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Advanced Bond-Strength Model of Active Sites on Oxide Catalysts

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Recent studies provide several examples of catalytic anisotropy of oxides in simple or oxidative dehydrogenation, dehydration, and oxidation reactions. Among others, these data include conversion of methanol, ethanol, and propylene on MoO_3 and conversion of propylene and *o*-xylene on $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$. The univocal ascription of the formation of a given product to the defined crystallographic face of catalyst makes it possible a more profound discussion of the possible structure of active sites. Catalytic reaction can develop if geometric and energetic fit is achieved between adsorbed molecule and the neighborhood of adsorption site. In the proposed model structural considerations concerning various planes of catalyst are based on crystallographic data and on known shapes and dimensions of organic molecules. Adsorption of reactants is assumed to take place on coordinatively unsaturated surface metal and oxygen atoms. Bond strength, calculated according to the bond-length–bond-strength concept, is taken as a measure of binding energy, and consequently (beside geometry) as a factor determining the catalytic reaction pathway. Elementary steps consisting in the exchange of hydrogen or oxygen atom between organic species and catalyst surface are thought to proceed on the condition that the indicated atoms are more firmly bonded to the presumed step product than to the substrate. On this basis the sites are indicated on which dehydrogenation, oxidation (oxygenation), deoxygenation, and water evolution steps may take place. Combination of dehydrogenation and deoxygenation is thought to result in dehydration. Possible mechanisms of catalyst reoxidation are also discussed qualitatively in terms of the proposed model.

INTRODUCTION

Recent studies provide several examples proving that performance of oxide catalysts in the reactions of simple and oxidative dehydrogenation, dehydration, and oxidation of hydrocarbons and their derivatives depends on the kind of crystallographic plane preferentially exposed by the grains of polycrystalline sample. These data include oxidation of propylene on MoO_3/graphite system (*1*), on WO_3 (*2*), and over $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$ (MV-X, X = 100*x*) solid solutions (*3*), oxidation of *o*-xylene on MV-X (*4*), V_2O_5 (*5*), V_2O_5/TiO_2 system (*6*), and conversion of methanol and ethanol over MoO_3 (*7, 8*). Most of the above quoted experiments were done on the relatively large grains of well developed and macroscopically flat surfaces. As claimed by Tatibouët and Germain (*7*) these are certainly the new examples of the *structure sensitive* reactions (*9*), but the term *catalytic anisotropy* introduced in (*10*) seems to reflect better the nature of the phenomenon.

Recent studies performed with use of such modern techniques as low energy electron diffraction (LEED) (*11*), high resolution transition electron microscopy (HRTEM), and laser diffraction (*12*) or extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) (*13*) prove that the arrangement of atoms in the surface layer of various metals, diamond, LiF, and TiO_2-anatase is essentially the same as in the bulk. This was observed even in the case if the samples were dispersed into the particles as small as 20–60 Å in diameter, and thus composed—as it were—of the surface layer only. In most cases the bond lengths or the upperlayer spacing perpendicular to the surface were found to be equal to the bulk values within reported accuracy of 0.3

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to 5%. These facts permit to assume that the surface structure of a well grown crystal (especially the ionic one) is usually the same as that of the bulk, the differences being limited to the consequences of the flat crystal cutting along the respective crystallographic plane, resulting in the coordinative undersaturation of atoms.

Consequently, in the case of catalytic anisotropy of oxides the ground of differentiation of their catalytic behavior should be looked for in the differences in geometry and energetics of various crystallographic planes. Individual properties of structurally nonequivalent atoms of the same kind should be especially taken into account. Relevant inspiration may be found in the famous Balandin's multiplet theory of heterogenous catalysis (*14*).

So far, two models of oxide catalyst surface have been offered, based on crystallographic considerations and on the modern bond-strength concept involving empirically established bond-length–bond-strength relation (*15, 16*). One of them has been proposed by Anderson and applied to the vanadium oxides (*17*). The other, called BSMAS (bond-strength model of active sites), has been formulated by the author of the present paper and applied to the oxidation of propylene (*18*) and *o*-xylene (*4*) on MV-X and to the oxidation of propylene on MoO_3 (*10*).

In the present paper BSMAS, applied so far to oxidation reactions, will be extended on dehydrogenation and dehydration reactions with use of the experimental data published by Tatibouët and Germain (*7, 8*). For this purpose some new concepts will be introduced to the model and thus it will be necessary to present briefly new formulation of BSMAS. A brief comment will be included at the end of the paper to demonstrate how the former discussion concerning oxidation reactions (*4, 10, 18*) can be ameliorated in terms of the new formulated model.

ADVANCED FORMULATION OF BSMAS

The model of surface of oxide catalyst is constructed by cutting the crystal along the respective crystallographic plane in such a manner as to break the weakest (i.e., the longest) bonds and to conserve the stoichiometric composition. The latter condition results from the fact that the catalysts discussed until now work in highly oxidized state; obviously this condition is not necessarily general. It is assumed that the configuration of atoms and the bond lengths at the surface are the same as in the bulk. In spite of crystal cutting, some of the surface atoms retain their normal, bulk coordination and they are regarded as inactive in adsorption or in catalytic transformations, contrary to those which become coordinatively unsaturated. Both coordinatively unsaturated metal and oxygen atoms may serve as adsorption sites (e.g., σ or π bonding of olefin, σ bonding of alcoxyl and adsorption of oxygen on metal atom; hydrogen bonding of hydrocarbon or alcohol on oxygen atom). As for a way of adsorption of a given molecule and its orientation with respect to the surface, available literature data are used as discussed in (*10, 18*).

The identification of the active centers on a given crystallographic plane of catalyst consists in looking for a geometric and energetic correspondence between the adsorbed molecule and the neighborhood of the adsorption site. While surface geometry and geometry of adsorption have been generally characterized above, the quantitative measurement of the energetic factor is to be more precise.

Various crystallographically nonequivalent surface oxygens (including those which lie above the surface, complete the polyhedra around metal atoms and are regarded as adsorbed oxygens) are characterized by the sums Σs_i of the strengths of bonds to them from the adjacent metal atoms. The individual s_i values are calculated according to the bond-length–bond-strength concept using the formula proposed by Brown and Wu (*16*):

$$s = (R/R_1)^{-N} \qquad (1)$$

where R is the length of a given bond and R_1

and N are the empirical constants determined for 84 different cations in oxygen environment and tabulated in (*16*). As an example the respective data for MoO_3 may be referred to Table 3. It may be useful to recall that according to Pauling's rule Σs_i around each bulk atom is equal to its valence.

It is assumed that Σs_i of surface oxygen atom may be taken as a measure of its binding energy E. In other words, E is thought to be an unknown function of Σs_i:

$$E = f(\Sigma s_i) \qquad (2)$$

The possible shape of this function will be discussed in a separate paper and the preliminary suggestions are given in Appendix 1.

In the equilibrium state the distribution of oxygen atoms over all possible surface oxygen positions (including both, lattice and adsorbed) should be ruled by the term $[1 - \exp(-f(\Sigma s_i)/RT)]$ and normalized to the actual oxidation state of crystal comprising possible nonstoichiometry. As far as adsorption of oxygen in monoatomic form is regarded there is no necessity and no univocal ground to make traditional difference between surface lattice and adsorbed oxygens.[1] In a stationary state (catalytic reaction conditions) kinetic terms should also play a role in determining the distribution. In both, equilibrium and stationary state, positions of firmly bonded oxygens ($\Sigma s_i \approx 2$) should be entirely occupied, while all other oxygen positions should be more or less vacant. Empty lattice positions of oxygen (= uncovered metal atoms) may act as additional adsorption sites for organic species.

The term $\exp(-f(\Sigma s_i)/RT)$ characterizes the probability of abstraction of oxygen from the surface to be used in oxidation of hydrocarbons. Thus the lower Σs_i of a given surface oxygen, the higher its catalytic activity. It is thought that incorporation of oxygen to the organic molecule is possible on condition that the strength of its bonding to the organic species s_{C-O} is higher than its Σs_i to the crystal surface.[2] The s_{C-O} can be calculated using formula (*1*), $R_1 = 1.378$, $N = 4.065$ for C–O bond given in (*16*) and the respective bond length R for the expected reaction product. The s_{C-O} values for some molecules are gathered in Table 1. As results from Table 1, e.g., acrolein can be formed with participation of surface oxygen of $\Sigma s_i < 1.70$; other examples will be discussed in the further paragraph of the paper.

Evolution of water formed in oxidation or oxidative dehydrogenation reactions may be discussed exactly in the same terms. Hydrogen atoms abstracted from the organic molecule are thought to diffuse along the surface and to combine with any surface oxygen of $\Sigma s_i < 1.62$ (the length of O–H bond in water is 0.9572 Å (*19*), which corresponds to $s_{O-H} = 0.81$).[3] As it will be

[1] In this paper the arbitrary differentiation will be maintained for convenience only, to distinguish between these oxygens which belong to the surface after stoichiometric cutting (lattice oxygens) and those which complete the polyhedra around cations (adsorbed oxygens).

[2] In other words, it is assumed that the rate of oxidation is higher than the rate of the reverse reaction on condition that $s_{C-O} > \Sigma s_i$ for the oxygen atom considered. This assumption is obviously only the first approximation as entropy factor is neglected. The simplification leads to the apparent conclusion that only exothermic elementary steps are allowed to proceed. We have thus to remember that the activity limit does not correspond exactly to $s_{C-O} = \Sigma s_i$ (as for simplicity and convenience we shall write below) but it is only close to the value determined in such a way. We have to take into account: (1) Entropy values and entropy changes are markedly reduced, as we regard molecules already adsorbed. (2) Our aim is to distinguish between active and inactive oxygens among a set, along which Σs_i varies markedly (cf. Table 3), and the more so the respective exponential expressions; therefore incorrectness resulting from neglecting entropy factor seems to be of minor importance. The above comments are valid also for other surface reactions which will be discussed below.

[3] $R_1 = 0.87$ and $N = 2.2$ for O–H bond were determined in (*16*) only for hydrogen bonds of 1.7–1.9 Å. Due to the necessity of extrapolation the indicated value of 1.62 is approximate.

TABLE 1

Lengths[a] and Strengths of C—O and O—H Bonds in Various Molecules

Molecule	C—O bond	
	Length [Å]	Strength [v.u.]
Carbon dioxide	1.16213	2.00
Carbon monoxide	1.128	2.26[b]
Average C=O		
In aldehydes, ketones, esters, carboxylic acids	1.23	1.59
In conjugated systems	1.207	1.72
Average C—O		
In epoxides	1.47	0.77
In carboxylic acids	1.36	1.05
Methanol	1.427	0.87
Ethanol	1.48	0.75
Isopropanol	1.45	0.81
Formaldehyde	1.2063	1.72
Acetaldehyde	1.216	1.66
Acrolein	1.21	1.70
Dimethyl ketone	1.215	1.67
Formic acid		
C=O	1.202	1.74
C—O	1.343	1.11
Ethylene oxide	1.436	0.85
Dimethyl ether	1.427	0.87
Methylal	1.42	0.88
Furan	1.3621	1.05
	O—H bond	
Water	0.958	0.81
Methanol	0.956	0.81
Formic acid	0.972	0.78

[a] Taken from (*19, 20*).

[b] This value is calculated using R_1 and N for C^{IV}; as results from paper (*16*) R_1 and N vary usually insignificantly with the valence state.

explained further, water produced in dehydration reactions is regarded to be evolved due to the same mechanism.

As follows from the above discussion, loosely bonded surface oxygens fulfilling the $\Sigma s_i < s_{C-O}$ or $\Sigma s_i < 2s_{O-H}$ conditions can be abstracted from the catalyst surface and used in oxidation of hydrocarbons or in formation of water, respectively. Contrarywise, if positions of loosely or moderately bonded oxygen is vacant it may work as a trap for oxygen originally belonging to the organic molecule. For example, methoxyl group formed as result of dissociative adsorption of methanol (*7, 21*) may be adsorbed here. If Σs_i of the discussed position is higher than s_{C-O} in methoxyl, i.e., higher than 0.87 (cf. Table 1), *deoxygenation* step may take place yielding methyl group. This group may react further, e.g., with other methoxyl to form dimethyl ether. This means that dehydration is regarded as a process composed of dehydrogenation and deoxygenation steps, the destiny of the abstracted hydrogens being entirely analogous to those discussed above in the context of oxidative dehydrogenation and oxidation reactions.

Finally we have to discuss dehydrogenation, the elementary step with which all above mentioned reactions begin, and which frequently repeats in further consecutive transformations of organic species. In analogy to the previously discussed reaction steps, dehydrogenation should be expected if $s_{C_m-H} < s_{O_s-H}$ or $s_{O_m-H} < s_{O_s-H}$ for hydrocarbons and alcohols, respectively, where indexes m and s denote molecule and surface. The s_{C-H} is, however, unknown and the second inequality may not be used in practice due to ambiguity in locating hydrogen atom. We may thus discuss the process only from the viewpoint of surface oxygen. It seems that the higher undersaturation of surface oxygen $(2 - \Sigma s_i)$, the higher should be the probability of dehydrogenation (this concept was inspired by Anderson (*17*)). Thus ability of surface oxygen to dehydrogenate should be ruled by term $[1 - \exp(-f(2 - \Sigma s_i)/RT)]$. Bearing in mind that s_{C-H} or s_{O-H} are presumably close to 1, only surface oxygens of $\Sigma s_i < 1$ were able to dehydrogenate (case 1). Such oxygen positions are, however, expected to be rarely occupied. It is more likely that in fact dehydrogenating oxygens are of Σs_i greater than 1 (presumably 1.5–1.8, for which reasonable coverage is expected),

but the process requires special activation of organic species (e.g., π-complex of olefin with convenient charge redistribution and weakening of C–H bond (*22*)) (case 2) or a bond strength redistribution in the system metal–oxygen–hydrogen (case 3). The nature of these last mentioned process is difficult to discuss at present in terms of BSMAS but the author's feeling (consistent with the suggestions of many authors) is that such redistribution could be expected especially in the case of oxygen atoms linked to one metal atom (Mo=O → Mo —O—H). It seems interesting to note that in each of the three cases mentioned above abstraction of hydrogen is difficult due to frequency (case 1) or energetic (cases 2, 3) factors, and it may be expected as a rate determining step of the reaction, as has been frequently pointed out.

To complete the description of surface processes we may briefly outline two other effects for which quantitative data are not available at present, but which could be discussed in detail if the E–s relation suggested in Appendix 1 was proved.

After oxidation or oxidative dehydrogenation reactions the surface of catalyst must be reoxidized with gaseous O_2 molecules. One may imagine that this process could proceed on two adjacent, vacant, surface oxygen positions fulfilling the condition $\Sigma_1 s_i + \Sigma_2 s_i > s_{O-O}$, where indexes 1 and 2 distinguish these two positions. The quoted positions should be located at a distance comparable with the bond length in the O_2 molecule, i.e., 1.207 Å (*19*). In the case of trapezoid complex the positions might be, however, more distant. After dissociative adsorption, oxygen atoms could diffuse along the surface. An alternative mechanism, similar to that proposed for oxidation of ethylene (*23, 24*) could consist in adsorption of O_2 molecules on one surface anion vacancy in orientation perpendicular to the surface and in consumption of protruding oxygen atom in any hydrocarbon oxidation reaction or in formation of water. In this case the energetic condition would be $\Sigma s_i + s_{C-O} > s_{O-O}$ or $\Sigma s_i + 2s_{O-H} > s_{O-O}$, respectively.

As already mentioned, coordinatively unsaturated metal atoms are regarded as adsorption sites for both oxygen and organic species. Bond strength of adsorbed oxygen characterizes as well a free strength of bonding of the metal atom, which may be used to adsorb an organic species if the discussed position is vacant. The higher free strength of bonding, the stronger should be the bond between metal atom and the greater the activation of the latter.

EXPERIMENTAL DATA

Tatibouët and Germain have studied conversion of methanol (*7*) and ethanol (*8*) over MoO_3. Several samples of orthorhombic MoO_3 were prepared by sublimation and sieving. They differed in grain morphology and statistical study of microphotographs made possible to determine the percentage (P) of (010), (100), (001), and (101) crystallographic planes in the external surface of the grains. Catalytic testing was performed in a flow system at low conversion (less than 5%), so as to determine the initial selectivities (S) to various products. A quantitative analysis of the obtained results (S–P correlations) enabled the quoted authors to ascribe the reaction products to the kind of exposed crystallographic plane, as recalled in Table 2. The present paper aims, among other things, at indicating a possible structure of active sites yielding the respective products.

APPLICATION OF BSMAS TO THE CONVERSION OF METHANOL AND ETHANOL ON VARIOUS CRYSTALLOGRAPHIC PLANES OF MoO_3

Crystallographic data for MoO_3, which forms the orthorhombic structure with layers built of edge sharing and corner sharing octahedra, are taken from the paper by Kihlborg (*25*). Surface structures corresponding to four crystallographic planes under discussion (analyzed already in detail in (*10*)) are shown in Figs. 1–4. Table 3

TABLE 2

Products of Conversion of Methanol and Ethanol Yielded at Short Contact Time on Different Planes of MoO_3 (*7*, *8*)

	Reaction substrate		
	Methanol	Ethanol	
	291°C MetOH/O_2/He = 8.2/19.7/72	215°C EtOH/He = 3.6/96.4	291°C EtOH/O_2/He = 3.6/20/76.4
(010) Plane	Formaldehyde	Acetaldehyde	Acetaldehyde[a]
(001) + (101) Planes	Dimethyl ether	Acetaldehyde	
(100) Plane	Methylal	Diethyl ether	
Remarks		[b]	[b]

[a] Strictly speaking, no significant differences were observed among samples of different morphology.
[b] Minor selectivity to ethylene was also observed without significant plane effect.

summarizes the Σs_i values for all surface oxygen atoms of MoO_3, as originally calculated in (*10*).

Figure 1 shows the arrangement of atoms on the (010) plane of MoO_3. It consists of corner sharing distorted square pyramids built of three structurally different atoms: two O_P(1.90), two O_R(1.98), and one O_S(2.04). The respective s_i values given in parentheses indicate that all of them are strongly bonded, and thus in terms of BSMAS all indicated positions should be entirely occupied and inactive. There is, however, the doubtless experimental fact that (010) plane yields aldehydes in oxidative dehydrogenation of alcohols (*7*, *8*). So far it was assumed (*10*) that terminal O_S oxygens belonging to so called Mo=O groups act as dehydrogenation centers after forming the hydrogen bonded intermediary complexes shown in Fig. 1 (situations 1 and 2). As Σs_i for O_S is high this interpretation may seem to remain in contradiction with the formulation of BSMAS given in one of the former paragraphs of this paper. This contradiction becomes apparent when taking into account the changes of the bond strength with temperature. As explained in Appendix 2 the bond strength of O_S is expected to be reduced to about 1.8 in the temperature range in which catalytic testing is performed. In such a way these oxygens become active in dehydrogenation.

If methanol is adsorbed with two hydrogen bonds to the surface, as shown in Fig. 1 (situation 1) it may be thus dehydrogenated to formaldehyde. Abstracted hydrogen at-

TABLE 3

Σs_i Values for Surface Oxygens on Various Planes of MoO_3 Calculated with Formula (*1*), $R_1 = 1.882$, $N = 6.0$ (16)

Oxygen	Σs_1	Oxygen	Σs_i
(100) Plane		(001) Plane	
O_A	1.90	O_K	1.98
O_B	2.04[a]	O_L	2.04[a]
O_C	2.04[a]	O_M	1.09
O_D	0.34	O_N	0.81
O_E	1.63		
O_F	0.34		
O_G	1.63		
(010) Plane		(101) Plane	
O_P	1.90	O_X	1.09
O_R	1.98	O_Y	1.63
O_S	2.04[a]	O_Z	2.04[a]
		O_W	0.8

[a] As explained in the text Σs_i of these atoms decreases with temperature and in the range of catalytic testing it is expected to be ~1.8.

oms are thought to move along the surface and combine with a loosely bonded surface oxygen to form water (Fig. 1, situation 4). Bond strength of O_S seems to be rather too high for its participation in formation of water. Thus hydrogens have rather to diffuse along the surface or through the bulk (*8*) to other planes where—as it will be shown further—loosely bonded oxygens are available.

As some O_S positions may be vacant, molecule of methanol initially adsorbed with one hydrogen bond on other O_S (Fig. 1, situation 2) and dehydrogenated to methoxyl may be there adsorbed (Fig. 1, situation 3) and deoxygenated to methyl. Methyl could react with other methoxyl to yield dimethyl ether with the mechanism analogous to that which will be discussed further for (001) and (101) planes. As, however, the population of vacant O_S positions is expected to be small (relatively high Σs_i) this reaction pathway seems to be of minor importance. The (010) plane should thus selectively yield formaldehyde.

Figure 2 shows a representative portion of (100) plane, the structure of which is a bit more complex. It is composed of parallel zigzag rows of edge sharing distorted squares formed of three O_A(1.90) and one

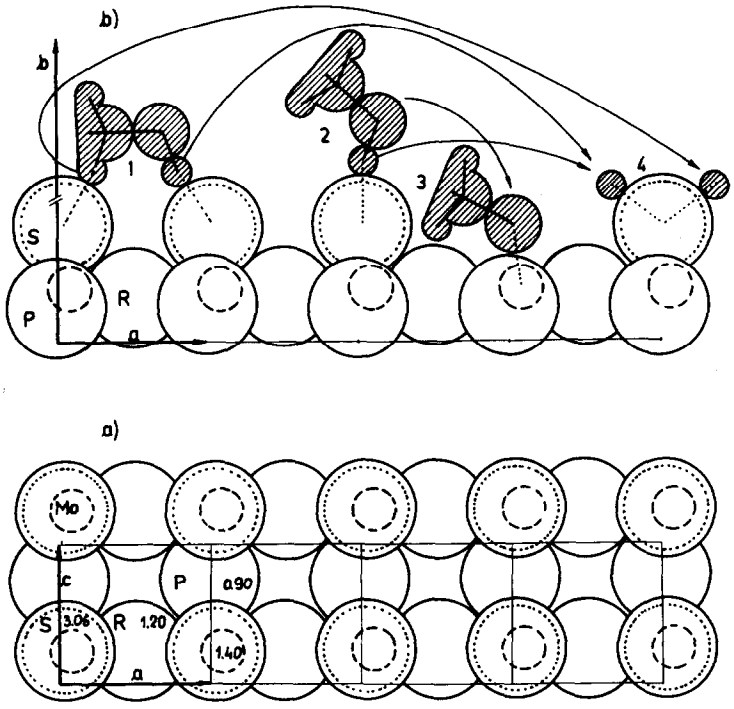


FIG. 1. Structure of (010) plane of MoO_3 (a) and its side view (b) with adsorbed methanol (1,2), methoxyl localized on O_S vacancy (3), and abstracted hydrogens combining with surface oxygen atom to form water (4). As for the last mentioned process see text. Figures 1–6 are drawn according to the following rules. Proportions resulting from ionic radii (solids), covalent radii (adsorbed molecules), crystallographic data, and bond lengths in organic molecules are respected. The numbers indicate the distance of atoms from the planes in Angstroms. Oxygen of methoxyl adsorbed on anion vacancy is localized at the same coordinates which would have the vacant anion. Inclination of C—O bond of methoxyl with respect to the surface is neglected. Capital letters distinguish the structurally nonequivalent oxygen atoms. Inactive oxygens are drawn with single line, active oxygens with double line, adsorbed oxygens with double dotted line. Oxygens of Mo=O groups are distinguished with inner pointed circle.

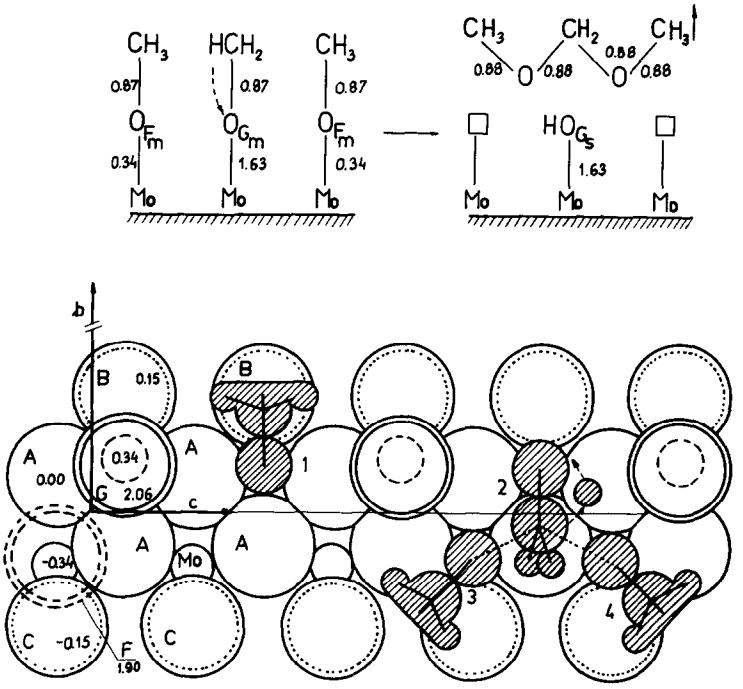


FIG. 2. (100) Plane of MoO_3 with methoxyl adsorbed on O_G vacancy (1) and three methoxyls (2,3,4) forming an active complex for methylal. Energetic scheme of methylal formation is given in the upper part of the figure (bond strengths in valence units).

$O_B(2.04 \rightarrow \sim 1.8)$ or one $O_C(2.04 \rightarrow \sim 1.8)$, with Mo atoms inside. $(O_A)_3O_B$ squares are completed with $O_G(1.63)$ to form square pyramides while over $(O_A)_3O_C$ squares $O_F(0.34)$ position exists which may be filled with adsorbed oxygen. Such zigzag rows are repeated each period along *b* axis. In between there are other zigzag rows in which $O_D(0.34)$ and $O_E(1.63)$ appear instead of O_F and O_G. The structure and energetics of that second type rows is entirely analogous to the above mentioned first type.

Molecule of methanol adsorbed first with hydrogen bond on O_B, O_C, O_G, or O_E may be dehydrogenated there. The abstracted hydrogen may form water with O_D and O_F (presumedly also with O_G and O_E). Methoxyl formed in dehydrogenation step may be adsorbed on vacant O_G or O_F positions, the former of these being able to act as deoxygenation center. The neighborhood of three methoxyls adsorbed in configuration shown in Fig. 2 seems especially interesting. As results from the energetic scheme included also in Fig. 2 the above mentioned configuration can play a role of active complex decomposing to methylal. In this processs the second hydrogen must be obviously abstracted from the central carbon atom. This could happen in advance with the help of, e.g., O_B. But the most plausible interpretation is the following: when oxygen atom belonging to the central methoxyl is abstracted it becomes lattice O_G atom and consequently it may act as dehydrogenation site. At the same time two C–H bonds have to change their orientation and carbon atom of central methoxyl has to interact with oxygen atoms of two adjacent methoxyls. It seems important to note that (100) plane is unique among the discussed morphological planes of MoO_3 on which three methoxyls may be adsorbed in configuration convenient to form directly methylal. The structure of (100) plane does not exclude the formation of some formaldehyde

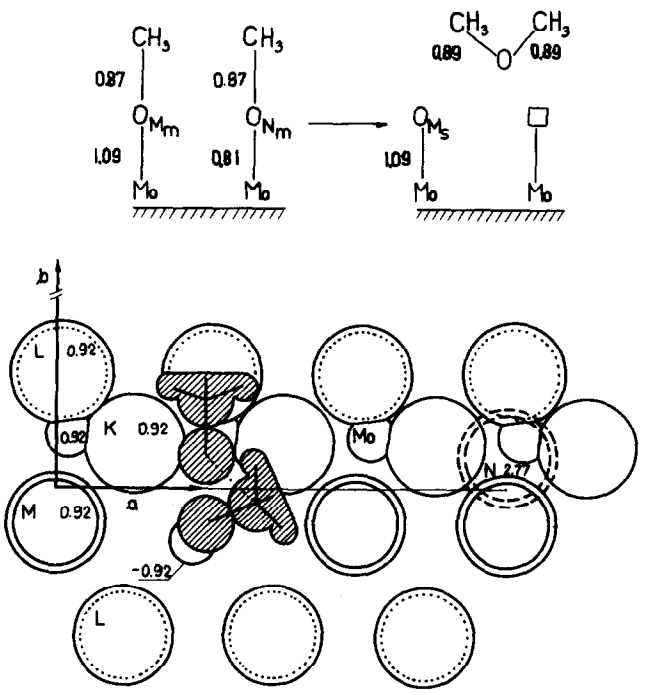


FIG. 3. (001) Plane of MoO_3 with two adsorbed methoxyls forming an active complex for dimethyl ether. Energetic scheme of formation of dimethyl ether is given in the upper part of the figure (bond strengths in valence units).

(active complex could be, e.g., O_B—H—CH_2—O—H—O_B) or some dimethylether (if only two methoxyls interact). Privileged formation of methylal on this plane is due probably to the very strong adsorption of methoxyl on O_G vacancy, and thus to relatively long lifetime of methoxyl adsorbed on this position. This question will be discussed again at the end of this paragraph.

Figure 3 shows a representative portion of (001) plane. It is composed of the parallel rows of corner sharing distorted squares built of two $O_K(1.98)$, one $O_L(2.04 \rightarrow \sim 1.8)$, and one $O_M(1.09)$ with Mo atoms inside, over which $O_N(0.81)$ may be adsorbed. As O_M are moderately bonded, large part of these positions is expected to be vacant. Consequently the second type of Mo atoms is uncovered and may serve as additional adsorption site for organic molecules. O_L, O_M, and O_N may act as dehydrogenation centers and the latter two may also participate in formation of water. Figure 3 shows the configuration of two methoxyls making the possible active complex yielding dimethyl ether. The respective energetic scheme included in Fig. 3 may be interpreted in a way analogous to that for (100) plane (Fig. 2) (deoxygenation on vacant O_M).

Figure 4 shows the arrangement of atoms on (101) plane. Along this plane two oxygens are lacking in each MoO_6 group the coordination of molybdenum becoming tetrahedral. Each Mo atom is linked with $O_X(1.09)$ and $O_Z(2.04 \rightarrow \sim 1.8)$ in the plane and with two other oxygens in the bulk. These tetrahedra form the zigzag rows. Between them $O_Y(1.63)$ atoms appear, being the apexes of MoO_6 groups localized below the surface. The fourth surface oxygen $O_W(0.8)$ may be adsorbed over Mo position. The above mentioned bulk oxygen atoms completing the surface MoO_4 tetrahedra are also drawn in Fig. 4 and are labeled as X_b, Y_b, and Z_b. This means that they are crys-

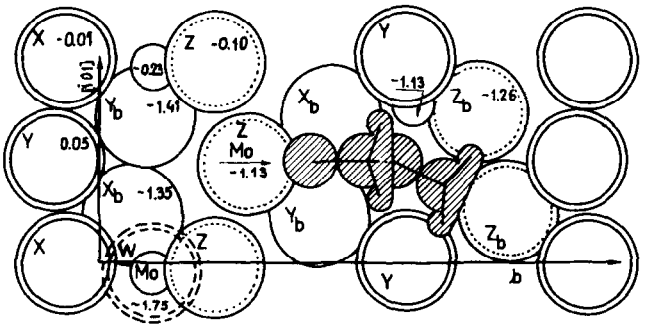


FIG. 4. (101) Plane of MoO_3 with two adsorbed methoxyls forming an active complex for dimethyl ether. Energetic scheme is the same as for (001) plane (cf. Fig. 3).

tallographically identical with the surface O_X, O_Y, and O_Z atoms, respectively, but their coordination is obviously complete and $\Sigma s_i \approx 2$. On the (101) surface O_X, O_Y, O_W, O_Z, and O_{z_b} may serve as dehydrogenation centers. O_X, O_W, and probably O_Y may participate in formation of water. The possible structure of active complex which may yield dimethyl ether is shown in Fig. 4. Its structure and energetics is exactly the same as that for (001) plane (Fig. 3). The structures of (001) and (101) planes do not exclude the formation of some formaldehyde. Active complex could be, e.g., O_L—H—CH_2—O—H—O_L and O_Z—H—CH_2—O—H—O_Z, respectively.

The above interpretation remains in complete agreement with the experimental facts given in (*7*). Localization of sites active in dehydrogenation and dehydration agrees also with the general idea suggested by Tatibouët and Germain (*7*). However, the sites are now indicated more precisely, especially those for specific formation of dimethyl ether and methylal, and energetic argumentation is given.

Conversion of ethanol on various planes of MoO_3 could be expected to follow exactly the same mechanism and thus acetaldehyde, acetal, and diethyl ether might be expected to be formed selectively on (010), (100), and (001) + (101) planes, respectively. This pattern does not agree, however, with the experimental data (Table 2). The discrepancy seems to result from two reasons.

First, experiments with ethanol were done either in the absence of oxygen or with the use of the reaction mixture which was much more oxidative as compared to methanol/oxygen mixture (cf. Table 2). Thus according to the opinion of Tatibouët and Germain (*8*) one may imagine that in the latter conditions positions of moderately bonded oxygens (working—if vacant—as deoxygenation centers) were highly covered. This resulted in hindrance of the reactions involving deoxygenation step, acetaldehyde and only small amounts of ethylene remaining as the reaction products. Similar effect was observed in conversion of methanol (*26*) where the rate of formation of dimethyl ether decreased with increasing partial pressure of oxygen in the reaction mixture. In view of the above mentioned facts and interpretations, experiments with ethanol performed at low oxygen content in the reaction mixture or even in its absence[4] reflect better the specificity of various faces of MoO_3. Further discussion will concern the experiments performed in the latter mentioned conditions.

Second, there are two important differences between molecules of methanol and ethanol: (1) s_{C-O} is about 15% smaller for ethanol than for methanol (Table 1), the de-

[4] It has been found (*8*) that dehydrogenation may proceed on MoO_3 in absence of oxygen. In this case hydrogen removed from ethanol is stored in a solid which is slowly converted to hydrogen–molybdena bronze.

oxygenation should be thus much more rapid; (2) one ethoxyl after deoxygenation may yield ethylene while in analogous reaction at least two methoxyls are required to form a stable chemical molecule. Consequently, ethoxyl, once adsorbed on $(100)O_G$, $(001)O_M$, $(101)O_X$, or $(010)O_S$ vacancy, does not necessarily wait for adsorption of other species beside, but it may decompose to ethylene, which is in fact observed experimentally, without significant plane dependence. Experimental facts (*8*) (Table 2) demonstrate that the lifetime of the adsorbed ethoxyl is sufficiently long for its interaction with another ethoxyl to happen and diethyl ether to be formed. On the other hand the probability of three ethoxyls meeting to form acetal is apparently insignificant. This is not the case with methanol, where oxygen is more firmly bonded. The lifetime of adsorbed methoxyl is longer and reaction probability is shifted in favor of methylal.

Finally, it seems important to remember that diethyl ether may be formed both on (001) + (101) and on (100) planes, but the sites on (100) plane are energetically more favorable (cf. the energetic schemes in Figs. 2 and 3). There is thus nothing strange in the fact that formation of diethyl ether has been ascribed mainly to (100) plane.

Some interesting conclusions may also be drawn from the specific reaction rates determined in (*7, 8*). As it has been found acetaldehyde is formed 44 times faster on (001) + (101) planes than on (010) plane. This is to be expected on the reasonable assumption that dehydrogenation or evolution of water is the rate determining step of this reaction at least on (010) plane where O_S atoms are relatively firmly bonded (cf. the respective discussion for methanol). Contrarywise, more loosely bonded oxygens on (001) and (100) planes (O_M, O_N, O_X, O_Y) are much more active in both steps mentioned above.

It has been found that diethyl ether is formed on (100) plane with the rate 25 times higher than acetaldehyde on (010) plane, while the rate ratio for formaldehyde (010), methylal (100), and dimethyl ether (001) + (101) is only 1 : 1 : 2.5. Bearing in mind that both alcohols should be dehydrogenated on OH group with comparable rate, these facts allow to conclude that apparently deoxygenation is the rate determining step in formation of methylal and dimethyl ether, while diethyl ether formation is rather rate determined by dehydrogenation or water evolution. This conclusion remains in complete agreement with the above discussion concerning the difference in s_{C-O} in methanol and ethanol.

COMMENTS CONCERNING OXIDATION REACTIONS

As already mentioned some oxidation reactions have been discussed in terms of BSMAS in (*4, 10, 18*). In this paragraph selected examples will be considered to show briefly how the former discussion may be ameliorated with the use of the new formulation of BSMAS.

Oxidation reactions are composed of adsorption, desorption, and four sensu stricto chemical elementary steps: dehydrogenation, evolution of water, oxidation, and reoxidation of catalyst surface. On the basis of literature data it has been assumed in (*4, 10, 18*) that propylene and *o*-xylene are adsorbed on coordinatively unsaturated metal atoms as π-complexes and the exact localization of adsorption sites on various planes of MoO_3 and MV-X has been discussed in the quoted papers. The structure of some representative sites are recalled in Figs. 5 and 6. Taking into account Σs_i values given in Table 3 and in Fig. 6 it is self-evident that in the vicinity of these sites there are moderately or weakly bonded oxygens which—in terms of BSMAS—fulfill the energetic condition for both: dehydrogenation and evolution of water. The selective formation of various oxygen-containing reaction products at short contact time depends on the number and configuration of active oxygens in the nearest vicinity of the adsorption site. According to the

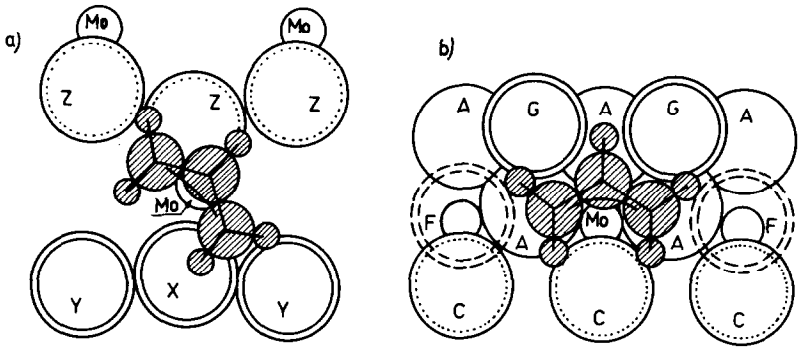


FIG. 5. π-Allyl adsorbed on (101) plane of MoO_3 (a) and on (100) plane of MoO_3 (b). Actions of these centers are described in the text.

present formulation of BSMAS these oxygens should fulfill the condition which may be generally formulated as $\Sigma s_i^{\text{substrate}} < \Sigma s_i^{\text{product}}$.

As results from Table 1 indicate, the formation of acrolein requires active oxygens of $\Sigma s_i < 1.70$. Acrolein-like intermediary species may be transformed to acrylic acid with participation of other oxygen (or OH group) bonded to the catalyst with a strength inferior to about 1.05–1.1. Figure 5a shows—as an example—π-allylic species adsorbed on (101) plane of MoO_3. It is evident that π-allyl may interact with $O_Y(1.63)$ or with $O_X(1.09)$ to form acrolein. Incorporation of two oxygens in the order O_Y, O_X to the same terminal carbon of allyl may not be excluded, but the probability of such a transformation seems to be much smaller. The center should thus yield selectively acrolein, which remains in agreement with experimental data (10).

Figure 6 shows one of the active centers on $(20\bar{2})$ plane of MV-X on which one site rake reaction is thought to proceed transforming *o*-xylene to C_8 products: tolualdehyde (TA), phthalide (PH), and phthalic anhydride (PA) (*4*). For this purpose one, two, or three active oxygens are required, respectively. Making use of the available data given in Table 1 one may estimate the strength of C=O bond in the above mentioned compounds to be 1.7–1.75 and the sum of the strengths of two C—O—C bonds to be 1.8–1.9. As seen in Fig. 6 conveniently arranged around methyl groups of *o*-xylene two $O_L(1.68)$ and one $O_M(1.58)$ atoms fulfill the geometric and energetic conditions for the formation of phthalic anhydride. Obviously, certain probability exists for desorption of less oxidized products (PH, TA). As calculated in (*4, 18*), on doping with MoO_3, i.e., on passing from MnV_2O_6 to MV-X solid solutions Σs_i values of some O_M and O_L statistically increase up to 1.81, i.e., some of them become even inactive in C=O bond formation. This is responsible for decrease of the yield of C_8 products as well as for decrease of PA/TA

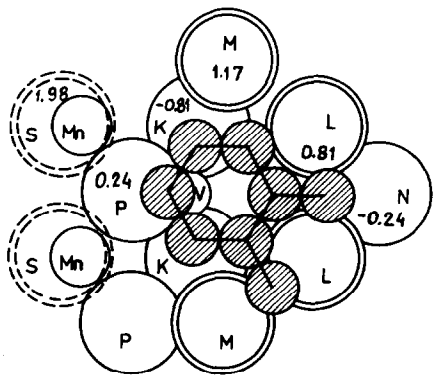


FIG. 6. *o*-Xylene adsorbed on one of active centers of $(20\bar{2})$ plane of MV-X. Bond strength sums for active oxygens are $O_M(1.58)$, $O_L(1.68)$, $O_S(0.39)$. On doping with MoO_3 s_i values of some O_M and O_L increase statistically up to 1.81. Action of the center is described in the text.

yield ratio, which is in fact observed experimentally (*4*).

Figure 5b shows the active center on the (100) plane of MoO_3 which is thought to be responsible for degradation and total combustion of propylene (*10*). This is due to the fact that at least two active oxygens $O_G(1.63)$ may attack both C–C bonds of π-allyl and sometimes its terminal carbons may react in addition with one or two adsorbed $O_F(0.34)$ atoms. According to Table 1 $s_{C-O} \geq 2$ for CO_2 and CO. This could suggest that even firmly bonded surface oxygens might take part in total combustion. Such process would require, however, complete dehydrogenation of carbon atom in advance, the process of extremely high activation energy and little frequency factor. It seems more likely that one-site direct combustion is composed of a series of transformations in which propylene (and similarly other organic molecules) is transformed at first, e.g., to formaldehyde and acetaldehyde; then aldehydes are decomposed successively to CO molecules. Only in the last step of this one-site rake reaction ($CO \rightarrow CO_2$) firmly bonded surface oxygen might take part. Obviously, generally the rake reaction leading to the total combustion does not necessarily develop on one site.

Possible mechanisms of catalyst reoxidation have already been discussed in one of the former paragraphs of the paper.

FINAL REMARKS

This paper gives a new formulation of the bond-strength model of active sites on oxide catalysts. The pathway of catalytic reaction is thought to depend on geometric and energetic correspondence between adsorbed reactants and the neighborhood of adsorption site. Structural considerations concerning various planes of catalysts are based on crystallographic data and on available dimensions of organic molecules. Adsorption of reactants is assumed to take place on coordinatively unsaturated surface metal and oxygen atoms. Bond strength is taken as a measure of binding energy. Elementary steps of catalytic reactions consisting in the exchange of hydrogen or oxygen atom between reactants and catalyst surface are thought to proceed on the condition that

$$\sum s_i^{\text{substrate}} \lesssim \sum s_i^{\text{product}}$$

On this basis the sites are indicated on which dehydrogenation (dhg), oxidation (oxygenation) (ox), deoxygenation (dox), evolution of water (we), and catalyst reoxidation (crox) may take place. Each reaction is commenced with substrate adsorption (sads) and its activation (act) and terminated with desorption of product (desp). Some of the reaction steps mentioned above are sometimes to be discussed together, e.g. (sads + act). The difference between the overall reaction result, e.g., oxidation (oxygenation) (OX), oxidative dehydrogenation (ODHG), or dehydration (DHD) and the nature of elementary steps of which the reaction is composed is clearly indicated in BSMAS and may be summarized as follows:

$$\text{ODHG} = \text{sads} + \text{act} + \text{dhg} + \text{desp} + \text{we} + \text{crox}$$

$$\text{OX} = \text{sads} + \text{act} + \text{dhg} + \text{ox} + \text{desp} + \text{we} + \text{crox}$$

$$\text{DHD} = \text{sads} + \text{act} + \text{dhg} + \text{dox} + \text{desp} + \text{we}$$

It seems especially interesting that the reaction steps regarded until now in red–ox or acid–base terms may be discussed at present in a uniform way.

It seems also noteworthy that deoxygenation step which plays an important role in BSMAS, resembles the essential step of sulfur removal postulated for hydrodesulfurization reactions (*27*).

In contrast to the most of the present theories, neither electron transfer, electrophilicity, and nucleophilicity of surface species are treated in BSMAS nor problems directly concerned with activation energy.

Catalytic reaction is considered as a process following down some energetic stairs. Strictly speaking, these are stairs along the free enthalpy axis, as explained in footnote 2, and reaction allowance condition (*3*) has an approximate character. The clearly distinguishable steps of the above mentioned stairs are discussed without considering the processes which certainly proceed in the meantime. It seems that this exclusion may be easily filled up provided that sufficiently convincing and general measures for the encountered quantities will be discovered.

In spite of simplifying assumptions the model makes it possible to draw some clear conclusions, especially concerning the selectivity of catalytic reactions. In some points BSMAS should still be improved. The mechanism of activation of the adsorbed reaction substrate and description of dehydrogenation step shall require a more profound discussion. Desorption step is discussed so far only from the viewpoint of the formation of energetically more stable reaction products, while in reality it is also favored at least by an entropy increase. Finally, the bond strength should be translated to the energy units as suggested in Appendix 1.

APPENDIX 1

It is difficult to determine the shape of $E = f(s)$ function as the energies of the individual bonds in crystals are not available. Fortunately, one can make use of $R_1 = 1.378$ and $N = 4.065$ for the C–O bond (*16*) and of known lengths and energies of C–O bonds in CO_2 and in some organic molecules (*19*). Such data drawn in E–s coordinates (Fig. 7) suggest the linear relation $E = Js$, with J_{C-O} equal to 102 kcal mol^{-1} vu^{-1} (vu = valence unit). Equation $E = Js$ could be supposed to have general significance.

APPENDIX 2

MoO_3 is known to show high anisotropy of thermal expansion, the coefficients along *a*, *b*, and *c* axes being, respectively, $(0.9\pm0.1) \times 10^{-5}$, $(18\pm2) \times 10^{-5}$, and 0 per

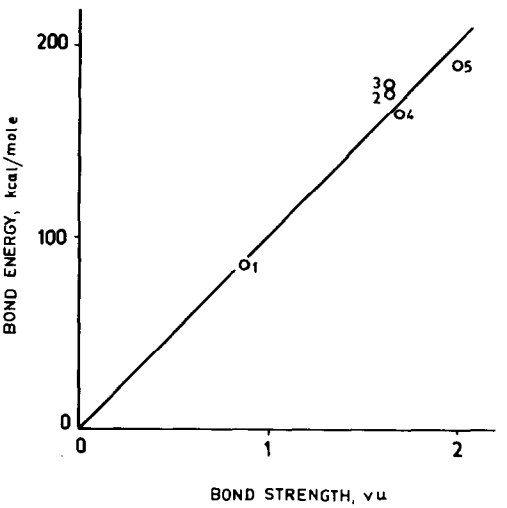


FIG. 7. Bond energy vs bond strength for C—O bonds. (1) Average C—O bond, (2) average C=O bond (aldehydes), (3) average C=O bond (ketones), (4) HCHO, (5) CO_2, $E = 102\ S$.

degree at 25 to 500°C (*28*). This means that on heating MoO_3 from room temperature up to, e.g., 200 or 400°C the interatomic distances along *a* and *c* axes (and consequently the bond strength values) remain practically unchanged, while those along *b* axis increase in average by 3.15 and 6.75%, respectively. If Mo=O bonds, situated along *b* axis, were elongated in the same proportion their lengths would increase from 1.671 Å (25°C) to 1.723 Å (200°C) or 1.784 Å (400°C) and their strengths would decrease from 2.04 (25°C) to 1.70 (200°C) or to 1.38 (400°C). The temperature effect evaluated in such a way is certainly exaggerated as the most part of temperature expansion along *b* axis should rather be ascribed to the increase of the distance between the layers in the MoO_3 structure which are situated perpendicularly to the *b* axis and bound together with weak van der Waals interactions.

To determine the effect of temperature on the Mo–O bonds within the layers of the MoO_3 structure the Raman spectra were recorded as function of temperature (Varian, Cary 82 instrument, laser beam of 5145 Å, self-made heating stage). Three bands were

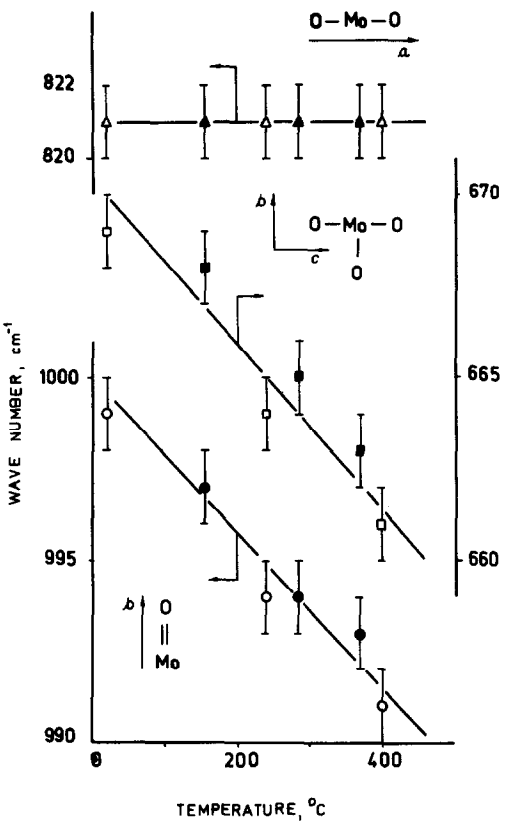
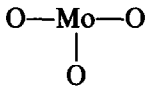


FIG. 8. Temperature dependence of the three Raman bands of MoO_3 corresponding to the three types of vibrations; open points—heating, black points—cooling.

considered (*29*): (1) band at 999 cm^{-1} derived from the stretching of Mo=O bond situated along *b* axis; (2) band at 821 cm^{-1} assigned to the simultaneous stretching and compressing of two O—Mo—O bonds situated along *a* axis; (3) band at 669 cm^{-1} ascribed to the simultaneous stretching and compressing of the three bonds:



situated in the *bc* plane. The obtained results are shown in Fig. 8. In agreement with the values of the coefficients of thermal expansion the bonds located in *b* direction are weakened with increasing temperature while those along *a* axis remain practically unchanged. This proves that the strength of Mo=O_S bond decreases with temperature. Combining the results obtained with both methods one may estimate the bond strength of O_S to be about 1.8 in the temperature range in which catalytic testing was performed (200–400°C). Taking into account the detailed data concerning calculations of Σs_i for other surface oxygens (*10*) one may expect that Σs_i values for O_A, O_M, and O_X should also decrease with increasing temperature as they involve a bond situated in *b* direction. The expected effect is, however, nearly negligible (~0.05) as the above mentioned bond is the longest one and it has a minor contribution in Σs_i. The Σs_i values of all other surface oxygens are practically independent of temperature.

ACKNOWLEDGMENT

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Note added in proof. The relation $E = Js$ mentioned in Appendix 1 has recently been confirmed for inorganic crystals. Two papers on this subject are in preparation. Due to the reviewing procedure all papers of the author that were cited (*3, 4, 10, 18*) were published in 1983. To follow the development of the author's ideas readers are kindly requested to compare the "Received" dates.

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