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Active and super active oxygen on metals in comparison with metal oxides

Gennady I. Panov*, Eugeny V. Starokon, Dmitry P. Ivanov, Larisa V. Pirutko, and Alexandr S. Kharitonov

Department of heterogeneous catalysis, Boreskov Institute of Catalysis, Novosibirsk, Russian Federation

ABSTRACT

In the context of heterogeneous catalysis, oxygen on metals and oxygen on metal oxides are often considered as two different phenomena that are little related to each other. The former is mainly investigated in the field of Surface Science and the calculation chemistry, while the latter in the field of conventional catalysis. In this review we performed a joint analysis of the literature data obtained in both fields, which showed that in many aspects these two types of oxygen are chemically similar. It is usually assumed that, as in the case of oxides, the reactivity of oxygen on metals is determined by its binding energy to the surface. Trying to confirm this idea by comparing the catalytic activity of metals with the heat of oxygen adsorption (Q_{O2}), we came across a paradox of excessive metal activity, which was associated with the presence of “hot” or super active (SA) oxygen. This oxygen is capable of oxidizing methane and other substances at cryogenic temperatures but does not make a significant contribution to Q_{O2}. A comparison of SA oxygen on metals with the $O^{\bullet -}$ radicals on oxides revealed a clear similarity of these species. This allows one to conclude that the oxygen on metals is a radical, which well explains its super high reactivity without using the idea of an energetically excited state. A hypothesis is proposed that not only $O^{\bullet -}$, but also the surface O^{2-} species have a certain degree of the radical nature. Results of low-temperature reactions of SA oxygen offer a more precise interpretation of the selectivity rule. Not the high or low reactivity of surface oxygen in itself is essential for the selective catalyst. A consent between the rates of the product formation and its desorption from the surface is of vital importance. This concept opens the possibility for new approaches in the development of selective catalysts, including those based on metals.

KEYWORDS
Oxygen on metals and oxides; “hot” oxygen; super active oxygen; heat of oxygen adsorption; selectivity

1. Introduction

Dioxygen takes part nearly in all gas-phase catalytic oxidations. Investigation of the mechanism of O_2 activation on the catalyst surface may give a key information for understanding general regularities of oxidation catalysis.[1]

CONTACT Gennady I. Panov gepan2014@mail.ru

*Retired. Present address: 19145 NE 66TH Way Redmond WA 98052-0565 USA. E-mail address: gennady.panov@outlook.com

Metals readily activate dioxygen. This makes them the efficient catalysts for deep oxidation processes. However, another important field of catalysis related to the selective (partial) oxidation remains inaccessible to metals and is based almost completely on the application of oxide catalysts.[2] The most notable exception is the process of ethylene oxidation to ethylene oxide, which proceeds with a high selectivity on metallic silver. This situation indicates that the catalytic potential of metals is far from being disclosed yet, and this can largely be due to the lack of our knowledge about oxygen on their surfaces.

In the case of oxides, the binding energy to a catalyst is the main parameter determining the reactivity of surface oxygen. It is believed that the decisive role of the binding energy can be automatically applied also to oxygen on metals. However, this idea has no experimental verification and its validity remains an open question. Having the intention to solve this problem, we made a comparison of the literature data on catalytic activity of metals with the binding energy of their surface oxygen. The resulting picture, as we will see, was very far from our expectations, leaving the question open.

An essential aspect of the problem is the role of the so-called “hot” or, in the general case, super active (SA) oxygen on metals, the nature of which is unclear and has been discussed for a long time in the literature. Such oxygen exists in the low-temperature region and exhibits an extremely high reactivity, performing oxidations near the temperature of liquid nitrogen. However, availability of SA oxygen is not the unique feature of metals. Such oxygen is available also on oxide systems, where its physical and chemical properties have successfully been studied for many years with virtually no relation to similar studies on metals.

In this work, we analyze jointly the literature data on the active and super active oxygen on the surface of metals and metal oxides. This makes it necessary to touch upon a wide range of issues, including those in which the authors are not experts. Therefore, the review in no way claims to give a complete analysis of the problems under consideration. In many cases, it should rather be taken as an invitation for further discussions in order to find the right answers.

The authors hope that this work will be interesting for researchers involved in studies of the oxygen activation on both metal and oxide surfaces. This could facilitate a closer interaction between ideas developed in both areas, contributing to more successful progress in oxidation catalysis.

2. Heat of dioxygen adsorption on metals and its role in catalytic oxidation. A comparison with oxides

2.1. Introductory comments

The adsorption of oxygen on metals can occur in both the molecular and atomic forms.[3–7] The molecular form is usually observed in the low-temperature region. As the temperature is raised to 200–300 K, the adsorbed O_2 molecules either desorb to the gas phase or dissociate to form atomic species. In oxidation catalysis, the role of molecular form seems to be inessential; adsorption and desorption in this form do not change the isotopic composition of ($^{18}O_2$ + $^{16}O_2$) molecules.[8]

The adsorption of dioxygen is accompanied by an increase in the electron work function. It means that during the adsorption electrons are transferred from a metal to oxygen atoms, which thus acquire a negative charge. As will be seen further, this circumstance is very important for the reactivity of surface oxygen.

Studies on single crystals revealed that at a small degree of surface coverage the adsorption of oxygen does not lead to substantial changes in interatomic bonds in a metal. The adsorbed oxygen atoms form a two-dimensional lattice, the structure of which is determined by the structure of metal surface. Such state of the oxygen is called the ideal adsorbed layer. As oxygen amount increases, the ideal adsorbed layer can transform into two-dimensional surface oxide. This phenomenon, accompanied by substantial changes in the surface structure, is called the reconstructive chemisorption. During such chemisorption, the valence state of the surface metal atoms changes significantly and can approach the state in bulk oxides, whereas the state of oxygen, accordingly, can approach the state of doubly charged O^{2-} anions. At elevated temperature, a dissolution of oxygen in the bulk of metal may occur, leading to the formation of a three-dimensional oxide.

2.2. *Heat of oxygen adsorption on metals*

Table 1 lists the values of O_2 adsorption heat on metals. The Table is based on a quite complete summary of the literature data reported in a rather old (1979) but quite complete review by Toyoshima and Somorjai.[4] By that time, Q_{O2} values have been measured virtually on all polycrystalline samples of metals that are interesting for catalysis, and on many single crystals. Results of Q_{O2} measurements made in the subsequent years were most likely consistent with the data presented in paper[4] and did not cause a significant change in the overall picture. This is evidenced by the lack of later reviews on this important issue. Therefore, when composing Table 1, we did not made an analysis of more recent studies, assuming that data reported in the review[4] quite adequately reflect the current situation, too.

The adsorption heats were obtained mostly by calorimetry and temperature-programmed desorption (TPD). If several results were available for a certain metal, the averaged values were taken. We discarded a few results that were obtained at low temperatures (below 273 K), where the molecular

Table 1. Heats of oxygen chemisorption on polycrystalline and single crystal metal samples, Q_{O2},[4] and heats of formation for the low valence oxides, Q_{oxide}[9].

Entry #	Metal	Q_{O2} (kcal/mol O_2)	Oxide	Q_{oxide} (kcal/mol O_2)
1	Al	211	Al_2O_3	267
2	Si	218	SiO_2	217
3	Ti	236	TiO	247
4	Cr	174	CrO	182
5	Mn	152	MnO	183
6	Fe	123	FeO	130
7	Ni	115	NiO	114
8	Co	100	CoO	114
9	Re	130	Re_2O_3	85
10	Cu	65	Cu_2O	81
	Cu(110)	50		
11	Ge	131	GeO_2	126
12	Nb	208	NbO	193
13	Mo	133	MoO_2	140
	Mo(100)	118		
14	Rh	120	–	–
15	Pd	55	PdO	41
	Pd(110)	59		
	Pd(100)	55		
16	Ag	42	AgO	14.5
	Ag(100)	40		
	Ag(111)	40		
17	Ta	212	Ta_2O_5	195
18	W	136	WO_2	140
	W(100)	141		
	W(110)	115		
19	Ir	72	IrO_2	66
	Ir(111)	65		
20	Pt	58	PtO	68
	Pt(111)	58		
21	Au		Au_2O_3	2.1

form of O_2 adsorption could occur. Table 1 includes both the polycrystalline samples (in this case, a metal is denoted only by the symbol of element) and single crystals with indication of their faces.

One can see that Q_{O2} values vary in a wide range, from 40 to 236 kcal/mol O_2. Table 1 also presents the heats of formation of the corresponding oxides, Q_{oxide}.[9] A graphical comparison of the Q_{O2} and Q_{oxide} is made in Figure 1. A straight line intersecting the Figure at an angle of 45° corresponds to the equality $Q_{O2} = Q_{oxide}$. As one can see, the results for both the polycrystalline samples and single crystals are located mostly around this line, which testifies that the values under consideration are approximately equal. Similar graphical comparison in a slightly different form was made earlier by Sachtler and Reijen,[3] Toyoshima and Somorjai,[4] and Savchenko.[5] (Figures S1, S2, S3 in the Supporting Material). In all cases, the authors concluded that Q_{O2} and Q_{oxide} are approximately equal.

In recent decades, methods of quantum-chemical calculations have been strongly developed.[10–14] At present, the advanced density functional theory (DFT) allows one to calculate with high accuracy the heats of adsorption of molecules on metal single crystals, including the adsorption heat of dioxygen,

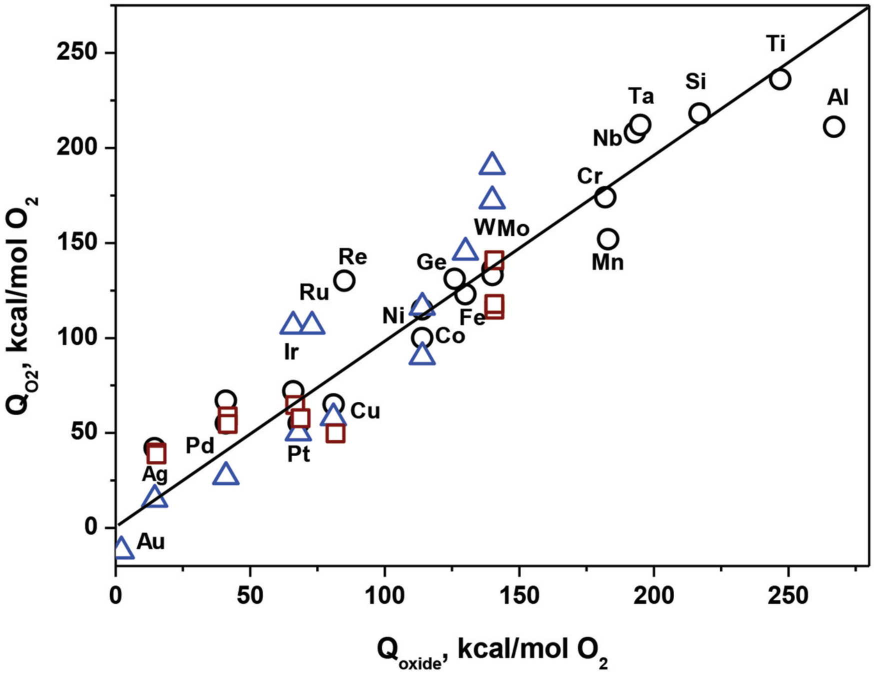


Figure 1. Heat of oxygen chemisorption on metals vs heat of the oxide formation: ○ – experimental heat on polycrystalline samples; □ – experimental heat on single crystals; Δ – calculated heat on single crystals. (Plotted with data of Tables 1 and 2).

$Q_{O2\ calc.}$[15–19] Systematic calculations of O_2 adsorption were performed by the Nørskov's group. Table 2 lists the values of $Q_{O2\ calc}$ on stepped surfaces of the 13 transition metals obtained by this group.[17] These results are displayed also in Figure 1 together with experimental data. The calculated heats roughly fall on the general dependence.

Note that the approximate equality $Q_{O2} = Q_{oxide}$ in Figure 1 is the result of averaging many data having a significant scatter due to the limited experimental accuracy. However, some of the deviations may have an objective reason related to the nature of the metal and the specific reactivity of its surface oxygen. Therefore, the principle of equality can hardly be used for a sophisticated analysis of the kinetics, but it can be a useful general guide in experimental catalytic studies.

Table 2. Calculated heats of oxygen chemisorption, $Q_{O2\ calc}$, on stepped surfaces of metals[17].

Metal[a)]	Fe	Co	Ni	Cu	Mo	Ru	Rh	Pd	Ag	W	Ir	Pt	Au
$Q_{O2\ calc}$ (kcal/mol O_2)	145	116	90	58	172	106	93	27	15	190	106	50	−12
Q_{oxide} (kcal/mol O_2)	130	114	114	81	140	73	–	41	15	140	66	68	2.1

[a)] The adsorption has been calculated on the fcc (211) surface in all cases except for Fe, Mo, and W, for which the calculations were done on bcc (210) surfaces.

2.3. Catalytic activity of metals in the oxidation of hydrogen

Most of metals are instable in the presence of dioxygen and transform into oxides. An exception is the platinum group metals, which retain metallic properties in the O_2 presence. A limited set of metals that are stable in oxygen is a serious difficulty in revealing the relationship between their catalytic activity in oxidation reactions and physicochemical characteristics, including the heat of oxygen adsorption.

A decisive attempt to overcome this difficulty was made by Boreskov and coauthors in their studies on the oxidation of hydrogen in the middle of 1950s.[20–23] The experiments were carried out at a temperature of 323–573 K in a flow-circulation setup at atmospheric pressure in flowing hydrogen. A very small amount of O_2 was added to the H_2 flow. It was supposed that a large H_2 excess would allow investigating a wide range of metals without the formation of oxide phases. Water product was frozen out in a trap at 195 K. Polycrystalline samples of metals were loaded in the reactor as chips, thin wire or platelets with the total surface area of 30–500 cm^2. Prior to the experiments, metals were thoroughly cleaned from oxygen by a long-term treatment in H_2 flow at 773 K.

The results are summarized in Table 3. At low concentrations of dioxygen (C_{O2}) the reaction on a considerable part of metals has the first order with respect to O_2. In the case of Fe, Co, and Ni the reaction rate breaks down when C_{O2} reaches a certain limit, as it is shown for nickel in Figure 2. This is accompanied by a change in the reaction order from 1 to 0, and by a significant increase in the activation energy, from 5 to 14 kcal/mol. Such a breakdown of activity is reversible. The limiting value of C_{O2} at which a breakdown occurs depends on the reaction temperature and the nature of metal. So, if at 453 K the first order of

Table 3. Oxidation of hydrogen on metals[23].

		W_{H2} a)			
Entry #	Metal	ml H_2/cm^2·h b)	10^{16} molec. H_2/cm^2 s c)	Reaction order on oxygen	Activation energy, kcal/mol
1	V	0.19	0.15	0.6	9.7
2	Cr	0.16	0.12	0.4	9.5
3	Mn	0.25	0.19	0.4	12.8
4	Fe	1.9 (low C_{O2})	1.4	1	4.3
		0.15 (high C_{O2})	0.12	0	10.0
5	Co	14.1 (low C_{O2})	11	1	7.4
		4.2 (high C_{O2})	3.0	0.38	
6	Ni	30 (low C_{O2})	23	1	5.3
		2.4 (high C_{O2})	1.8	0	14
7	Cu	0.4	0.3	–	12.1
8	Rh	16	12	–	–
9	Pd	63	48	1	11.2
10	Ag	0.22	0.17	–	–
11	Pt	74	56	1	11
12	Au	0.28	0.20	–	–

a) Reaction conditions: flow-circulating unit with freezing product H_2O at 195 K; reaction temperature 458 K; 0.5 mol % O_2 in H_2 flow. b) Taken from.[23] c) Recalculated by us.

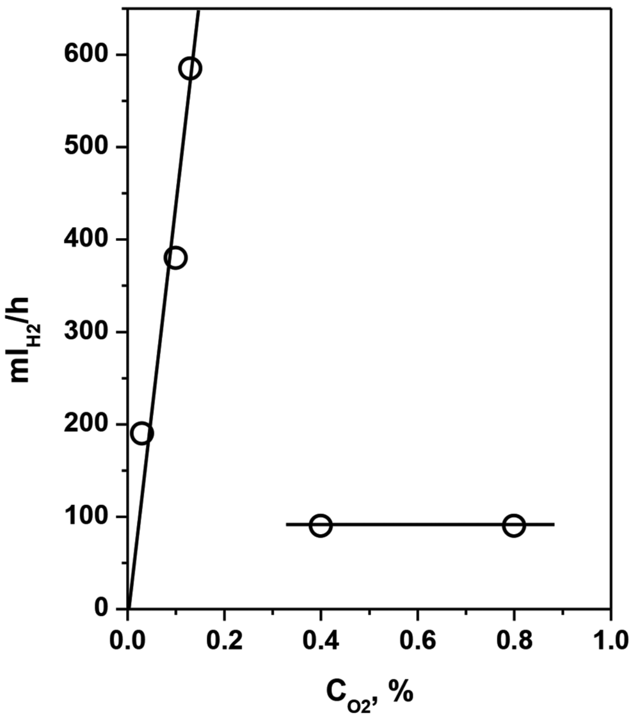


Figure 2. Reaction rate of hydrogen oxidation on Ni vs concentration of oxygen. (Adapted from paper[23]).

the reaction on nickel is retained up to about 0.2% O_2, then on iron only up to 0.06% O_2. At 408 K, for all the tested C_{O2} values, the order of the reaction on iron is zero.

The IV period metals located before iron (V, Cr, Mn) are oxidized under the reaction conditions. Their activity is approximately 10 times lower as compared to iron.

Oxygen exerts a considerable effect also on noble metals, including platinum, which catalytic activity are described in detail in a summarizing paper.[23] After treatment in H_2 at 773 K, the steady state activity of Pt wire at 373 K was 250 ml H_2/cm^2 h and remained constant for 54 hours of continuous operation. As a result of a repeated treatment in hydrogen, the initial activity of the sample increased five-fold, but was unstable and after a long-term operation decreased to 640 ml H_2/cm^2 h. An additional treatment with hydrogen increased the activity again, but after several hours of operation it decreased to 950 ml H_2 $/cm^2$ h. A contact with air at 373 K sharply decreased the reaction rate, which after 36 hours of operation at 453 K slowly increased to 200 ml H_2/cm^2 h.

These experiments demonstrate that it is difficult to obtain reliable data on the steady state activity even for Pt, not to mention metals prone to a more intense interaction with O_2. Therefore, the results in Table 3 are of a qualitative nature and indicate only the lower limit of the metals activity. The real activity may be much higher.

The oxidation rate of hydrogen on Ti and Zn turned out to be immeasurably low at all temperatures studied and, probably, reflects the activity of surface oxide films.

An attempt to relate the data of Table 3 with various characteristics of metals, including their position in the Periodic Table, the type of crystal lattice, the work function, and the number of unpaired electrons, did not lead to distinct correlations.[23] A comparison with Q_{O2} was not made because such data were virtually absent at that time.

To our knowledge, the works by Boreskov and coauthors [20–23] are the only systematic study where activity of a significant number of metals was estimated under comparable conditions of real catalysis. Note that the H_2 oxidation is probably the only reasonable choice for such a study. For example, the oxidation of carbon monoxide with its large excess can be complicated by CO dissociation (the Boudart reaction), leading to carbonization of the metal surface, not to mention the oxidation of more complex molecules like methane or other hydrocarbons.

Although Boreskov's results[20–23] are of qualitative nature, they are of great interest for comparison with the catalytic activity of oxides.

2.4. Heat of oxygen adsorption and catalytic activity of oxides

It is generally accepted,[24–28] that oxidation reactions proceed by the Mars–Van Krevelen mechanism, in which the catalyst plays the role of a carrier of an oxygen atom from O_2 molecule to an oxidized molecule R. The mechanism includes two main steps: the adsorption of dioxygen with the formation of MO particles (M is the active site containing a metal atom), and the oxidation of R by MO oxygen:

$$M + {}^{1}\!/_{2}O_2 \rightarrow MO \tag{1}$$

$$R + MO \rightarrow RO + M \tag{2}$$

Already early attempts to elucidate regularities in oxidation reactions were based on the idea that the catalyst activity is determined by the M-O binding energy and hence by the corresponding value of Q_{O2}. This idea was convincingly supported in the studies by Boreskov, Popovsky and coauthors on the deep oxidation of various substances over a wide series of oxides.[29–32] It should be emphasized that in these works the reaction rate, W_R, was measured in a great excess of dioxygen at low concentrations of R_i (in a flow of O_2 or air). At such condition, the reaction order with respect to R was usually equal to unity and the order with respect to O_2 was equal to zero. It is assumed that the presence of a small amount of a substance R_i does not affect the state of the oxide surface, which can be considered to be completely oxidized. It means that the surface state at the reaction study is close to that at measuring the adsorption heat. This is a critical condition, which should be always satisfied for a correct comparison of W_R and Q_{O2} values.

The authors[6,33] showed that on oxides the relationship between the activation energy of oxidation reactions, E, and Q_{O2} corresponds to a Brönsted-Evans-Polanyi (BEP) correlation:

$$E = E_0 + \beta Q_{O2} \tag{3}$$

In equation (3), E_0 is the constant depending on the nature of the substance to be oxidized, β is the Brönsted coefficient, which value is about 0.5 for all reactions. Equation (3) leads to a linear dependence of log W_R on Q_{O2}, which holds for various oxidizable substances. In Figure 3 such a dependence is displayed for the oxidation of hydrogen. This reaction was taken as an example because it is the only reaction that was studied on both the metals and oxides. One can see that the highest W_{H2} value is observed on Co_3O_4, which has the minimum Q_{O2} value (15 kcal/mol O_2). With the growth of Q_{O2}, the activity shows an exponential decrease. On TiO_2, which has the highest adsorption heat (60 kcal/mol O_2), the reaction rate drops by six orders of magnitude.

Note that, in distinction to the calculated BEP correlations for elementary reactions,[14,35] including adsorption of O_2, BEP correlations for overal catalytic reactions do not have a satisfactory explanation.[33]

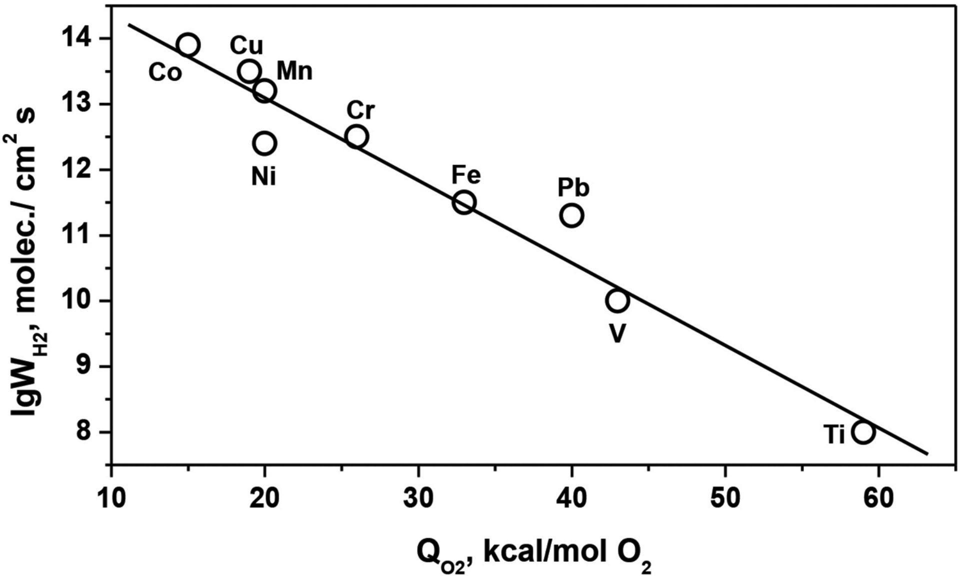


Figure 3. The reaction rate of hydrogen oxidation on metal oxides (573 K, 1.0 mol % H_2 in air flow) vs the heat of oxygen adsorption (Plotted with the data of paper[34]).

2.5. Comparison of the catalytic activity of metals and oxides. A paradox of excessive activity of metals

Earlier, the catalytic activity of metals has not been compared with Q_{O2}. Using the Boreskov's results on the H_2 oxidation (Table 3), we made such a comparison taking Q_{oxide} as the heat of O_2 adsorption. In Figure 4, one can notice a certain tendency toward a decrease in activity with increasing Q_{O2}, which, however, does not look as convincing as in the case of oxides. Indeed, the highest reaction rate is observed for Pd and Pt with small values of Q_{O2} (41 and 68 kcal/mol O_2); the lowest rate is on Mn, V, and Cr with the largest values of Q_{O2} (182–206 kcal/mol O_2). However, other three metals – Ag, Au and Cu – have nearly the same low rate as the three last metals but much smaller Q_{O2}. Therefore, their activity is far from a hypothetical dependence indicated by the dotted line.

It is interesting to note that the five metals of the highest activity (from Fe to Pd) have an oxygen reaction order of 1. The low-active metals in the lower part of the Figure have the order of 0.4–0.6, which indicates that oxygen on their surface has a greater deactivating effect.

In addition to the absence of a clear relationship between W_{H2} and Q_{O2}, metals have another remarkable distinction from oxides. On metals, Q_{O2} values are much larger than in the case of oxides. This is clearly seen in Table 4, where data on Q_{O2} are given for the "oxide–metal" pairs (for example, Co_3O_4 – Co; CuO – Cu; etc.). Thus, for cobalt, upon transition from oxide to metal, Q_{O2} increases from 15 to 100; for copper, from 19 to 110 kcal/mol O_2, etc. For the series of oxide catalysts, an

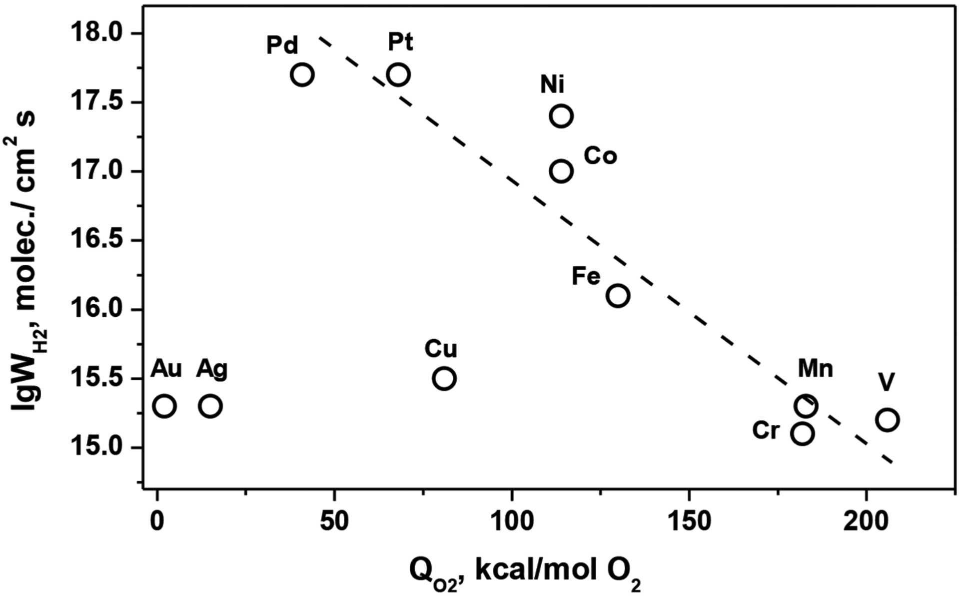


Figure 4. The reaction rate of hydrogen oxidation on metals (453 K, 0,5 mol % O_2 in H_2 flow) vs the heat of oxygen adsorption (Plotted with the data of Tables 1 and 3).

Table 4. Heat of oxygen adsorption and the rate of H_2 oxidation a) for the "oxide-metal" pairs.

Parameter	Co_3O_4	Co	CuO	Cu	NiO	Ni	MnO_2	Mn	Cr_2O_3	Cr	Fe_2O_3	Fe
Q_{O2} (kcal/mol O_2)	15	100	19	110	20	123	20	152	26	174	33	128
lg W_{H2} (molec/cm^2·s)	12.8	17.0	12.4	15.5	11.0	17.4	11.9	15.3	11.0	15.1	9.4	16.1

a) Reaction temperature 458 K; reaction mixture for oxides: 0.5% H_2 in air flow;[34] reaction mixture for metals: 0.5% O_2 in H_2 flow.[23]

increase in Q_{O2} by 45 kcal/mol O_2 produces a decrease in W_{H2} by six orders of magnitude (Figure 3). When going from oxide to metal, an increase in Q_{O2} is much greater, in the range of 85–148 kcal/mol O_2. If the activity of metals and oxides follows the same regularity, the oxidation rate on metals should be lower by 11–20 orders of magnitude than on oxides, i.e. it should be immeasurably small. However, the transition from an oxide to a metal does not decrease the reaction rate at all. On the contrary, the rate increases by 3–6 orders of magnitude (Table 4). One may call this phenomenon the paradox of excessive catalytic activity of metals.

At first glance, it seems that this paradox is easy to explain by assuming that metals can effectively activate dihydrogen by its adsorption into the atomic form, while oxides cannot. However, a more detailed consideration, which will be given later, does not confirm this explanation.

A more likely reason for the paradox may be as follows. On metals, the reaction can involve some other oxygen, then the oxygen involved in measurements of the adsorption heat. Indeed, the so-called "hot" oxygen is known to exist on metals; it occurs in the low-temperature region and exhibits a remarkably high reactivity. The nature of the "hot" oxygen is not quite clear. One might think that it is this oxygen that can cause the paradox of excessive activity of metals. The properties of "hot" oxygen will be considered in the next section.

3. "Hot" oxygen on metals and its low-temperature reactions

The mechanism of oxygen adsorption on metals is the subject of many studies, especially in the field of Surface Science.[6,7,11,1436–38] Such studies using sophisticated surface sensitive physical methods make it possible to obtain unique atom-resolved information about processes that occur on clean surfaces under ultrahigh vacuum (10^{-12} Torr). Currently, the term "hot" oxygen is used quite widely, although there are significant differences in the understanding of this term. The most extensive studies related to hot oxygen were carried out by two groups of researchers: by Ertl et al. and by Roberts et al., whose work we will consider in more detail.

3.1. "Hot" oxygen in works by Ertl

In the previous section, we saw that the adsorption of O_2 on metals is accompanied by the release of a large amount of energy. It is usually assumed that this energy quickly dissipates on the metal, and the adsorbed particles immediately go into a thermally equilibrium state. However, there are observations that are not consistent with this assumption and suggest that some time (relaxation time) is required for the transition to equilibrium.

A number of striking examples of this situation were obtained by Ertl and coauthors using Scanning Tunneling Microscopy (STM). The study of the O_2 adsorption by this method on the Pt(111) face has led the authors[39–41] to a conclusion that initially oxygen is adsorbed in the form of O_2^- peroxo species, which then dissociate to form a pair of negatively charged O atoms. At 180 K and lower temperatures, oxygen atoms are fixed on the platinum surface and do not change their position for a long time. So, it can be expected that the dissociative adsorption of O_2 performed at a temperature below 180 K would produce a pair of O atoms residing exactly at the dissociation site, i.e. on adjacent metal atoms.

However, the actual picture appeared to be different. Figure 5 shows an STM image from the Pt(111) surface with atomic resolution, which had been exposed to a small dose of O_2 molecules at 165 K. Apart from the periodic arrangement of Pt atoms on the perfect (111) plane, the image exhibits additional features, namely, pairs of chemisorbed O atoms. Contrary to expectations, oxygen atoms in each pair are located not on adjacent Pt atoms but at a considerable distance from each other, up to 0.5–0.8 nm. This fly apart of particles indicates that the formed O atoms are "hot" for some time, that is, they retain excess energy on themselves, which is the reason for their movement on the surface. A rough estimate made by Ertl[36,42] from the adsorption energy and the fly-apart distance of hot oxygen atoms gave the average relaxation time of $\sim 3\ 10^{-13}$ s.

An especially impressive phenomenon was observed by Ertl and coauthors on the Al(111) surface, where hot oxygen atoms fly apart at a huge distance, up to 10 nm,[44,45] which is difficult to interpret theoretically. Moreover, in addition to the strongly separated pairs, even the isolated O atoms are observed in this case. To explain this unusual phenomenon, some researchers proposed the hypothesis of the so-called "abstractive chemisorption".[46,47] During such chemisorption, one atom from O_2 molecule is supposed to remain on the surface, while another atom is ejected to the gas phase, from which it is re-adsorbed randomly on a surface site.

This hypothesis was supported by experiments. Using laser spectroscopy and resonance-enhanced multiphoton ionization (REMPI) method, Hasselbrink et - al.[48–50] have registered oxygen atoms in the gas phase during O_2 adsorption on Al(111). Such a phenomenon with the ejection of O atoms to the gas phase was observed also by Ertl et al. for the O_2 adsorption on cerium.[51] The phenomenon of abstractive chemisorption is probably characteristic of metals with strongly exothermic oxygen adsorption, which include Al and Ce with a Q_{O2} of 267 and 286 kcal/mol O_2, respectively. (Hereinafter, we will use Q_{oxide} as Q_{O2}).

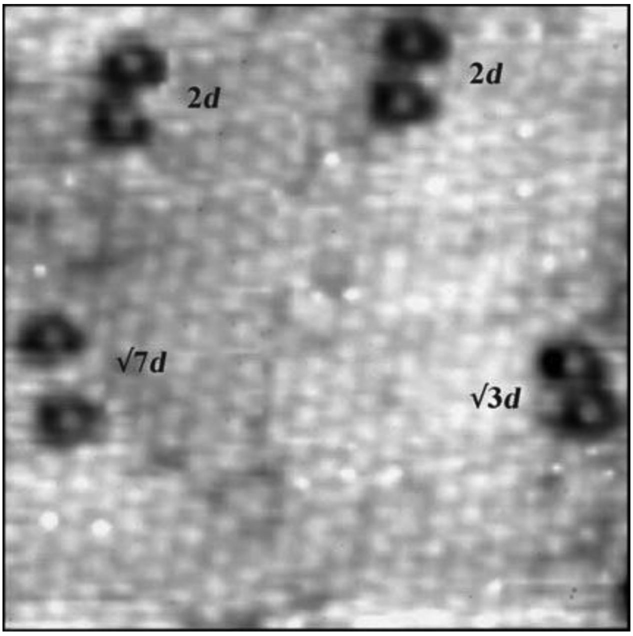


Figure 5. STM image from a Pt(111) with chemisorbed O atoms resulting from dissociative chemisorption of O_2. (Reproduced from paper[43] with permission of Wiley-VCH Verlag GmbH & Co. KGaA).

It is natural to assume that oxygen in the hot state should be highly reactive. Ertl[37] (p. 63) writes:

"These "hot" adatoms are more energetic than they would be if accommodated with the surface, and hence they are expected to be more reactive. Experimental evidence for such effects involving adsorbed oxygen was presented by Roberts et al.[52,53] and becomes even more evident in several studies on the oxidation of CO on Pt".[54–57]

As a particularly convincing example, Ertl presents the results by Matsushima[54] for the oxidation of CO on Pt(111) and interprets them as evidence for the involvement of hot oxygen in the reaction. These results are illustrated in Figure 6 by the TPD spectra of CO_2 taken upon oxidation of CO by accommodated, (O + CO), and by "hot" oxygen adatoms, (O_2 + CO). In the first case, the adsorption of O_2 on Pt(111) was carried out at 125 K.

Oxygen at this temperature is adsorbed in the molecular form, which turns into atomic form upon heating to 150 K. If such platinum sample containing thermolyzed oxygen atoms is cooled again to 125 K and CO is fed to the system, the CO_2 peak with the maximum temperature of 300 K (peak β) will appear in the TPD spectrum of (O + CO). A different pattern is observed if O_2 and CO are simultaneously adsorbed on a clean surface at 125 K. In this case, apart from peak β, the spectrum contains an additional α-peak of CO_2 at 150 K. This is exactly the temperature at which dissociation

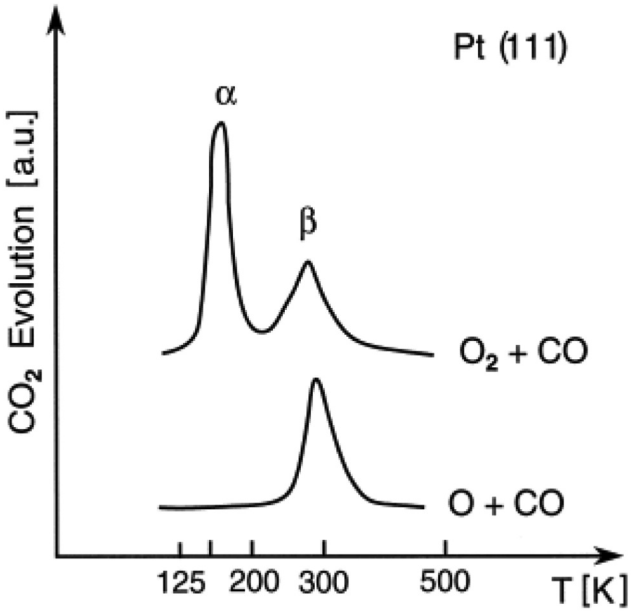


Figure 6. Temperature-programmed reaction spectroscopy characterizing CO_2 formation on Pt (111), demonstrating the participation of hot O adatoms. (Reproduced from paper[36] with permission of Elsevier).

of O_2 molecules takes place and hence the formation of hot oxygen atoms. A part of the hot oxygen atoms reacts with CO, which results in the low-temperature α-peak of CO_2. The other part goes into a thermolyzed state, which, due to reduced activity, reacts with CO at a higher temperature, giving a β-peak.

3.2. *"Hot" oxygen in works by Roberts*

Unlike Ertl, Roberts' works were mainly performed on non-platinum metals, prone to the formation of oxide phases. Roberts was probably the first to discover or at least pay serious attention to the existence of two states of atomic oxygen on metal surfaces, which manifest themselves in different ways in oxidation reactions. One is a transient metastable state with very high activity, which Roberts et al. call "hot oxygen" (sometimes "oxygen transient" or "hot oxygen atomic transient") and which is usually referred to as $O^{\delta-}$. Another is a stable state similar to oxide-like oxygen O^{2-}, which has low activity.[5358–60]

3.2.1. *The reaction of hot oxygen with water and ammonia*

One of the striking results indicating the existence of hot oxygen and its involvement in the reaction was obtained by Roberts et al.[61] upon contacting NO with a molecular layer of H_2O on a Cu(110) single crystal. Despite the low temperature

(160 K), this contact led to the surface hydroxy groups detected by XPS (X-ray photo electron spectroscopy). This testified to NO dissociation with the formation of very active oxygen that can abstract H atom from water molecule. The process of hydrogen abstraction from H_2O was observed also on Zn(0001). Further evidence in favor of the existence of $O^{\delta-}$ was obtained upon interaction of water with oxygen, which was chemisorbed at 80 K on a nickel single crystal Ni (210) and on a Pb film deposited onto stainless steel.[62] At a minor temperature elevation (150–170 K), the formation of surface hydroxy groups was observed in both systems, indicating the occurrence of the following reaction:

$$H_2O + O^{\delta-} \rightarrow OH + OH \tag{4}$$

Considering a very high O–H bond energy in H_2O (118 kcal/mol), this fact shows an extremely strong tendency of hot oxygen to abstract the H atom. The role of water in heterogeneous catalytic reactions is discussed in the review by Davis[63] which was published as a tribute to Prof. Roberts.

Convincing confirmation of the presence of two surface forms was obtained by studying the O_2 adsorption on nickel single crystals Ni(100) and Ni(210) at room temperature.[64] At a low surface coverage, the state of oxygen is observed having the O(1 s) electron binding energy of 531 eV. This form does not cause any changes in the state of Ni^0. The second state with the O(1 s) binding energy of 529.5 eV occurs as a result of longer exposure to oxygen. This state gives rise to signals in the region of 855–857 eV, which correspond to the formation of Ni^{2+} and Ni^{3+}. The first state of oxygen was attributed to $O^{\delta-}$ species, the second to O^{2-} species.

Of particular interest was the metastable state $O^{\delta-}$, which is connected to Ni^0. Using NH_3 as a probe molecule, Roberts et al.[53,65] showed that it is oxygen $O^{\delta-}$ that reacts, causing a decrease in the O(1s) signal at 531 eV and the appearance of dehydrated ammonia species: NH_2, NH and N. The oxide-like O^{2-} oxygen does not participate in the reaction; the intensity of its O(1s) signal remains unchanged.

Quite a detailed study on the oxidation of ammonia was carried out with Cu (110).[58,59,66] According to STM data, the O_2 adsorption at 120 K and low coverage results in the formation of isolated oxygen atoms located at a large distance from each other (0.8–2.5 nm). As the coverage increases, a disordered layer of atomic oxygen is formed on the surface. When the temperature is raised to 290 K, the disordered layer transforms into a well-ordered structure Cu(2x1). Testing with NH_3 revealed that activity is exhibited only by the disordered layer that contains a transient $O^{\delta-}$ species. The ordered layer containing O^{2-} species is inactive.

The mechanism of ammonia oxidation can be presented as a scheme including two parallel routes (Figure 7). Route 1 leads to the transformation of metastable species $O^{\delta-}$ (ms) into a stable inactive oxide-like form O^{2-} (s);

route 2 – to the reaction of $O^{\delta-}$ (ms) with ammonia, whose molecules act as an interceptor of hot oxygen on the way of its conversion into O^{2-} (s).

3.2.2. Oxidation of methane and propene

The Mg(0001) single crystal turned out to be a convenient object for studying hot oxygen, on which, in addition to ammonia,[52] the oxidation of methane[53] and propene[67] was studied. The oxidation of methane was performed by co-adsorption of CH_4+ NO (50:1) or CH_4+ O_2 (60:1) with a gradual increase in temperature starting from 80 K. The reaction became noticeable already at 100 K, which was indicated by the formation of carbonyl groups that showed up as the C(1s) signal at 291.3 eV.

In a study of propene oxidation on Mg(0001), the authors[67] tried to elucidate the effect of hot oxygen on the reaction selectivity. The study included two main experiments. In the first experiment, C_3H_6 was pre-adsorbed on the surface at 78 K. After that, an O_2 flow was fed to the reaction system at a pressure of 1×10^{-6} Torr, and the temperature was gradually raised. The reaction started at above 160 K, giving rise to XPS signals indicating the formation of carbonyl groups. The second experiment was carried out as a "catalytic reaction" at 295 K. In this case, a flow of the (O_2 + C_3H_6) mixture (1:1) was immediately fed at a pressure of 1×10^{-6} Torr on a pure Mg (0001) surface for 300 s. Mass spectrometric analysis showed that the reaction was accompanied by a release to the gas phase of benzene and compounds with mass numbers 54–56, which can be attributed to C_4 products. According to XPS spectra, allylic-type and carbidic-type species appeared on the surface. The state of magnesium changed from Mg^0 to Mg^{2+}.

As in the case of ammonia oxidation, the authors believe that the results are related with the participation of hot oxygen. The major role of $O^{\delta-}$ consists in the abstraction of hydrogen from propene molecules, which leads to dimerization in benzene. The formation of carbonyl groups and carbon deposits indicates that hot oxygen may initiate also the cleavage of C-C bonds. Both reaction types are likely to affect the process selectivity in the oxidation of propene to propene oxide.

Table 5. shows a broad (although probably incomplete) list of systems studied by Roberts et al. in connection with hot oxygen.

3.3. Does Ertl's hot oxygen participate in the reactions?

Since Ertl's non-thermolyzed oxygen contains excess energy, it can rightfully be called hot. In order for such oxygen to participate in surface reactions, the time of its energetically excited state must be sufficiently large, comparable with the time of the reaction act (~10^{-12} s). According to the Ertl's estimate, mentioned earlier, the lifetime of hot oxygen is ~3×10^{-13} s. Therefore, its participation in the reactions does not seem obvious.

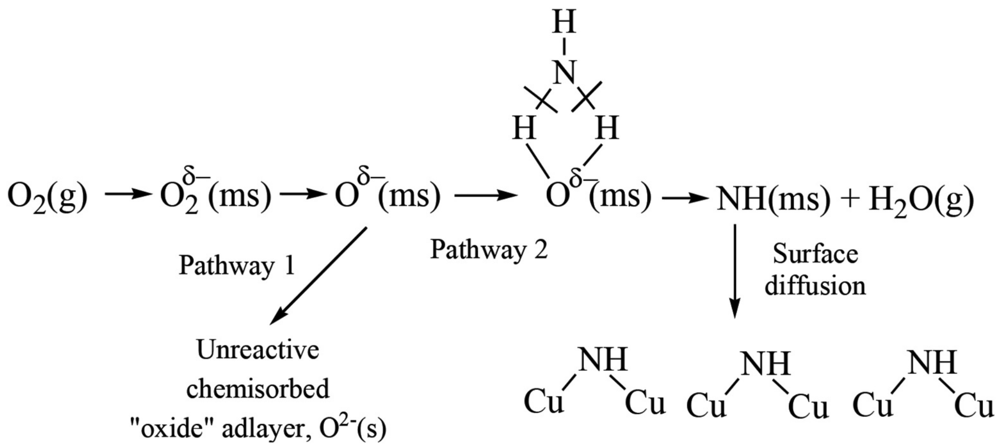


Figure 7. Model of the coadsorption of oxygen and ammonia on Cu(110) at 295 K. (Adapted from paper[60]).

Table 5. Surface chemistry mediated *via* oxygen transients: evidence from surface spectroscopy (1986–1999)[60].

Mg(0001)	O_2: NH_3	Facile H-abstraction
Mg(0001)	O_2: C_3H_6	C-H activation and H-abstraction
Al(pc)	O_2: CO	Low energy pathway to C-O bond cleavage
Zn(0001)	O_2: C_5H_5 N	Facile route to dioxygen bond cleavage
Cu(110)	O_2: NH_3	Selective oxydehydrogenation reactions giving N, NH or NH_2 species
Cu(110)	O_2: CH_3OH	Selectivity for HCHO or surface formate
Ag(110)	O_2: NH_3	Dioxygen states stabilized in the presence of NH_3
Zn(0001)	O_2: CH_3OH	C-O bond cleavage at 80 K
Cu(111)	O_2: H_2O	Facile surface hydroxylation
Ni(110)	O_2: H_2O	Surface hydroxylation at low temperatures
Ni(110)	O_2: NH_3	Oxydehydrogenation to give NH species
Cu(100)	O_2: H_2O	Facile hydroxylation at low temperatures

The idea about participation of energetically excited particles in surface reactions was discussed many times in the literature, especially in the 70–80s of the last century. In particular, some authors[68–70] investigated whether the energy released during adsorption can be transferred to the step of desorption. Excellent works by Ertl et al., which convincingly showed the existence of non-thermolyzed hot oxygen, would seem to give this idea a fundamental basis and make its experimental confirmation more likely. However, these difficult experiments did not give unambiguous results.

At the same time, there are many studies[8,71–75] where the high reactivity of oxygen particles is obviously not connected with their excited state. Among such studies is another work by Matsushima[71] on CO oxidation that was carried out with a Pt(110)(1x2) sample. Here, the surface layer of atomic oxygen was created at 250 K, in the absence of molecular adsorption. After cooling to 110 K, CO was adsorbed on the thermolyzed layer of atomic oxygen with subsequent heating of the sample and detection of CO_2 desorbed to the gas phase. It was found that the main release of CO_2 occurs at 170 K. This only slightly differs from the temperature of the peak at 150 K reported by Matsushima in his paper,[54] which was earlier interpreted by Ertl[37] as evidence for the participation of hot oxygen.

In some studies,[8,74,75] high activity of pre-adsorbed thermolyzed oxygen atoms was tested in the oxidation of hydrogen. On Pt and Ir surfaces, the reaction proceeds at 150–170 K resulting in a complete removal of oxygen from the surface. The absence of adsorbed O_2 molecules excludes a possible involvement of hot oxygen.

The problem of energy transfer from one reaction step to another was considered by Zhdanov and Zamaraev in their thorough review.[76] Summarizing, the authors made the following conclusion (p. 408):

“The available theoretical and experimental data on the rates of vibrational relaxation of adsorbed molecules indicate that direct acceleration of one surface reaction by the energy evolved in another surface reaction is possible in principle, but it is likely to take place only in exceptional situations. Thus, in most cases the mechanisms of heterogeneous catalysis are not expected to be based on the use of the energy evolved in one step (e.g., adsorption) for the direct acceleration of another (rate-determining) step of the catalytic process".

We think that this conclusion is valid for non-thermolyzed hot oxygen on metals. Therefore, the hypothesis of an excited state of oxygen can hardly explain the low-temperature oxidations discussed above.

3.4. Is Roberts' "hot" oxygen really hot?

Both Ertl et al. and Roberts et al. believe that their studies on hot oxygen supplement each other This is evidenced by their mutual references. Thus, Ertl[36] (p. 23) writes:

"These hot adatoms are more energetic than they would be if accommodated with the surface and are hence also expected to be more reactive. Such effects were suggested by Au and Roberts[52] for reactions between molecular oxygen and ammonia on MgO surfaces and later for Cu single crystal surfaces".[77]

For their part, Roberts et al.[66] (p. 349) write:

"Recently Ertl and coworkers [78] have provided more direct experimental evidence for such oxygen transients in scanning tunneling microscopic studies of oxygen chemisorption at AI(lll) surfaces. … That such oxygen atoms possess high chemical reactivities relevant to the mechanism of metal catalyzed reactions is already well documented through their reactions with ammonia,[52] carbon monoxide,[79] propene and water".[80]

However, it is easy to verify that these references describe different states of oxygen, which exist on different time scales. Indeed, lifetime of the Ertl's hot oxygen is ~3×10^{-13} s, after which it passes to the thermally equilibrium state.[36] Lifetime of the Roberts' hot oxygen is ~10^{-8} s in the case of Mg[53] with its very high Q_{O2} value (288 kcal/mol O_2). On metals with a lower adsorption heat, stability of $O^{\delta-}$ should be even higher. Indeed, in the case of nickel[64] and copper[58,59] ($Q_{O2} = 114$ and 81 kcal/mol O_2, respectively), hot oxygen is observed not only in the case of co-adsorption (O_2+ NH_3), but also in the case of atomic oxygen pre-adsorption (O+ NH_3). Especially significant is the experiment on the interaction of ethylene with atomic oxygen on cesium,[81] where according to XPS data the reaction proceeds even at 80 K. It is clear that the lifetime of $O^{\delta-}$ in these cases is measured at least in minutes. Otherwise, such experiments would be impossible to perform.

A similar result, showing a considerable lifetime of active oxygen, was obtained by Iwasawa et al.[82] on copper single crystal Cu(110). Using HREELS, LEED and TPD methods, the authors revealed that the low-temperature adsorption of O_2 on Cu(110) leads to the formation of atomic oxygen that can oxidize CO at 100 K. Such a state was called "*as-exposed* oxygen”. Upon heating to 200 K, the disordered structure of “*ex-exposed* oxygen” turns into the ordered surface phase (2x1)-O in which oxygen is inactive.

Noteworthy are the works by Khasin et al.[83,84] devoted to oxygen reactivity on silver. In these studies, the adsorption of O_2 in the atomic form took place at 293 K, which was followed by the reaction (O_{ads} + H_2). Although oxygen on the silver surface was less active as compared to other metals, its reactivity is quite high. The reaction with hydrogen proceeds at 195 K resulting in the formation of hydroxy groups.

Most likely, “hot oxygen” of Roberts, “*ex-exposed* oxygen” of Iwasawa, and O_{ads} oxygen of Khasin are modifications of the same highly active form of oxygen. Such oxygen species, which can perform oxidations at cryogenic temperatures (below 273 K), we will call further the super active (SA) oxygen and denote by symbol O^*.

Since SA oxygen (possibly with rare exceptions) is in thermal equilibrium, and therefore not hot, this again raises the question of the reason for its surprisingly high reactivity. This issue is relevant not only for metals. Oxygen with an equally high reactivity also exists on oxide systems, where it is the subject of numerous studies using other approaches than in the case of metals. Next, we briefly review the results of these studies for subsequent comparison with SA oxygen on metal surfaces.

4. Super active oxygen ($O^{\bullet -}$ radical anion) on oxide systems and its low-temperature reactions

To have high reactivity, reacting species need not be energetically excited. An example is various radicals, which, due to the availability of unpaired electrons, exhibit an extremely high reactivity, being in thermal equilibrium. This fully applies to the oxygen radical anion $O^{\bullet -}$ on oxide systems. Investigations of $O^{\bullet -}$ were begun in the 60s of the last century, that is, at about the same time as studies of “hot” oxygen on metals. Unfortunately, these works were carried out without any connection with each other, as evidenced by the almost complete absence of cross-references.

In this section, we briefly review the results obtained on oxide systems, including metal-containing zeolites, among which FeZSM-5 zeolite is a particularly successful model for studying $O^{\bullet -}$ radicals.

4.1. Radical anion $O^{\bullet -}$ on supported oxide catalysts

The results of early studies of oxygen radicals on oxides by the electron spin resonance method (ESR) were discussed in reviews.[85–88] Radicals $O^{\bullet -}$ are usually obtained in two ways:

1. UV irradiation of samples having low oxygen mobility (e.g. MgO, TiO_2) in the presence of N_2O or O_2.

2. Reduction of oxides V_2O_5, MoO_3, WO_3 deposited on SiO_2, followed by adsorption of N_2O or O_2 at room temperature:

$$N_2O + Mo^{V} \rightarrow Mo^{VI}O^{\bullet -} + N_2 \quad (5)$$

The concentration of $O^{\bullet -}$ radicals on the surface of oxides is very small, 10^{15}–10^{16} spices per gram of catalyst. However, due to the presence of unpaired electrons, these paramagnetic spices can be easily detected by the ESR having a very high sensitivity.

The study of the $O^{\bullet -}$ reactivity is usually carried out by "titration" of the oxide surface using various test molecules.[89–92] The reaction of $O^{\bullet -}$ with H_2 and CO on V_2O_5/SiO_2 is observed even at liquid nitrogen temperature, leading to disappearance of the corresponding ESR signal.[91] In the case of methane, the $O^{\bullet -}$ signal disappears at 120–140 K, ethane at 183–193, propane at 233–253 and butane at 263–273 K.[90] The indicated temperatures are close to the boiling points of the corresponding hydrocarbons. This may indicate that the reaction is limited by the surface diffusion of the hydrocarbons to $O^{\bullet -}$ radicals.

In the works by Kazansky et al.,[93,94] the oxidation of ethylene was studied in detail. Adsorption of C_2H_4 on MoO_3/SiO_2 at the temperature of liquid nitrogen does not lead to its reaction with $O^{\bullet -}$ radical. The reaction begins at 110 K and accompanied by the appearance of new signals, which the authors associate with the formation of epoxy-like $C_2H_4O^-$ complexes. A further temperature increase leads to decomposition of these complexes by the abstraction of hydrogen, resulting in OH groups and adsorbed vinyl radicals. Close results were obtained by Lunsford et al.[95] for the reaction ($C_2H_4 + O^{\bullet -}$) on MgO.

In addition to low-temperature reactions, $O^{\bullet -}$ radicals are also very likely to take part in the high-temperature (725–870 K) selective catalytic oxidation of methane by nitrous oxide on supported V and Mo oxides. As shown by Somorjai et al.[96,97] and Lunsford et al.[89,98] at low methane conversions (<1%), the selectivity of the reaction ($CH_4 + N_2O$) by the sum of methanol and formaldehyde attains 100%.

4.2. *SA oxygen on metal-containing zeolites*

If the reactivity of oxygen radicals on oxides can be readily studied by ESR, then studying its chemical properties, which assumes identification of the resulting products, is a more difficult task, since not all products have paramagnetic properties and can be observed by this method. The discovery of anion radical oxygen on Fe-containing zeolites such as FeZSM-5, FeZSM-11, Fe-BEA and some others has created new opportunities in this area. FeZSM-5 zeolite attracted the greatest attention of researchers. The concentration of $O^{\bullet-}$ radicals on this zeolite can be 3 orders of magnitude higher than that on conventional oxide catalysts.[99] In the micropore space of FeZSM-5, stable complexes of bivalent iron $(Fe^{II})_\alpha$, (α-sites) can be created. By reaction with nitrous oxide (eq. 6), the α-sites can be converted to oxidized α-complexes $(Fe^{III} - O^{\bullet-})_\alpha$, containing $O^{\bullet-}$ radicals, called α-oxygen in this system, O_α:

$$N_2O + \left(Fe^{II}\right)_\alpha \rightarrow \left(Fe^{III} - O^{\bullet-}\right)_\alpha + N_2 \tag{6}$$

The formation of $(Fe^{III}–O^{\bullet-})_\alpha$ complexes was confirmed by Mössbauer measurements in combination with measurements of the amount of α-oxygen and α-cites,[100,101] as well as by the methods of RIXS (resonant inelastic X-ray scattering)[102,103] and ESR.[104,105]

Note that the oxyl complexes $(Fe^{III}–O^{\bullet-})_\alpha$ are electronic isomers of ferryl complexes $(Fe^{IV} = O)_\alpha$, which in biological and biomimetic studies are considered as key intermediates capable of hydroxylating a wide range of hydrocarbons, with the exception of methane.[106] Possible parameters affecting the mutual transition $(Fe^{III} - O^{\bullet-})_\alpha \leftrightarrow (Fe^{IV} = O)_\alpha$ were considered in papers.[107,108] In a recent review, Mahyuddin et al.,[109] analyzing the arguments in favor of one or another structure, came to the conclusion that it is difficult to decide which one is the ground state of the α sites, even with the use of DFT calculations. However, considering the results of paper,[110] obtained by MCD (magnetic circular dichroism) the authors[109] are inclined to give preference to the $(Fe^{IV} = O)_\alpha$ structure. This issue is also discussed in detail in a comprehensive review by Snyder et al.[111]

Nevertheless, the question of the α-site structure does not seem to be completely resolved. As an additional argument in favor of the $(Fe^{III}–O^{\cdot-})_\alpha$, one can refer to the similarity of the properties of α-oxygen with the properties of SA-oxygen on V and Mo oxides, whose radical nature is not in doubt. This similarity goes so far as to even include the fact of their unusual behavior in relation to methane and hydrogen. Namely, the reaction of both O_α and $O^{\bullet-}$ species with methane proceeds at least an order of magnitude faster than with hydrogen.[92,112] Moreover, it can also be noted that a ferryl structure does not guarantee the ability of its oxygen to oxidize methane. In the biomimetic chemistry, a variety of ferryl complexes were synthesized,[106] however, as far as we know, attempts to oxidize methane with these complexes were unsuccessful. At the same time, α-oxygen can easily perform this reaction at cryogenic temperatures. Therefore, further we will consider α-sites as oxyl complexes $(Fe^{III} - O^{\bullet-})_\alpha$ containing radical anions $O^{\bullet-}$

Using calorimetry, Sobolev et al.[113] measured the value of Q_{O2} for α-oxygen, i. e. the heat of a hypothetical reaction of the O_α formation from O_2 (eq. 7):

$$\tfrac{1}{2}O_2 + \left(Fe^{II}\right)_\alpha \rightarrow \left(Fe^{III} - O^{\bullet -}\right)_\alpha \quad (7)$$

The reaction heat was found to be 2–5 kcal/mol O_2. Such a small value of Q_{O2} explains the reason why the deposition of α-oxygen is impossible from O_2, but possible from endothermic molecules N_2O and H_2O_2.[114]

The discovery of α-oxygen and α-sites stimulated many attempts to create such sites by introducing other metals, especially Cu, Co and Ni, into zeolite matrices. Recent results in this area are discussed in the excellent review by Mahyuddin et al.[109] mentioned above, which focuses mainly on the structure of active sites and their reactivity in the oxidation of methane. These metal-zeolite systems can be activated by heating in dioxygen,[111,115,116] which makes them attractive in practical aspect. However, methane oxidation on their surfaces occurs only at above 373 K. This indicates the lack of SA oxygen species similar to O_α in these systems and makes them less interesting for our consideration.

4.3. Chemical properties of α-oxygen in low-temperature oxidation reactions

Figure 8a shows an experiment in a vacuum static unit (10^{-7} Torr) on the deposition of α-oxygen on a FeZSM-5 sample having a concentration of α sites C_α = 6 10^{19} site/g. The reaction leads to a decrease in N_2O pressure and an equivalent increase in N_2 pressure. The oxygen formed is not released into the gas phase but is quantitatively spent on the oxidation of α-sites. At heating, α-oxygen desorbs as O_2 peak at 598 K (Figure 8b). A high concentration of O_α makes the amount of titration products so large, that they can be extracted from the surface and reliably analyzed using gas chromatography (GC), chromatography-mass spectrometry (GC-MS), nuclear magnetic resonance (NMR) and other analytical methods. Many experimental and theoretical studies,[117–126] as well as several reviews[99,101,109,111,124,127] are devoted to α-oxygen and α-sites. With the participation of O_α, various high-temperature catalytic reactions occur on FeZSM-5,[127] including the steady state oxidation of benzene to phenol with a selectivity close to 100%. In this section, we restrict ourselves to a brief description of only the low-temperature reactions, which clearly show the features of the $O^{\bullet -}$ oxidation chemistry, as well as its similarity with SA oxygen on metals.

4.3.1. Oxidation of alkanes

Methane oxidation ($CH_4 + O_\alpha$) is one of the most studied reactions of α-oxygen. Figure 9 shows the IR spectra of FeZSM-5 (C_{Fe} = 2.0 wt. %; C_α = 6 10^{19} site/g) after methane reaction at room temperature with different amounts of pre-deposited O_α. The reaction leads to the appearance of new absorption bands associated with the formation of methoxy and hydroxy groups, containing α-oxygen:

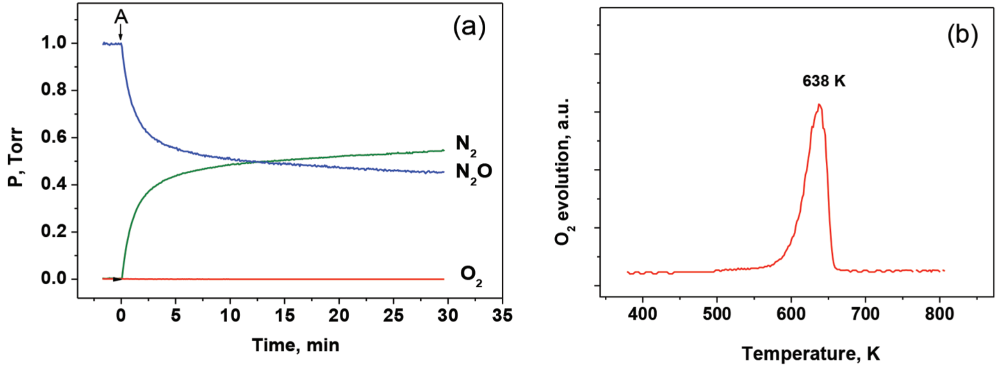


Figure 8. Deposition of α-oxygen by N_2O decomposition at 503 K (a) and its desorption from FeZSM-5 zeolite (b) (C_{Fe} = 2.0 wt.%, C_α = 6 10^{19} site/g); **A**: time of opening the microreactor. (Reproduced from paper[117] with permission of American Chemical Society).

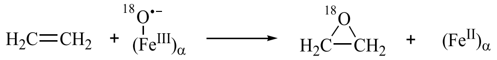
$$CH_4 + 2\left(Fe^{III} - O^{\bullet -}\right)_\alpha \rightarrow \left(Fe^{III} - OCH_3\right)_\alpha + \left(Fe^{III} - OH\right)_\alpha \qquad (8)$$

This means that the reaction proceeds by the hydrogen abstraction mechanism. Extraction with a solvent (acetonitrile + 10% H_2O) leads to methanol, the formation of which occurs due to the hydrolysis of methoxy groups.[117,119] The methanol yield is 75% of the amount of reacted methane.

Rodkin et. al.[128] investigated the oxidation of several other alkanes, such as ethane, propane, n-hexane and 2-methylhexane. The extraction in all cases showed the formation of alcohols. The oxidation preferably proceeds over a weaker secondary C-H bond. So, in the case of propane, the amount of isopropanol is approximately twice the amount of n-propanol.

4.3.2. Oxidation of alkenes

As already noted, the oxidation of ethylene by the $O^{\bullet -}$ radical anion on MoO_3 /SiO_2 proceeds via the C = C bond, giving an epoxy-like complex.[94] It can be expected that oxidation by α-oxygen should proceed in a similar way. The reaction of (C_2H_4 + O_α) on FeZSM-5 was investigated in detail by Starokon et al.[129] An experiment at room temperature showed that the total yield of products referred to the α-oxygen amount is only 3.5%, which indicates intense side processes leading to heavy, non-extractable compounds. However, a noticeable amount (~ 8%) of ethylene oxide, EO, was present in the extract. Modification of the sample with sodium and lowering the reaction temperature led to a significant suppression of side processes. At 213 K, the yield of extracted products was 40%, and the selectivity for EO was 84%. Experiment with the $^{18}O_\alpha$ isotope showed that the formation of EO proceeds by the direct addition of O_α via the C = C bond:



(9)

The chemical properties of α-oxygen in the oxidation of propene is of particular interest. Unlike ethylene, the C_3H_6 molecule has a weak allyl C-H bond (86 vs 111 kcal/mol), which is expected to be the main point for the O_α attack. In the general opinion, it is the presence of this easily broken bond that causes the low selectivity of silver catalysts in the process of propene oxidation to propene oxide (PO).[130] However, contrary to expectations, the results were close to those obtained with ethylene. At 213 K, the yield of extracted products was 50–52%, and the selectivity for PO was 60–63%.[131] The nature of the side compounds (these are the products of PO isomerization), as well as IR spectra indicated that the primary reaction proceeds only by the epoxidation mechanism. For making this important result more evident, Figure 10 shows the spectra of Na-modified FeZSM-5 zeolite. In contrast to methane (section a), the oxidation of propene (section b) proceeds in the complete absence of absorption bands related to the formation of OH groups, which indicates the

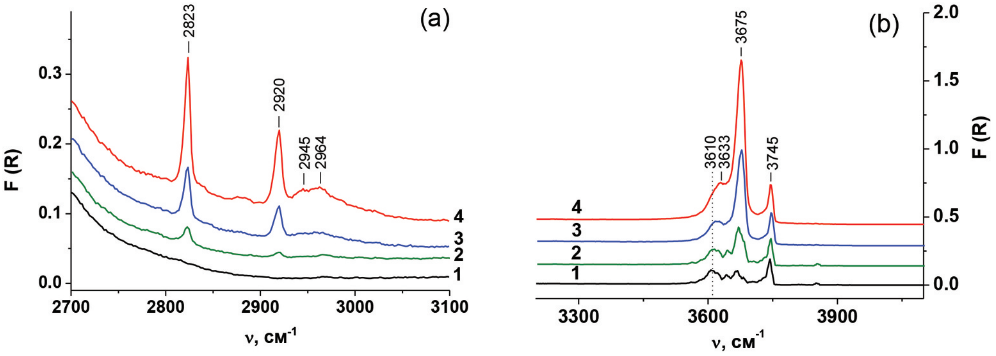


Figure 9. IR spectra of FeZSM-5 (C_{Fe} = 2.0 wt.%, C_α = 6 10^{19} site/g) in C-H (**a**) and O-H (**b**) vibration regions after RT reaction of methane with different amount of α-oxygen: 1 – no O_α; 2–20 μmol O_α/g; 3–50 μmol O_α/g; 4–100 μmol O_α/g. (Reproduced from paper[117] with permission of American Chemical Society).

lack of the hydrogen abstraction mechanism. Similar results were obtained for the oxidation of 1-butene.[132]

Note that the results on the oxidation of alkenes with α-oxygen differ from the results of Roberts et al., who observed the formation of carbonate groups and carbon deposits upon the oxidation of propene with "hot" oxygen.[67] Obviously, these products are result of several oxidative events and do not allow one to conclude on the primary reaction. It is quite possible that the primary reaction in this case also proceed with addition of O^* species via the C = C bond, which is difficult to register by XPS method.

4.3.3. *Oxidation of water*

The oxidation of water in studies by Roberts[61,62] was probably the first unusual result, indicating the existence of hot oxygen on metals. Panov et al.[133] studied this reaction with the participation of α-oxygen ($H_2O + O_\alpha$) on FeZSM-5 in the temperature range 278–473 K. Adsorption of H_2O on the initial sample is accompanied by hydroxylation of the surface, including α-cites. Adsorption onto a sample with pre-deposited α-oxygen gives a quite different result; along with the surface hydroxylation, O_2 is released into the gas phase. Using volumetric measurements, IR, TPD, and isotopic methods, the authors[133] showed that this phenomenon is associated not with the displacement of pre-deposited O_α, but with the water oxidation, which, like in the case of methane, proceeds via the hydrogen abstraction mechanism:

$$H_2O + 2(Fe^{III} - O^{\bullet -})_\alpha \rightarrow 2(Fe^{III} - OH^-)_\alpha + \tfrac{1}{2}O_2 \qquad (10)$$

The amount of O_2 formed does not depend on the reaction temperature and is equal to half the amount of α-oxygen.

4.3.4. *Kinetic isotope effects*

The kinetic isotope effect (KIE) allows obtaining additional information on the reaction mechanism. For the case of α-oxygen, KIE measurements were carried out in the oxidation of hydrogen,[112] methane, and benzene.[134] The results are shown in Table 6. Depending on the reaction temperature, the KIE for hydrogen is 3.5–41, and for methane 1.9–5.5. The high KIE values indicate that the limiting steps of these reactions include the cleavage of hydrogen containing bonds. This confirms the H abstraction mechanism in the methane oxidation.

It is interesting that the oxidation of benzene proceeds without a KIE. This indicates a different reaction mechanism, which involves the formation of an intermediate that does not require abstraction of hydrogen. One can assume that although bonds in the aromatic ring of benzene are not completely double, this mechanism is similar to that in the oxidation of alkenes. The reaction probably occurs through the addition of O_α via the carbon – carbon

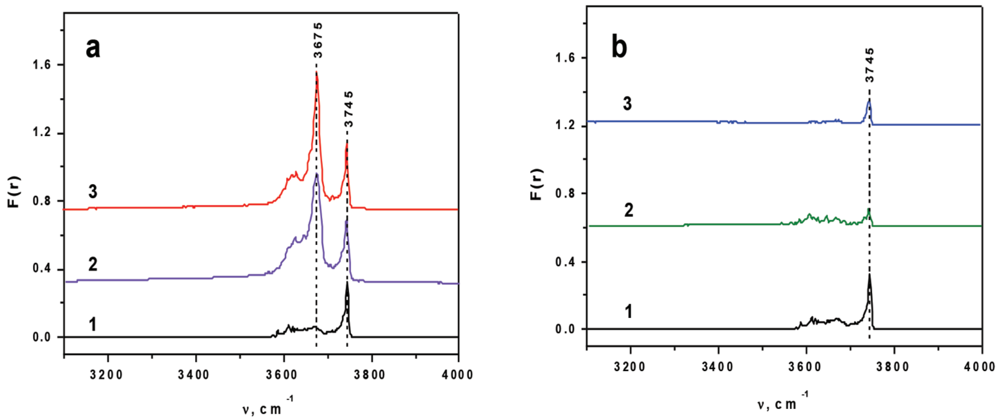


Figure 10. IR spectra of Na-modified FeZSM-5 (C_{Na} = 0.2 wt.%, C_{Fe} = 2.0 wt.%, $C_\alpha = 3.5\ 10^{19}$ site/g) after reaction $CH_4 + O_\alpha$ (**a**) and $C_3H_6 + O_\alpha$ (**b**): 1 - spectra before reaction; 2 - after reaction at 298 K; 3 - after reaction at 213 K. (Reproduced from paper[131] with permission of Elsevier B.V.)

Table 6. Kinetic isotope effects (KIE) in α-oxygen oxidation of H_2, CH_4, and C_6H_6[112,134].

	KIE (k_H/k_D)		
Reaction temperature, K	H_2	CH_4	C_6H_6
373	–	1.9	–
298	3.5	3.2	1.0
263	–	4.0	–
253	8	–	–
223	14	5.5	–
203	23	–	–
173	41	–	–

bond with the intermediate formation of arene oxide, which isomerizes into phenol.[123,134]

5. Comments on the role of active and super active oxygen in oxidation catalysis

This final part of the review is rather speculative. Here, we suggest some hypotheses and comments on questions that were previously left without discussion in order to keep a general logic of the presentation clear. We consider these comments not as complete solutions, but rather as an invitation to further discussion for a deeper understanding of the fundamental role, which different forms of surface oxygen may play in oxidation catalysis on both metals and oxides.

5.1. On the paradox of excessive catalytic activity of metals

In the case of oxides, an increase in the heat of oxygen adsorption leads to an exponential decrease in the catalytic activity. Trying to verify this BEP-type relationship for metals, we encountered an unusual phenomenon (Section 2.5). It turned out that at the transition from oxides to metals, despite a large increase in Q_{O2}, the catalytic activity not only did not fall by the expected 11–20 orders of magnitude, but, on the contrary, increased 10^3–10^6 times. We called this phenomenon a paradox of excessive catalytic activity of metals. As the first hypothesis, we assumed that metals can efficiently activate dihydrogen by adsorbing it into an atomic form, which explains their high catalytic activity. Below we will consider this idea in more detail.

Indeed, the dissociation of H_2 on metals, except for *sp* metals, occurs at very low temperatures, including in some cases even the temperature of liquid helium.[135–137] However, atomic hydrogen does not have sufficient reactivity to react with oxygen molecules. In contrast, atomic oxygen O^* readily reacts with both atomic and molecular hydrogen. Roberts' studies,[61–63] performed on a number of metals (Cu, Zn, Ni, Pb, Mg), showed that O^* species can oxidize also other inactivated molecules such as H_2O, CH_4, NH_3, at

130–170 K, whose H atom is bonded much more strongly than in H_2 molecule. These results are in good agreement with the data obtained on oxide and zeolite systems. Experiments with the sample of V_2O_5/SiO_2 are especially indicative, since the H_2 oxidation by $O^{-\bullet}$ radicals occurs here at a temperature of 78 K,[91] at which the molecular form of adsorbed hydrogen is evidenced by the lack of the H_2/D_2 isotopic excange. (See below).

The problem of H_2 activation on oxides has been studied much less. In the resting state, the oxide surface is usually covered with hydroxyl groups. The H_2 dissociation on such a surface at low temperatures does not take place; heating to high temperatures leads to the reduction of oxide.

A convenient test for the activation of dihydrogen is the reaction of its isotopic H_2/D_2 exchange. Studies carried out mainly in the 50–70s of the last century[136,138] showed that most metals are highly active in this simple catalytic reaction, which often proceeds at a temperature of 78 K. Copper and gold exhibit less activity. The exchange here becomes noticeable only at 250–270 K.[139] As for metal oxides, they are not active in their resting state in the H_2/D_2 exchange. However, after dehydration of their surface in vacuum at 673 K, the picture changes dramatically. This is convincingly shown by Dowden et al.,[140] who studied this reaction for 13 oxides of the first transition period, at 78–273 K. The activity of many oxides turned out to be high and comparable with the activity of metals. The exchange on Cr_2O_3, Co_3O_4 and NiO proceeds at a temperature of 78 K. Interestingly, two oxides, V_2O_5 and TiO_2, were inactive.

Thus, for oxidation on both metals and oxides, dihydrogen activation is not a necessary step. Therefore, even if we assume that metals really have greater efficiency in the H_2 activation (which is not obvious), this can hardly explain the paradox of their excessive catalytic activity.

We think that a more likely explanation of the paradox is due to the peculiar features of hot oxygen. Indeed, SA oxygen has an extremely high reactivity, but a limited lifetime even at low temperatures. A longer time or heating above room temperature, leads to the transformation of O^* species into a low-active state, which is usually attributed to the oxide-like form O^{2-}. Therefore, participating in catalytic reactions, SA oxygen may not show up in experiments on measuring Q_{O2}. Really, a calorimetric measurement requires a quite long time; TPD measurement involves the heating to a high temperature. In both cases, the value of Q_{O2} will most likely correspond to the oxygen adsorption into the most stable form, leading to the approximate equality $Q_{O2} = Q_{oxide}$.

More generally, the cause of the paradox is related to the fact that on metals, unlike oxides, it is not possible to ensure the same state of the surface when measuring W_R and Q_{O2}. Therefore, the comparison of these parameters does not make sense since they refer to different states of oxygen. The real value of Q_{O2} for SA oxygen on metals is probably much lower than the values shown in Table 1. As in the case of α-oxygen on FeZSM-5,[113] these values should probably also lie in the region of few kcal/mol O_2. It would correlate well with the super-high activity of O^* species, without causing an apparent paradox.

5.2. The radical nature of SA oxygen on metals

Based on theoretical calculations, the authors[141] suggested an idea that the molecular form of oxygen can act as a transient species. This makes it possible to explain the co-adsorption experiments by Roberts without the involvement of "hot" oxygen. However, most experimental results do not confirm this idea. When discussing the low-temperature reactions, we saw that oxygen molecules adsorbed on metals react only after conversion into atomic form.[8,54,75,82] Moreover, the molecular form, even partially activated as the O_2^- anion, is not able to participate in the isotope exchange,[87,142] and can hardly act as an oxidizing agent. Thus, we traditionally will consider SA oxygen as an atomic species.

The properties of the atomic $O^{\bullet -}$ radicals on oxide systems, discussed in Section 4, largely coincide with the properties of SA oxygen on metals. The very fact that each of these species has such a unique feature as super high activity is an important argument in favor of their kinship.

Another argument is their pronounced tendency to perform the oxidation of saturated compounds by the mechanism of hydrogen abstraction. This tendency is manifested not only with alkanes, including methane ($E_{C\text{-}H}$ = 105 kcal/mol), but also with ammonia ($E_{N\text{-}H}$ = 108 kcal/mol), and even water having especially strongly bound hydrogen ($E_{O\text{-}H}$ = 118 kcal/mol). It is difficult to think that the properties of some two oxygen forms of different nature could coincide accidentally in such a way that both of them were able to not only enter into chemical reactions at deep cryogenic temperatures, but also to do this by a similar mechanism. This allows one to conclude that, as in the case of oxides, SA oxygen on metals is the $O^{\bullet -}$ radical with its extremely high reactivity. The stability of radical species may depend on the metal nature and the local environment.

Note that the gas phase reaction of the free radical $O^{\bullet -}$ with methane and ammonia also proceeds via the hydrogen abstraction mechanism,[143] which is in line with the conclusion on radical nature of SA oxygen.

5.3. On the unified nature of active and super active oxygen

As already noted, SA oxygen O^* on metals exists at low temperatures. When heated to 300 K, it converts into a low active oxide-like form O^{2-}. This circumstance casts doubt on the participation of O^* species in real catalytic reactions, which are usually carried out at higher temperatures. So, in the works by Boreskov et al.,[20–23] the oxidation of hydrogen was studied in a temperature range of 323–575 K, at which SA oxygen can hardly exist. But from the data for oxides (Table 4), it is clear that at these temperatures the O^{2-}

form cannot provide the oxidation. Therefore, if we reject the unlikely hypothesis that some new form of oxygen appears, we have to admit that the catalytic oxidation of hydrogen[20–23] still occurs with the participation of SA oxygen, although its reactivity should be significantly reduced compared to the Surface Science conditions.

To compare the reactivity of SA oxygen in real catalysis and under the Surface Science conditions, one can compare rates of H_2 oxidation in the work by Boreskov[23] and in that one by Gorodetsky et al.[8] In the last work, the rate of steady state H_2 oxidation was measured at 150–300 K using an ultrahigh vacuum unit with a pressure of flowing stoichiometric (H_2 + O_2) mixture 1.5 10^{-7} Torr. The temperature dependence of W_{H2} is well described by the Arrhenius plot, from which it follows that the activation energy of the reaction is 3 kcal/mol. Extrapolation of these data to 453 K (the reference temperature in Boreskov's work) shows that the specific activity of the Pt wire in paper[8] is 2.5 orders of magnitude higher than the activity of the Pt wire in paper.[23] This means that the transition from the Surface Science conditions to real catalysis leads to a significant decrease in the reactivity of O^* species. This may be due either to a change in temperature or to a change in O_2 concentration. Since the temperature ranges in the considered studies almost overlap, the decrease in activity is most likely associated with a change in C_{O2}, which is almost 10^8 times greater in paper[23] than in paper.[8]

As shown by Kazansky et al.[92] and Lunsford et al.,[144] the reactivity of $O^{\bullet -}$ radicals on oxides are not constant and can vary significantly. Thus, on supported oxides of V, Mo, and W, the reaction rate of $O^{\bullet -}$ with H_2 and CH_4 increases in the order W < Mo <V.[92] Moreover, the reactivity of $O^{\bullet -}$ can differ even on the same oxide. So, on MoO_3/SiO_2 at a temperature of 173 K, 70% of the radicals react with H_2 within 30 minutes, and then the reaction practically stops. With increasing temperature, the extent of $O^{\bullet -}$ reaction increases. The least active part of $O^{\bullet -}$ is removed from the surface only at 270 K.

It is assumed that the change in $O^{\bullet -}$ reactivity is associated with the delocalization of an unpaired electron. According to Lunsford et al.,[90] $O^{\bullet -}$ radical on MgO possesses the least stability (and the highest reactivity) since an unpaired electron is almost completely localized on the *p*-orbital of the O^- ion. On the surface of MoO_3/SiO_2, partial delocalization of the unpaired electron occurs on the molybdenum ion, which makes the $O^{\bullet -}$ radical more stable.[144] Kazansky et al.[145] believe that delocalization can occur not only on metal atoms, but also on oxygen atoms.

The idea that a degree of delocalization of an unpaired electron affects the reactivity is probably applicable to $O^{\bullet -}$ radicals on metals. An increase in the amount of oxygen in the surface and sub-surface layers of the metal can cause an increasing delocalization of unpaired electrons, leading to the degeneration of radical properties and a decrease in the oxygen reactivity.

So, in the process of metal oxidation, its surface oxygen gradually approaches the state of oxide-like O^{2-} species having weakly expressed radical characteristics. We can hypothesize that all forms of surface oxygen have a certain degree of radical nature, which allows considering $O^{\bullet-}$ and O^{2-} species as fundamentally kindred forms of oxygen. The catalytic activity of metals in the Boreskov's studies,[20–23] apparently, is associated with some intermediate state of oxygen, the reactivity of which lies between $O^{\bullet-}$ and O^{2-} species.

Note that in addition to the degree of delocalization of unpaired electrons discussed by Lunsford[144] and Kazansky,[145] the reactivity of radicals may also be affected by other properties of the catalyst. This issue merits further study.

We think it is worth giving a comment regarding the term "oxide-like oxygen". The term is often used for the surface oxygen form, which is commonly designated as O^{2-}. Lattice oxygen of oxides has the same designation, although there are large differences between these forms, for instance in the binding energy. This is well evidenced by comparing the values of Q_{O2} and Q_{oxide}. E.g., for CuO these values are 19 and 75; for MnO_2 – 20 and 183; for Fe_2O_3 – 33 and 131 kcal/mol O_2, respectively. Lattice oxygen can hardly be a radical, while some radical properties may be a typical feature of the surface O^{2-} species.

5.4. Reactivity of surface oxygen and the catalyst selectivity

Currently, the development of catalysts for selective oxidation reactions is mainly based on an empirical rule, which was successfully used for many decades.[1,2[24–26] According to the rule, a selective catalyst must have a strongly bound surface oxygen of low reactivity. Such catalysts usually include oxides of Mo, V, and some other metals having Q_{O2} values in the range of 40–50 kcal/mol O_2. In contrast, oxides of Co, Cu, and Ni having Q_{O2} = 15–20 kcal/mol O_2 are nonselective and provide the deep oxidation. The oxygen of these oxides is considered to be very active and can unpredictably attack any bond of the molecule to be oxidized. Under this rule, metals with their SA oxygen *a priori* cannot be selective catalysts.

However, the results of the low-temperature surface reactions that we discuss above (sections 3 and 4) do not support this consideration. On the contrary, SA oxygen exhibits a quit predictable chemistry. So, its alkane oxidation always occurs by the mechanism of hydrogen abstraction; the attack is primarily aimed at weaker secondary C-H bonds. In the case of alkenes, the reaction mechanism is different. Here, instead of hydrogen abstraction, O^* species directly adds over a double C = C bond to form an epoxy cycle. These examples show quite regular behavior of SA oxygen. Due to its electrophilic nature, O* primarily reacts to those bonds of oxidizable molecules that have the highest electron density.

So, the data on low-temperature surface reactions indicate that not only high, but even super-high oxygen activity is not an obstacle to the formation of selective oxidation products. However, to complete the catalytic cycle, these products must be removed from the surface. This step is probably the critical point for the selectivity. On catalysts with high active (and the more so super active) oxygen, oxidation proceeds at low temperatures, when the partially oxidized products cannot desorb to the gas phase. On catalysts with low active oxygen, the reaction occurs at elevated temperatures, when the products are easily removed from the surface, avoiding the overoxidation and ensuring a selectivity of the process.

This consideration allows one to give a new interpretation of the selectivity rule. For a selective catalyst, it is not the high or low activity of surface oxygen that is important, but the consistency between the rates of formation and desorption of oxidized products. This interpretation does not deny the traditional rule, but makes it broader, thus providing an opportunity for new approaches in the development of selective catalysts, including those based on metals.

6. Conclusion

At first glance, it seems that properties of oxygen on the surface of metals and on the surface of metal oxides display a deep gap, so that their joint consideration can hardly be a rewarding matter. Really, by studying atomically adsorbed oxygen, say, on the surface of copper, one can hardly assume the oxygen properties on copper oxide. However, analysis of the literature data shows that these differences are not so dramatic. Indeed, following the changes in the surface oxygen during a gradual oxidation of a metal into an oxide, we can hardly draw a line where the metal ends and where the oxide begins. Between these two extreme states of the system, there are many transition states with intermediate oxygen properties.

We think this unifying concept may stimulate new approaches for in-depth study of various forms of surface oxygen, as well as their role in oxidation catalysis.

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Disclosure statement

The authors declare no competing financial interest.

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