\cdot P_2O_5$	0.59	1.9	2.8	16.0	17.0
$2Fe_2O_3\cdot P_2O_5$	1.18	0.2	0.2	16.0	23.0
over aerosyl	0.82	1.53	0.8	17.0	22.0
$Fe_2O_3\cdot P_2O_5$	1.15	0.4			
over SiO_2	0.85	1.5	1.95	16.0	25.0
SnO_2	1.68 ± 0.02	0.02	16.0	—	—
$SnO_2\cdot Sb_2O_4$	1.92	17.0	7.0	—	—
$SnO_2\cdot MoO_3$	2.04	14.0	6.0	—	—
$SnO_2\cdot Fe_2O_3$	2.12	0.4	2.0	21.0	18.0

TABLE 6
Adsorption of Oxygen and Propene on Tin Catalysts

Catalysts	°C	The coverage ratio of O_2/C_3H_6 Individual adsorption	The coverage ratio of O_2/C_3H_6 Successive adsorption	Pressure
SnO_2	200	0.8	2.0	Initial
$SnO_2 \cdot Sb_2O_4$	200	0.4	0.8	pressure
$SnO_2 \cdot MoO_3$	170	0.3	0.7	3-5 Torr

lurium oxides and halides, to the partial oxidation catalyst is known to increase the process selectivity by suppression of the complete oxidation reaction (*1*). Various explanations were proposed for the action of additives: Changes of collective electronic properties of the solid surface result in lower coverage by actively charged forms responsible for complete oxidation of hydrocarbons, blocking of active surface sites, etc.

As the negatively charged oxygen–hydrocarbon complexes were found to form under pre-catalysis conditions, the effect of additives on complex formation at the surface was studied for a tin-molybdenum catalyst. Comparison of the activities of mixed tin catalysts, SnO_2–Sb_2O_4, SnO_2–MoO_3, with pure tin dioxide, has shown that the tetravalent tin ions are those most effective for complete oxidation. It follows from the data on oxygen and propene adsorption on these catalysts (Table 6), that oxygen concentration on a tin-dioxide surface is higher than that of the irreversibly adsorbed hydrocarbon.

Addition of electronegative elements decreases oxygen adsorption and at the same time causes a deviation from charge symmetry around the tin nucleus. The quadrupole splitting value increases and the rate of complete propene oxidation decreases, as shown by γ-resonance spectroscopy.

With partial oxidation the promoting action of a small amount of an additive would probably involve, besides the above factors, disturbance of electron exchange between ions of the catalyst, for example of tin-molybdenum, and this would increase the probability of the formation of oxygen–hydrocarbon complexes limiting the rate of partial oxidation.

Heterogeneous oxidation in the gas phase was conducted mainly for two classes of hydrocarbons: for olefins and aromatics, i.e., those capable of forming complexes with transition metals of different electronic structure. This capability seems to be the reason of failure in attempting to conduct partial oxidation of hydrocarbons in the gas phase. Thus, further development in the field of partial oxidation of organic compounds less active in complex formation would require investigations on their complexing capacity.

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