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REACTIVITY OF OXYGEN IN CATALYSTS FOR SELECTIVE OXIDATION

REACTIVIDADE DO OXIGÉNIO EM CATALISADORES DE OXIDAÇÃO SELECTIVA

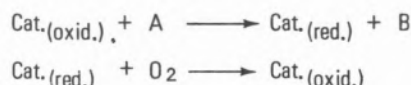
1. THE ROLE OF THE REACTIVITY OF OXYGEN IN OXIDATION CATALYSTS AND PRESENT STATE OF THE METHODS FOR ITS DETERMINATION

The oxidation-reduction catalytic reactions are of significant theoretical interest. At the same time they are of primary importance for modern chemical industry.

In the past two decades great attention has been devoted to the reactions of selective oxidation. Numerous investigations directed to the selective oxidation of olefines, primary alcohols, etc. have been carried out (1,2).

It has been shown by many authors, that a large group of this class of reactions proceed according to a redox mechanism. The kinetic equations derived by assuming an oxidation-reduction mechanism describe the experimental data quite satisfactorily (3, 4). Puls-chromatographic and direct kinetic methods have been applied for measuring not only the rate of the catalytic reaction, but also the rate of reduction and reoxidation of the catalyst surface by the reagents (39). A comparison of these rates for a series of reactions confirmed a predominating reduction-oxidation mechanism.

This mechanism involves, as intermediate stages, desorption of oxygen from the surface of the catalyst, facilitated by the formation of an intermediate complex with the molecule to be oxidized and consequent reoxidation of the active sites, i.e.:



In view of this it seems reasonable to assume, that the activity and selectivity of the oxidation catalysts will be influenced by the reactivity of oxygen in their surface layer. On the other hand reactivity should depend on the bonding energy of oxygen and the type of this bond. Such a conception was formulated in our works at the beginning of the 60-thies as well as in the works of some other authors (5-9). It found later an wide confirmation.

For determination of the bonding energy of oxygen in the surface layer of oxide catalysts different methods have been suggested. Some of them are summarized in table 1.

Table 1

Principle of the method
1. Thermochemical calculations $\Delta H_f^\circ / n$; $\Delta H_f^\circ (\text{Me}_n \text{O}_m - 1/2 \text{O}_2)$
2. Kinetics or initial temperature of reduction of the catalysts
3. Thermodesorption of oxygen
4. Determination of the dissociation pressure of surface oxygen
5. Calorimetric measurements of the heats of oxygen adsorption
6. Oxygen isotopic exchange
7. Quantum-chemical calculations

The method based on thermochemical calculations and used up to now by some authors should be rejected. Here the main objection is that the catalytic reactions are not accompanied by phase

transitions. In addition to this different bonding energies should correspond to oxygen atoms in multivalent oxides (8). The method suggested by Boreskov et al. possesses definite advantages (9). It is direct and based on determination of the temperature dependence of the surface oxygen dissociation pressure.

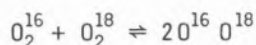
The distribution of surface oxygen with respect to its bonding energy can be determined by consecutive elimination of parts of a monolayer.

Valuable information concerning the reactivity of surface oxygen can be obtained by application of the oxygen isotopic exchange method. I would also like to mention in advance, that useful information can be obtained by some relatively simple methods. In support of this view, data on the bonding energy of surface oxygen in metal oxides and data on the initial temperature of their reduction with hydrogen are compared in fig. 2. As can be seen, a satisfactory correlation exists between these two parameters.

The application of the oxygen isotopic exchange permits not only the bonding energy of oxygen in the surface layer of oxide catalysts to be estimated, but also the degree and the character of the surface heterogeneity and the rate of oxygen self-diffusion to be studied.

It is reasonable to apply :

a) Homomolecular exchange :



b) Heteroexchange :



where $O_{(surf.)}$ are oxygen atoms on the surface of the catalysts. I shall discuss our results obtained mainly by the method of heteroexchange.

Our studies as well as the works of Winter (10), Boreskov & Muzykantov (11), Jiru & Novakova (12) show that, with respect to the kinetics of exchange, oxide catalysts can be subdivided into 2 groups :

- The reactivity of surface oxygen differed significantly from that of the lattice oxygen for a large number of oxides. In most cases the surface oxygen was more readily exchanged. Moreover within the limits of one monolayer a sharp decrease in the rate of exchange was observed (fig. 3), which indicates that the surface oxygen is energetically non-uniform (13).
- On the other hand, the oxides Fe_2O_3 , Bi_2O_3 , V_2O_5 , MoO_3 , Nb_2O_5 , WO_3 exchanged their surface oxygen and part or all of their lattice oxygen with a practically constant rate (fig. 4). This kinetic behaviour could be regarded as an indication of a high rate of the oxygen self-diffusion in the most of these solid catalysts.

It is noteworthy that a measurable difference between the reactivity of the surface and bulk oxygen is mainly observed for oxides of multivalent metals. Typical of this class of compounds is that they can contain cations whose valency is higher than the

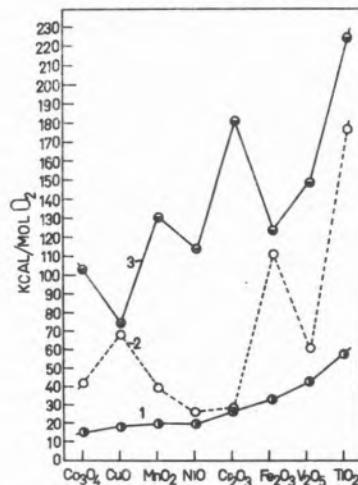


Fig. 1

Comparison of data on the bonding energy of oxygen in metal oxides (kcal/g.-mol O₂), determined by different methods :

curve 1 — based on data determined from the temperature dependence of the oxygen dissociation pressure.

curve 2 — based on data calculated from the enthalpy change during the transition from a higher to a lower oxide (data for the transitions : $Co_2O_3 \rightarrow Co_3O_4$; $CuO \rightarrow Cu_2O$; $MnO_2 \rightarrow Mn_2O_3$; $Ni_2O_3 \rightarrow NiO$; $CrO_2 \rightarrow Cr_2O_3$; $Fe_2O_3 \rightarrow Fe_3O_4$; $V_2O_5 \rightarrow V_2O_4$; $TiO_2 \rightarrow Ti_2O_3$).

curve 3 — based on data calculated from the standard heats of formation of the oxides.

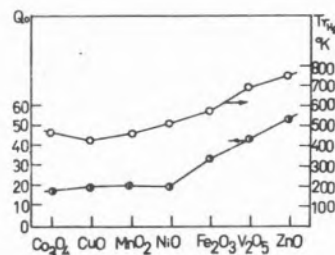


Fig. 2

A comparison between the bonding energy of oxygen in the surface layer of metal oxides and the initial temperatures of their reduction with hydrogen (T_r)

predominating one, and measurable amounts of non-stoichiometric oxygen. Boreskov & Popovskii assumed the existence of parallelism between the rate of the oxygen isotopic exchange and the content of non-stoichiometric oxygen in oxide catalysts. It was of interest to check this idea. Some of our results treating this problem will be discussed.

2. DEVIATIONS IN THE STOICHIOMETRY OF OXIDE CATALYSTS AND THE REACTIVITY OF THEIR OXYGEN

The idea about the existence of a parallelism between the rate of the

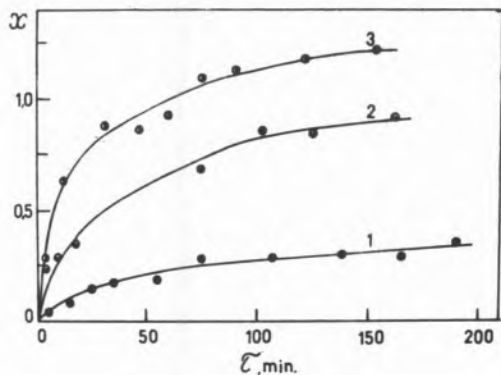


Fig. 3

Exchanged fraction of the surface oxygen of NiO, X , as a function of the time of exchange at different temperatures ($P_{O_2} = 10$ Torr).

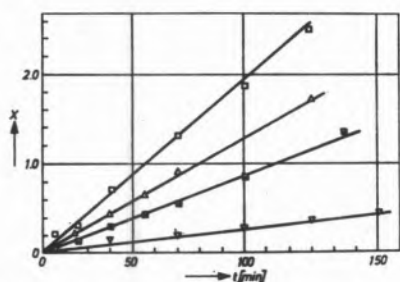


Fig. 4

The dependence of the fraction of surface oxygen attaining the isotopic composition of the gas phase, X , on time of exchange ($P_{O_2} = 10$ Torr, ∇ - 637°C, \square - 673°C, \square - 685°C, Δ - 697°C, $2X$ values plotted for 637° and 673°C).

oxygen isotopic exchange and the content of non-stoichiometric oxygen in metal oxides was suggested in 1960 (15). Unfortunately, the verification of this assumption was connected, for a long period, with experimental complications. The proposed experimental methods for determination of non-stoichiometric oxygen in oxide catalysts are indicated and the obtained results have in general a low reproducibility. The main method for such determinations is the iodometric one (16). It consists in determination of the content of metal cations with a higher valency than the basic one in metal oxides. It is assumed that their additional charge is compensated by the ions of the non-stoichiometric oxygen. The calculations are, however, complicated by the fact that the non-stoichiometric oxygen can exist not only in the form of O^{2-} but also in the form of O^- . As was shown by Bielanski (16), the ratio between these forms vary in a wide range, being a function of the conditions. In view of this, an attempt was made in our laboratory to develop a new direct thermodesorption method for determination of non-stoichiometric oxygen in oxide catalysts. The method is based on the difference between the bonding energies of stoichiometric and non-stoichiometric oxygen. The different bonding energies determine different dissociation pressures of both types of oxygen. The non-stoichiometric oxygen is usually held in an adsorbed form or in the form of impurities of higher oxides or peroxides. In principle its bond is weaker and it possesses a higher reactivity. The

method proposed by us consists in realization of quantitative desorption of oxygen in excess of the stoichiometric amount and determination of this oxygen by a volumetric or other methods (17). Thermodesorption should be performed under the following conditions:

$$P_{O_2(n.s.o.)} > P_{O_2(g.ph.)} > P_{O_2(s.o.)}$$

where $P_{O_2(n.s.o.)}$ and $P_{O_2(s.o.)}$ are the pressures of the non-stoichiometric and stoichiometric oxygen respectively, and $P_{O_2(g.ph.)}$ the pressure of oxygen in the gaseous phase.

Systematic investigations of the content of non-stoichiometric oxygen in a series of transition metal oxides have been carried out. I shall discuss the stoichiometric deviations in NiO and Cr_2O_3 catalysts of different dispersity. Fig. 5 shows data on the content of non-stoichiometric oxygen in specimens of NiO with different specific surface areas calcined at different temperatures in the range 300-700°C. As can be seen, the content of non-stoichiometric

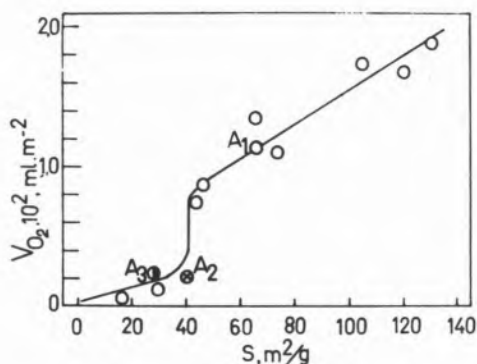


Fig. 5

Desorbed amount of oxygen versus the specific surface area of NiO specimens

oxygen decreases with the decrease of the specific surface area. This conclusion has also been confirmed in the study of nickel oxide samples obtained by calcination of nickel hydroxide at 450°C and different time intervals (fig. 6).

It is important to note that in specific surface areas ranging from 45 to 130 m^2/g , the content of non-stoichiometric oxygen per unit surface area is several times higher than the one established for specimens with smaller specific surface areas. Since the sintering process can lead to structural changes and accompanying changes in the magnetic state of nickel oxide, the magnetic susceptibility of specimens of the transition region was measured. It was found (fig. 7) that the sharp decrease in the content of non-stoichiometric oxygen corresponds to the transition from a paramagnetic to an antiferromagnetic state. A similar effect was described previously by Bliznakov (18). These results show that the non-stoichiometric oxygen in nickel oxide is held in an adsorbed form mainly and that its content changes sharply during phase transitions.

As was noted previously, the non-stoichiometric oxygen can also be held in the form of higher oxides. Our data on Cr_2O_3 calcined for 5 h in air at different temperatures can be given as an example. As can be seen from fig. 8, the content of excess oxygen sharply

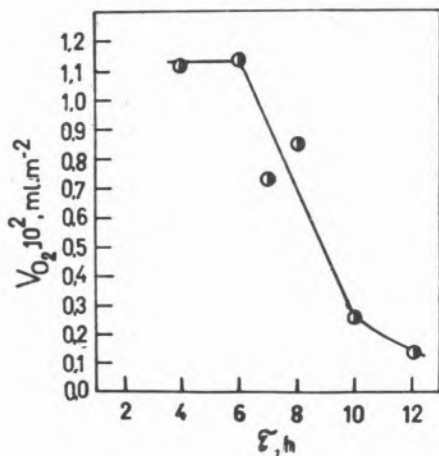


Fig. 6

Desorbed amount of oxygen from NiO specimens versus time of calcination at 450 °C

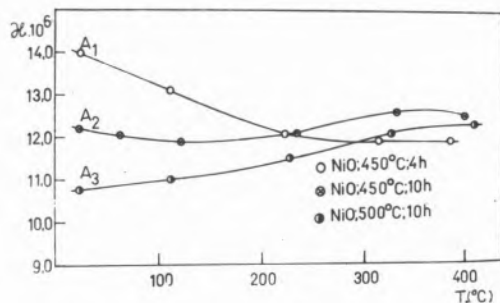


Fig. 7

Temperature dependence of the magnetic susceptibility of NiO specimens.

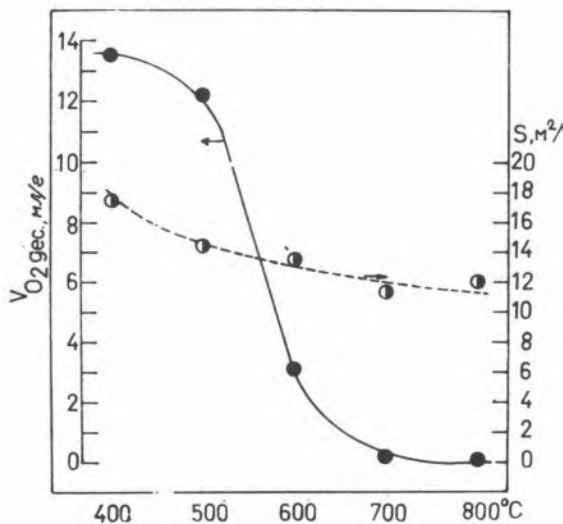


Fig. 8

Desorbed amount of oxygen from Cr_2O_3 specimens calcined for 5 h in air at different temperatures and variation of the specific surface area

changes with the increase of the temperature of calcination. For the samples calcined at 400 °C it reaches 14 ml/g. The samples calcined at 700 °C have practically stoichiometric composition. At the same time, the specific surface area of the specimens changes slowly and decreases less than 2 times. The temperature range of the sharp decrease in the content of non-stoichiometric oxygen corresponds in general to the temperature range of decomposition of the higher chromium oxides (19). This permits the assumption that the high content of non-stoichiometric oxygen in specimens obtained by calcination of chromium hydroxide at relatively low temperatures is due to the impurities of higher chromium oxides formed under these conditions.

Experiments with Al_2O_3 did not show the presence of non-stoichiometric oxygen in this oxide.

A more general conclusion can be drawn, namely, that a significant content of non-stoichiometric oxygen will be observed in oxide catalysts in which the appearance of cations with higher valency than the basic one or formation of peroxides is possible (Co_3O_4 , Cr_2O_3 , Mn_2O_3 , BaO , etc.).

The above data show that the content of non-stoichiometric oxygen in Cr_2O_3 can be significantly higher than in the case of NiO. At the same time, the specific rate of exchange of molecular oxygen with the oxygen of nickel oxide is significantly higher than in the case of chromium oxide (11,20). This leads to the conclusion that the reactivity of oxygen in oxide catalysts, which is connected with the presence of non-stoichiometric oxygen depends predominantly on the strength and type of its bond with the solid surface.

About ten years ago we showed (21) that the existence of more loosely bound and highly reactive oxygen in oxide catalysts favours the proceeding of oxidation catalytic reactions up to products of complete oxidation. This conception is in good agreement with experimental data obtained later.

3. THE INFLUENCE OF THE PROMOTING ON THE REACTIVITY OF OXYGEN IN OXIDE CATALYSTS

The possibility of variation of the reactivity of oxygen in oxide catalysts by introduction of additives is of both theoretical and practical interest. In many cases the influence of the additive can hardly be predicted and mainly the analogies and comparisons are used. However, definite tendencies can be observed in some cases. Some of our results and the results of other authors (22-2) obtained by other methods support this view. I shall briefly discuss the influence of compounds of alkali and alkali-earth metals on the reactivity of oxygen in vanadium oxide catalysts. The reactivity of oxygen has been estimated by studying the kinetics of the catalysts reduction by hydrogen and the kinetics of oxygen desorption from the same specimens under isothermal conditions. The kinetic isotherms of reduction of vanadium pentoxide and vanadium pentoxide containing alkali metal sulfates in a molar ratio $\text{V}_2\text{O}_5 \cdot 0,1 \text{M}_2\text{SO}_4$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) are shown in fig. 9. The kinetic curves of oxygen desorption at 450 °C from the same specimens are shown in fig. 10. As can be seen from these figures, the specific rate of reduction sharply changes with the increase of the atomic number of the alkali metal. It is noteworthy that the desorbability of oxygen changes in the same sequence. The anion component of the alkali compounds added has a weaker effect on the reactivity of oxygen in vanadium pentoxide. Our experiments

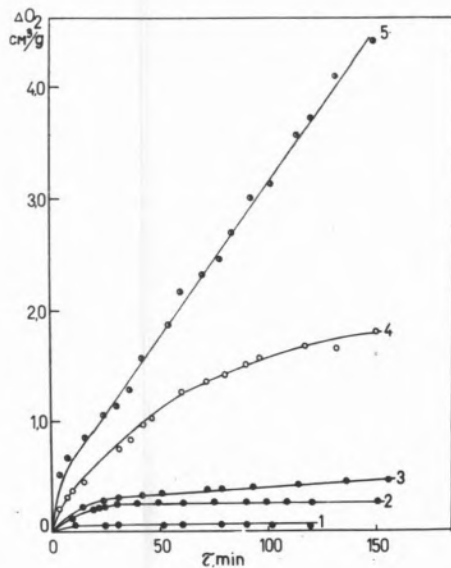


Fig. 9

Kinetic curves of the reduction of V_2O_5 containing alkali sulfates, at $416^\circ C$ and an initial pressure of hydrogen $P_{H_2} = 33$ Torr.

curve 1 - V_2O_5 ; 2 - $V_2O_5 \cdot 0,1Li_2SO_4$; 3 - $V_2O_5 \cdot 0,1Na_2SO_4$; 4 - $V_2O_5 \cdot 0,1K_2SO_4$; 5 - $V_2O_5 \cdot 0,1Cs_2SO_4$

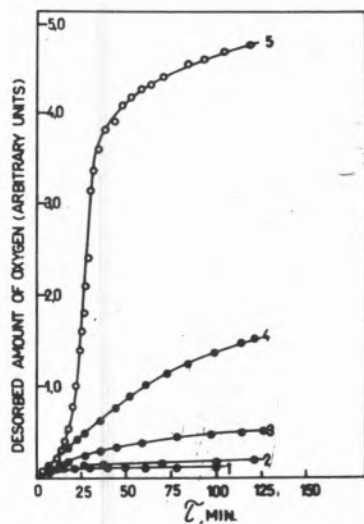


Fig. 10

Kinetic curves of oxygen desorption at $450^\circ C$ (1 - V_2O_5 ; 2 - $V_2O_5 \cdot 0,1Li_2SO_4$; 3 - $V_2O_5 \cdot 0,1Na_2SO_4$; 4 - $V_2O_5 \cdot 0,1K_2SO_4$; 5 - $V_2O_5 \cdot 0,1Cs_2SO_4$)

with addition of alkali metal hydroxides showed an analogical tendency, i. e. an increase in the rate of reduction with the increase in the atomic number of the alkali metal. It is interesting to note that during a study of the influence of sulfates of alkali-earth metals on the desorbability of oxygen from vanadium pentoxide the same tendency was observed (25). In this case the effect increased again from magnesium to barium, i. e. with the increase of the atomic

number of the alkali-earth metal. As was noted previously by Boreskov, with the increase of the atomic number of the alkali metal some of its important parameters (ionic radius, electronegativity, etc.) change. As can be seen from fig. 11 the variation of the reactivity of oxygen correlates well with the variation of these parameters. The experimental results, however, are still insufficient for the formulation of rules concerning promoting. It is hard to predict, for instance, a similar effect of the same additives to molybdena. Studies in this direction are now in progress.

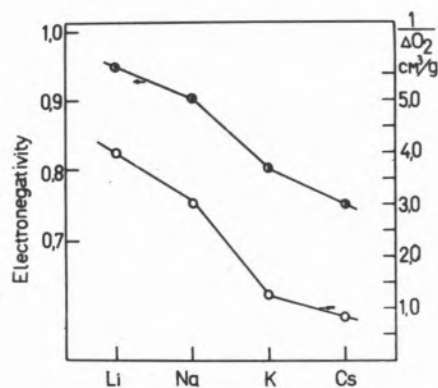


Fig. 11

Relationship between the electronegativity of the alkali metal and the amount of oxygen removed after 30 min of reduction at $416^\circ C$ and $P_{H_2} (init.) = 33$ Torr

It should also be noted that the promoting leads not only to a change of the reactivity of oxygen in the surface layer of the oxide catalysts. The chemical composition of the solid surface also undergoes changes and, in principle, this should additionally affect the activity and selectivity of the catalysts.

According to some current conceptions, the increase in the reactivity of oxygen in vanadium pentoxide under the effect of the alkali metal compounds is associated with a labilization of one of the V-O bonds having the character of a double bond. Irrespective of the fact that numerous data obtained mainly by infra-red spectroscopy support such a conception our opinion is that additional data are necessary for elucidating this problem.

4. REACTIVITY OF OXYGEN IN OXYSALTS AND BINARY OXIDE SYSTEMS

Numerous oxysalts and especially molybdates, tungstates, antimonates and phosphates have found an increasing application as catalysts for selective oxidation. Due to this fact it is of interest to study the reactivity of oxygen in their surface layer. Moreover, systematic studies in this field are very scarce.

Recently, the normal molybdates of metals from the IVth period of the Periodic Table and the normal molybdates of the rare-earth elements from the cerium subgroup as well as bismuth molybdates have been studied systematically (27-30). High purity samples were synthesized, as was confirmed by X-rays analysis, chemical analysis, infra-red spectroscopy and by other methods. The kinetics of exchange of their surface oxygen with oxygen from the gaseous

phase was systematically studied. The following results were obtained :

a) Transition metal molybdates

It was established that the kinetics of the exchange obeys the exponential law, i. e. it is satisfactorily described by the expression :

$$R = \frac{-2,303 N_s \lg (1-F)}{S(1+\lambda) \tau} \quad (1)$$

where F is the extent to which equilibrium has been approached and is defined as $F = (C_0 - C)/(C_0 - C_\infty)$. C_0 is the initial concentration of O^{18} (at. %) in the gaseous phase, C is the concentration of O^{18} in the time t and C_∞ is the equilibrium concentration of O^{18} (at. %) defined on the basis of a material balance. Thus, $C_\infty = (C_0 + 0,2)/(1+\lambda)$ where 0,2 is the natural content of O^{18} (at. %), $\lambda = N_s/N_g$ where N_s is the number (or mass) of the exchangeable oxygen atoms in the oxide sample, and N_g is the number (or mass) of the oxygen atoms in the gas phase. S is the total surface area of the sample (cm^2) and R is the exchange rate per unit area in molecules cm^{-2}, sec^{-1} .

The fraction, X, of the surface oxygen atoms attaining the isotopic composition of the gas phase was calculated from a material balance of the experimental data according to the equation :

$$X = \frac{C_0 - C}{(C - 0,2)} \quad (2)$$

where $X = (N_{surf}/N_g)$, is the ratio of the quantities of oxygen in the surface layer of the oxide and in the gas phase.

A small deviation from the linear dependence of $\lg(1-F) = f(t)$ was observed in the case of cupric molybdate calcined above $750^\circ C$. The applicability of eq. (1) is illustrated with data on one of the molybdates studied in fig. 12. The validity of this equation shows that the oxygen of the molybdates under consideration behaves as energetically uniform. The linear dependence $\lg(1-F) = f(t)$ up to degrees of exchange corresponding to several monolayers indicates a high rate of oxygen self-diffusion in the compounds studied.

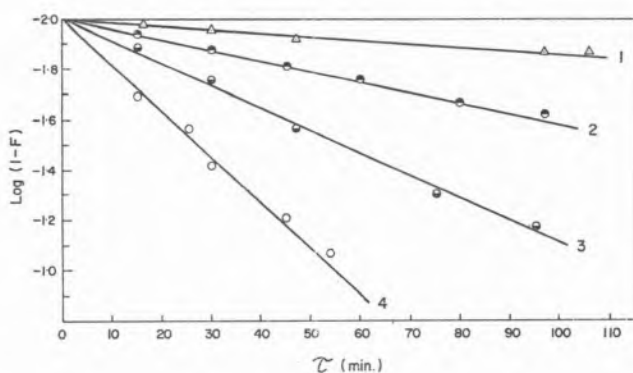


Fig. 12

The dependence of $\text{Log}(1-F)$ on time of exchange for $CuMoO_4$: $1,522^\circ$; $2,540^\circ$; $3,501^\circ$ and $4,601^\circ C$ (the values of $\log(1-F)$ at $501^\circ C$ are multiplied 10 times)

A comparison of the activation energies of exchange for different molybdates and the corresponding oxides presents a special interest. As is known, in the case of simple oxides the activation energy of

exchange varies in wide limits (from 16 kcal/mol for Co_3O_4 to about 60 kcal/mol for TiO_2). For the corresponding molybdates the variation is in very narrow limits (from 42 kcal/mol for cupric molybdate to 56 kcal/mol for $MnMoO_4$). If we take into account the lower thermal stability of cupric molybdate (for which the lowest activation energy of exchange was found) the interval of the variation of the activation energy is still narrower. The difference between the simple oxides and the molybdates with respect to the specific rates of exchange is even more pronounced. While in the case of simple oxides the above parameter varies at isothermal conditions within the range of 5 orders of magnitude, with the corresponding molybdates the changes are in the narrow limits of 1 order magnitude.

Another peculiarity should also be mentioned. In the case of some simple oxides which can be regarded as precursors of the corresponding molybdates the surface oxygen behaves as strongly non-uniform with respect to the oxygen isotopic exchange. It also differs in reactivity from lattice oxygen. This difference is practically not observed in the case of the metal molybdates under investigation. A general characteristic of these compounds is that the reactivity of oxygen in their surface layer is very close to the reactivity of oxygen in MoO_3 . At the same time it is influenced to a significantly smaller extent by the presence of cations of the second metal.

b) Rare-earth molybdates

The reactivity of oxygen has been studied in cooperation with the laboratory of prof. Minachev (30). The exchange of oxygen in CO_2^{18} with the oxygen of the corresponding molybdates was used as a test reaction. In this case it was also established that the specific rate of exchange varies within relatively narrow limits during the transition from one molybdate to another. The values found are very close to the value established for pure MoO_3 . These results can be regarded as indicative of a more general tendency, namely, the reactivity of oxygen in complex oxide catalysts (oxysalts) is usually close to the reactivity of the oxide which forms the anion component. In the case of molybdates, the reactivity of the surface oxygen is closer to that of molybdena, in the case of vanadates to that of vanadium pentoxide, etc. However, this tendency cannot be regarded as a strict rule. Sharp changes in the reactivity of oxygen in the limits of one kind of oxysalts are also possible. The molybdates of bismuth should be mentioned as an example.

c) Bismuth molybdates

In table 2 some preliminary data on the activation energy of exchange of molecular oxygen with the oxygen of different bismuth molybdates are summarized.

Table 2

Composition	Ea of exchange kcal/mol
Bi_2O_3	38
MoO_3	56
$Bi_2O_3 \cdot MoO_3$	58
$Bi_2O_3 \cdot 2MoO_3$	105
$Bi_2O_3 \cdot 3MoO_3$	67
$2Bi_2O_3 \cdot MoO_3$	40

As can be seen from this table the activation energy of exchange for a $2\text{MoO}_3 \cdot \text{Bi}_2\text{O}_3$ composition is strongly different from the activation energies found for Bi_2O_3 and MoO_3 .

Evidently, the formation of this new compound leads to a sharp increase of the bonding energy of oxygen, and to a sharp decrease of

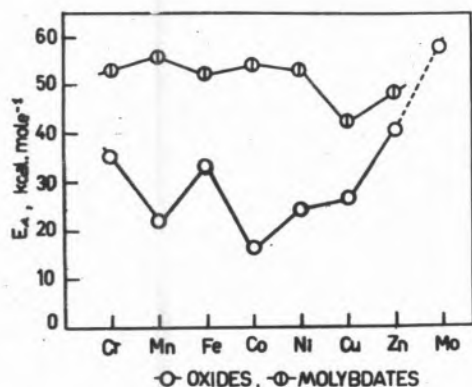


Fig. 13

Activation energies of exchange (kcal/mol) for metal oxides (Cr_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO , CuO , ZnO , MoO_3) and for metal molybdates

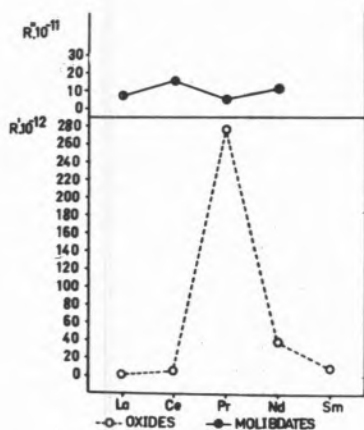


Fig. 14

A comparison between the specific rates of exchange of molecular oxygen with the oxygen of oxides of rare-earth elements (370°C , $P_{\text{O}_2} = 40$ Torr) and the specific rates of exchange of oxygen in CO_2^{18} with the oxygen of rare-earth molybdates ($P_{\text{CO}_2} = 5$ Torr, 450°C)

the reactivity of surface oxygen, respectively. This our conclusion is also supported by the results of Gelbstein (37).

Evidently, the reactivity of oxygen depends on the space orientation and the character of the oxygen bonds. According to some current conceptions, the oxygen in molybdates which is most active in catalytic processes is bound only to one metal atom. The theoretical

calculations of Popovskii et al. show that binding to more than one metal atoms leads to a sharp increase of the binding energy. Since the activity of the molybdates studied with respect to the oxygen isotopic exchange is close to that of MoO_3 , it seems reasonable to assume that the most active oxygen is bound to one molybdenum atom. This assumption supports the view that one of the molybdenum-oxygen bonds having a double bond character plays predominating role in molybdates (31). This conception needs, however additional experimental confirmation.

5. CORRELATION BETWEEN THE REACTIVITY OF OXYGEN IN OXIDE CATALYSTS AND THEIR CATALYTIC ACTIVITY AND SELECTIVITY

The kinetics of exchange of molecular oxygen with the oxygen of oxide catalysts reflects the strength of the oxygen bond in the surface layer and to some extent, the character of the oxygen bond. A general tendency can be noted. The oxides which exchange their oxygen with a relatively low rate and high activation energy are predominantly acidic and can usually be regarded as anhydrides of the corresponding acids. Besides, the metal-oxygen bonds in these oxides have a more pronounced covalent character.

The «degree of covalency» of the metal-oxygen bonds may be estimated from the polarizing powers of the metal and oxygen ions and a very useful information for the polarizing power of the cation may be obtained from the charge/radius ratio. Table 3 presents these ratios for a particular oxide group along with data on the rates (14) and activation energies of exchange.

Table 3

Oxide	Charge/radius ratio for cation	Activation energy of exchange kcal/mol	Lg (rate of exchange 300°C , 10 Torr molecules $\text{O}_2 / \text{cm}^2 \cdot \text{sec}$)
TiO_2^*	6,0	60	5,1
V_2O_5^*	8,4	46	7,1
MoO_3	9,7	52	8,4
WO_3	9,2	51	-
Nb_2O_5	7,1	61	-

There appears to be no simple proportionality between the surface acidity and the mobility of surface oxygen in these oxides. Vanadium pentoxide, for example, is more acidic than niobium (V) oxide but possesses more reactive oxygen. However, it may be concluded that the kinetics of the isotopic exchange reflects not only the bonding energy of oxygen in the oxides but, to some extent, also the type of this bond. In this connection it is noteworthy that the reactivity of oxygen in oxides of group II^a changes in the order $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO}$ (10) and it may be observed that the ionicity of the metal/oxygen bond in this series changes in the same sequence.

According to current conceptions a correlation may exist between the binding energy of oxygen in the surface layer of oxide catalysts

and their activity and selectivity in a large group of redox type reactions. In the case of loosely bound and highly reactive surface oxygen oxidation processes lead mainly to products of complete oxidation. Surface oxygen possessing lower reactivity favours partial oxidation processes. This general tendency has been discussed in previous publications of ours (20, 33) and proved to be in a good agreement with numerous experimental data.

Concerning the catalytic activity for a series of oxidation reactions, the valid use of a Brønsted-Polanyi expression :

$$E = E_0 \pm q$$

has been demonstrated (39), where E is the activation energy of the catalyzed reaction and q is the binding energy of oxygen in the surface layer of the catalysts. The established relationship between q and the activation energy of the oxygen isotopic exchange E_e :

$$E_e = bq$$

($b \approx 1$ for the 3^d mechanism of exchange) permits the activation energy and the rate of exchange to be used for a prognosis of the properties of oxidation catalysts, if the mechanism of exchange is known. An almost linear decrease of the activation energy of numerous oxidation reactions with the decrease of the binding energy of oxygen in the surface layer of oxide catalysts has been experimentally observed (39). Some deviations are also possible due mainly to surface modification and surface heterogeneity.

In fig. 15 the selectivities of a series of metal oxides with respect to the oxidation of methanol to formaldehyde are compared with the binding energy of oxygen in their surface layer. It has also been established in our laboratory that the molybdates studied, which possess surface oxygen with relatively low reactivity are all selective in the oxidation of methanol to formaldehyde. Their selectivity varies from ~ 60 to 100 %.

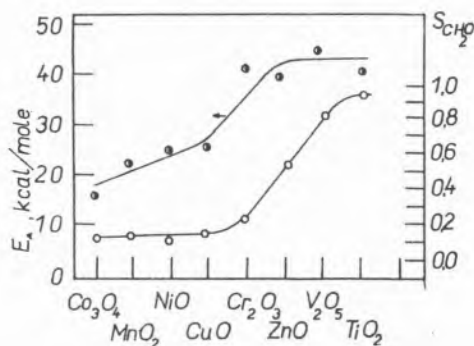


Fig. 15

Relationship between activation energy of isotopic exchange in molecular oxygen on the surface of metal oxides and the selectivity of their catalytic action in oxidation of methanol to formaldehyde

In agreement with the above conceptions our results show that the weak bond and the high reactivity of the surface oxygen favours a complete oxidation. A lower reactivity of the surface oxygen is a necessary condition for a selective oxidation. This is a more general tendency, which can be explained by the fact that the lower reactivity of oxygen suppresses a destructive oxidation and a consecutive oxidation of the products of selective oxidation to products of complete oxidation.

It is necessary to note, however, that the selectivity of oxidation should also depend on the specific activation of the molecule to be oxidized. Nevertheless, information concerning the reactivity of surface oxygen permits an approximate prognosis of the selectivity of oxide type catalysts with respect to reactions of partial oxidation. This facilitates the search of efficient catalysts for important industrial processes and especially, for partial oxidation, oxidative dehydrogenation and oxidative ammonolysis of olefines as well as partial oxidation of primary alcohols.

REFERENCES

- MARGOLIS, L. YA; Heterogeneous Catalytic Oxidation of Hydrocarbons, Ed. Chemistry (1967) (Russ.).
- D. J. HUCKNALL; Selective Oxidation of Hydrocarbons, Acad. Press, London (1974).
- P. JIRU, B. WICHTERLOWA and J. TICHY; Proceedings of the 3^d Internat. Congress on Catalysis, Elsevier Publ. Co., Amsterdam, vol. 1, p. 199 (1965).
- G. BLIZNAKOV, P. JIRU and D. KLISSURSKI; Collect. Czechoslov. Chem. Commun., 31, 2995 (1966).
- S. KYNEV, D. KLISSURSKI and E. VATEVA; Commun. Institute of Physics, Bulgarian Acad. Sci., vol. 9, p. 57 (1962).
- G. I. GOLODETS and V. A. ROITER; Ukrainski Khim. Zhurnal (Russ.), 29, 667 (1963).
- G. I. GOLODETS; Teoret. i Experm. Khimia (Russ.), 2, 755 (1966).
- D. G. KLISSURSKI and R. P. DIKOVA; Zeitschr. für Phys. Chem., 241, 101 (1969).
- V. A. SAZONOV, V. V. POPOVSKII and G. K. BORESKOV; Reports of the Academy of Sciences of USSR (Russ.), 176, 1331 (1967).
- E. R. S. WINTER; J. Chem. Soc. (London), Sec. A, 2889 (1968).
- BORESKOV, G. K. and V. S. MUZYKANTOV; Annal New York Acad. Sci., 137, 213 (1973).
- J. NOVAKOVA; Catalysis Reviews, vol. 4, 77 (1971).
- D. G. KLISSURSKI; Internat. Chem. Engineering (U.S.A.), 5, No. 1, 19 (1965).
- D. G. KLISSURSKI, R. A. ROSS and T. J. GRIFFITH; Zeitschr. Phys. Chem. N. F., 86, 50 (1973).
- G. K. BORESKOV and V. V. POPOVSKII; Kinetics and Catalysis (Russ.), 1, 530 (1960).
- A. BIELANSKI and M. NAJBAR; J. Catalysis, 25, 398 (1972).
- D. G. KLISSURSKI and N. K. NUAN; Proceedings of the 8th Internat. Symposium on the Reactivity of Solids (Preprints), Gothenburg (1976).
- G. M. BLIZNAKOV; Chimica Chronica (Athens), 30 A, 112 (1965).
- J. DEREN, J. HABER; Studies on the physico-chemical and surface properties of Chromium Oxides, Ed. PAN, Krakow (1969).
- E. F. McCAFFREY, D. G. KLISSURSKI and R. A. ROSE; Proceedings of the Vth Internat. Congress on Catalysis, Miami Beach (U.S.A.) (1972), Elsevier Publ. Co., Amsterdam (1973).
- D. KLISSURSKI; Comptes rendus de l'Academie Bulgare des Sciences, 19, 297 (1966).
- G. K. BORESKOV, L. A. KASATKINA, V. V. POPOVSKII, YU. A. BALOVNEV; Kinetics and Catalysis, 1, 229 (1960).

23. P. JIRU, D. TOMKOVA and V. JARA; *Zeitschr. anorg. allgem. Chem.*, 375, 24 (1960).
24. D. G. KLISSURSKI and N. ABADZHIJEVA; *React. Kinet. and Catalysis Letters*, 2, No. 4, 431 (1975).
25. D. G. KLISSURSKI, M. KANCHEVA, N. ABADZHIJEVA and N. K. NUAN; in press.
26. K. TARAMA et al.; *Proceedings of the 3d Internat. Congress on Catalysis*, Amsterdam, Elsevier Publ. Co. (1965).
27. D. G. KLISSURSKI, R. A. ROSS and T. J. GRIFFITH; *Can J. Chemistry*, 52, No. 23, 3847 (1975).
28. D. G. KLISSURSKI and R. A. ROSS; *Proceedings of the VIth Internat. Congress on Catalysis*, London, paper P 10 (1976).
29. D. G. KLISSURSKI and M. KANCHEVA; *React. Kinetics and Catalysis Letters*, vol. 6 (in press).
30. MINACHEV KH. M., D. G. KLISSURSKI, G. V. ANTOSHIN, N. TS. ABADZHIJEVA and N. GUIN; *Proceedings of the 3d Internat. Conference on Catalysis*, Varna (1975).
31. F. TRIFIRO, I. PASQUON and P. CENTOLA; *J. Catalysis*, 10, 86 (1968).
32. N. N. BULGAKOV, YU. A. BORISOV and V. V. POPOVSKII; *Kinetics and Catalysis*, 14, 468 (1973).
33. D. G. KLISSURSKI; *Proceedings of the IVth Internat. Congress on Catalysis*, Moscow (1968), Ed. Akad. Kiado, Budapest, vol. I, p. 477 (1970).
34. B. I. POPOV and V. N. BIBIN; *React. Kinetics and Catalysis Letters*, vol. 3, No. 3, 337 (1975).
35. D. G. KLISSURSKI; *Kinetics and Catalysis*, II, No. 1, 263 (1970).
36. P. JIRU, F. TRIFIRO, D. G. KLISSURSKI and I. PASQUON; *Dinamica reazioni Chim.*, p. 313, CNR, Roma (1967).
37. YU. A. MISCHTENKO, N. D. GOL'DSTEIN and A. I. GEL'BSCHTEIN; *Zhur. fiz. Khim.* 47, 511 (1973).
38. G. K. BORESKOV, V. S. MUZYKANTOV, G. I. PANOV and V. V. POPOVSKII; *Kinetics and Catalysis*, 10, No. 5, 1043 (1969).

DISCUSSION

J. HERRMANN: In connection with our communication at the present symposium, I would like to point out that oxygen isotopic exchange, catalyzed by UV irradiated TiO₂ (anatase) at room temperature proceeds only via the mechanism which involves the exchange of one O₂ molecule from the gas phase with one surface oxygen atom at a time.

Accordingly, it seems that activation by UV light may be highly selective as compared with thermal activation which generally results in a mixture of the various mechanisms.

D. G. KLISSURSKI: Thank you for your interesting comments. Such experiments could facilitate a better understanding of the mechanism of some reactions of selective oxidation.

I. MATSUURA: Generally, Bismuth Molybdates 2/1, 1/1 and 2/3 (Bi/Mo ratio) has high selectivity for olefins oxidation. In London Congress Prof. Kolks suggested the activity for these reaction depends to the oxygen diffusion rate in bulk. 2/1 is higher diffusion rate of oxygen than 2/3 correlated to catalytic activity. Would you give me your comment to the relation between the bulk oxygen diffusion and oxygen exchange rate on surface.

D. G. KLISSURSKI: On the basis of the available experimental data one can hardly assume a simple proportionality between the total activity of oxide type catalysts in oxidation reactions and the rate of oxygen self-diffusion. E.g., the rate of oxygen self-diffusion in Co₃O₄ is relatively low at temperatures at which it

shows a maximum catalytic activity with respect to a large group of oxidation reactions. From a more general point of view, however, the effect of oxygen self-diffusion in oxygen containing catalysts on the selectivity of catalytic oxidation can be motivated.

G. MUNUERA: What possibility exist that some of the results you ascribe to non-stoichiometric oxygen phases at the surface are really due to formation of new phases? For instance, in the alkalyne oxides the formation of new surface phases of peroxides or superoxides.

D. G. KLISSURSKI: Thank you for your valuable remarks. The considered oxide systems do not form peroxide compounds under the described conditions. The formation of peroxide phases can be established by spectroscopic methods.

H. NOLLER: Do you think that oxygen on the surface can only exist either in the form O²⁻ or in the form O⁻². Would you not make any allowance of intermediate charges?

D. G. KLISSURSKI: Our method permits the quantity of non-stoichiometric oxygen to be determined. The concentration of cations with a higher valency than the basic one can be determined by the iodometric method. By comparing these data, the effective charge of the chemisorbed oxygen can be calculated. As was shown by Bielanski et al. in the case of NiO and CoO, the ratio between O²⁻ and O⁻² can vary in a wide range depending on the experimental conditions during the preparation of the specimens.