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The Chemisorption of Oxygen and the Oxidation of Carbon Monoxide on Metals

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Data on the chemisorption of oxygen on a number of metals (Pt, Pd, Ir, Ru, Ni, etc.), obtained by SED, EAS, XES, etc., have been reviewed. The bond energies and principal properties of the two types of O_{ads} on metals (non-reconstructive and reconstructive), and also the conditions for the realisation of each type of adsorption, have been examined.
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I. INTRODUCTION

The nature of the chemisorption compounds, the energy of the bonds formed, and hence the mechanism and kinetics of the reactions depend on the chemical composition and structure of the metal surface. Many authors[1-3] have noted a similarity between the properties of chemisorption compounds and complex compounds or oxides, carbides, and nitrides. For example, in the chemisorption of oxygen, a whole series of compounds may be formed, from molecular forms to three-dimensional oxides. The heats of adsorption of the molecular forms O_{2ads} are 40–50 kJ mole^{-1}; their desorption temperature is low, T_{des} = 120–150 K; and the reactivity of O_{2ads} is low.[4] The forms of greatest interest for catalysis on metals are adsorbed atomic forms of oxygen at degrees of covering less than a monolayer, which are present on the surface at the temperatures of "real" catalysis (300–800 K).

One of the most important questions is whether the chemisorption of oxygen atoms takes place on the surface or whether they are inserted into the surface layer, with a simultaneous displacement of the metal atoms. The possibility of adsorption in the non-reconstructive (type I) or reconstructive (corrosion) (type II) forms was examined in Ref.1. Subsequently, as a result of the development of physical methods for studying surfaces (slow electron diffraction (SED), electronic Auger spectroscopy (EAS), X-ray electron spectroscopy (XES), thermal desorption (TD), low-energy electron characteristic loss spectroscopy, etc.), this question was discussed by a large number of authors. As emphasised by Boreskov,[5] "in a solid catalyst–reactant system, transformations are undergone not only by the reactants under the influence of the catalyst, but also by the catalyst as a result of chemical interaction with the reactants". The reaction medium will obviously have a greater effect on the catalyst when at least one of the reactants under the reaction conditions is chemisorbed in the reconstructive form (type II). Thus the phenomena of catalytic corrosion have been related to reconstructive adsorption.[6] The nature of the chemisorption (type I or II) apparently influences the reactivity of the species and the form of the kinetic relationships describing the adsorption and the catalytic reaction.

The present review examines data on the influence of the nature and structure of the surface on the state of adsorbed oxygen species and the oxidation of CO on a number of metals (Pt, Pd, Ir, Ru, Ni), obtained by SED, TD, and electron spectroscopy.

On all the above metals, carbon monoxide is adsorbed in molecular forms (linear and bridged) with approximately identical heats of adsorption ΔH between −100 kJ mole^{-1} and −150 kJ mole^{-1}; the influence of the structure of the surface is even stronger than the influence of the nature of the metal. The bond between CO and the metals is a donor–acceptor bond. Photoelectron spectroscopy (PES) has shown[7,8] that the CO_{ads} molecules are joined to the metal through the carbon atom and are arranged at right angles to the surface.

On the other hand, the energies of the bonds formed by oxygen with the above metals vary from 180–220 kJ mole^{-1} (Pt) to 500 kJ mole^{-1} (Ni). This indicates that a decisive role in the change in the catalytic activity in this series of metals is played by the change in the bond energy and state of the adsorbed oxygen. In the present review, therefore, particular attention is paid to the chemisorption of oxygen on metals.

II. MECHANISM OF THE ADSORPTION OF OXYGEN ON METALS

When oxygen is chemisorbed on the surface of metal single crystals, the O_{ads} atoms are not arranged randomly, but form definite structures. The diffraction patterns obtained by SED may result from the scattering of electrons on ordered oxygen atoms on the surface (adsorption of type I) or on metal atoms which have undergone ordered displacements on reconstructive (corrosion) chemisorption (adsorption of type II). It can also be said that in chemisorption of type II, surface oxides are formed, since a mixed layer consisting of oxygen and metal atoms is produced.

In the nineteen-sixties, on the basis of the concept of the once-only scattering of electrons (the kinematic theory of diffraction), it was concluded[9] that the adsorption of oxygen on nickel is reconstructive, for example, it was assumed that in the structure Ni(100)–c(2 × 2)O, every second nickel atom is replaced by an oxygen atom. Later calculations[10] carried out in accordance with the complete program of the dynamic theory of diffraction, that is with allowance for multiple scattering of the electrons, led to a model of the adsorption of type I in which the oxygen atoms are situated at a distance of 0.9 Å above the metal. This adsorption scheme, however, is not consistent with the data obtained by other methods, for example ion-neutralisation spectroscopy.[11] Thus in Ref.12

it was noted that the c(2 × 2)O structure can probably be produced in adsorption of both type I and type II.

Criteria for establishing the type of adsorption may be provided by the following data: 1) the change in the work function: $\Delta\phi \cong 0.5-1.0$ eV for adsorption of type I, and $\Delta\phi < 0$ eV for adsorption of type II; 2) the form of the EAS spectrum, namely the change in the ratio of the peaks in the Auger spectrum of oxygen. Thus the Auger spectrum of oxygen in the Ni(111)–(2 × 2)O structure practically consists of two peaks, whereas for reconstructive chemisorption and for oxygen in nickel oxide, the Auger spectrum shows three peaks: KL_1L_1, KL_1L_2, and KL_2L_2; 3) the temperature dependence of the intensity of additonal reflections. For reconstructive adsorption, this relationship approximately coincides with the temperature dependence of the principal reflections, for example for the structure W(100)–(2 × 1)O, whereas for non-reconstructive adsorption in the (4 × 1)O structure there is a sharp decrease in intensity with increase in temperature, due to the production of disorder in the adsorption layer.[13]

1. The Chemisorption of Oxygen on Pt, Pd, Ir, Ru, and Ni

a) Adsorption on nickel

According to EAS data, the kinetic curve for the adsorption of O_2 on the (111), (110), and (100) faces of Ni at 300 K consists of two main regions:[14,15] the first corresponds to rapid chemisorption, and the second is associated with the nucleation of isolated regions of the phase NiO (induction period) and the subsequent growth of the isolated regions to form a continuous NiO film with a thickness of 2–3 monolayers.

A detailed study of the kinetics of the chemisorption of O_2 at a low pressure ($p(O_2) = 2 \times 10^{-7}$ Pa) on Ni(100) at 433 K showed[15] that after the p(2 × 2)O structure is completely filled with oxygen; a slight induction period is observed, followed by an increase in the rate of chemisorption with the growth of the isolated regions of the c(2 × 2)O structure. The topochemical character of the kinetics of the chemisorption with the formation of the c(2 × 2)O structure, analogous to the kinetics of the formation of NiO, indicates that the adsorption in this case is reconstructive, that is a two-dimensional oxide is formed. To investigate the nature of the adsorption when the Ni(100)–c(2 × 2)O structure is formed, oxygen was adsorbed at 170 K to a degree of covering $\theta = 0.5$.[16] A structure was not formed, but the work function increased by 0.5 eV. Next, the crystal was stepwise heated to 600 K. Formation of the c(2 × 2)O structure at 250–300 K was accompanied by a decrease of the work function by 0.3 eV in comparison with that of a clean Ni(100) surface. It may be noted that the "order–disorder" transformation in layers of type I does not lead to a change in the work function. This was shown in analogous experiments[17] for the non-reconstructive adsorption of oxygen on an Ru(0001) face. Thus the decrease in the work function when the Ni(100)–c(2 × 2)O structure is formed must be due to the insertion of O_{ads} into the lattice, that is to the formation of a layer of type II.

It was found qualitatively (visual estimation) that there is no significant decrease in the intensity of the SED pattern on p(2 × 2)O and c(2 × 2)O when the crystal is heated to 700 K. It was recently found[18] that disorder is produced in the Ni(100)–c(2 × 2)O structure only at 900 K, and that simultaneously, judging from the EAS data, oxygen disappears from the surface, that is the production of disorder in the layers of this type is due to the breakdown of the lattice (2D) of the oxide and the solution of oxygen in the bulk of the metal.

Quantum-chemical calculations by the generalised valence bond method[19] led to the conclusion that two states of oxygen can exist on an Ni(100) surface: in the first, radical-like state (O^-_{ads}), the oxygen atom is at a distance $d = 0.9$ Å from the surface (adsorption of type I), and in the second state (O^{2-}_{ads}) the oxygen atom of the surface oxide is at distance $d = 0.23$ Å from the surface (adsorption of type II). The oxygen bond energy in state II is 60 kJ mole^{-1} greater than that in state I. State I is possibly produced on Ni(100) at $T \leq 250$ K, and state II in the c(2 × 2)O structure. The change from O_{ads}(I) to O_{ads}(II) for a given degree of covering ($\theta = 0.5$) leads to appreciable suppression of the adsorption of CO.[20]

When O_2 is adsorbed on Ni(110), a succession of structures appears: (3 × 1)O, (2 × 1)O, (3 × 1)O again, p(9 × 4)O, and finally (100)NiO. Their ranges of existence are separated by short induction periods.[21] Ion-scattering spectroscopy showed[22,23] that the Ni(110)–(2 × 1)O structure consists of alternating (at intervals of one) rows of nickel atoms, as suggested in Ref. 9.

Fig. 1 gives a representation of the structural transformations taking place when O_2 is adsorbed on Ni(111).[24] The start of adsorption at 300 K gives the (2 × 2)O structure, in which oxygen is probably adsorbed according to type I, since the Auger spectrum differs from that of oxygen in NiO, the work function increases by 0.5 eV on adsorption, and the temperature at which disorder is produced in the layer is 480 K. The production of disorder in the layer is accompanied by the reversible transfer of some of the O_{ads} into the

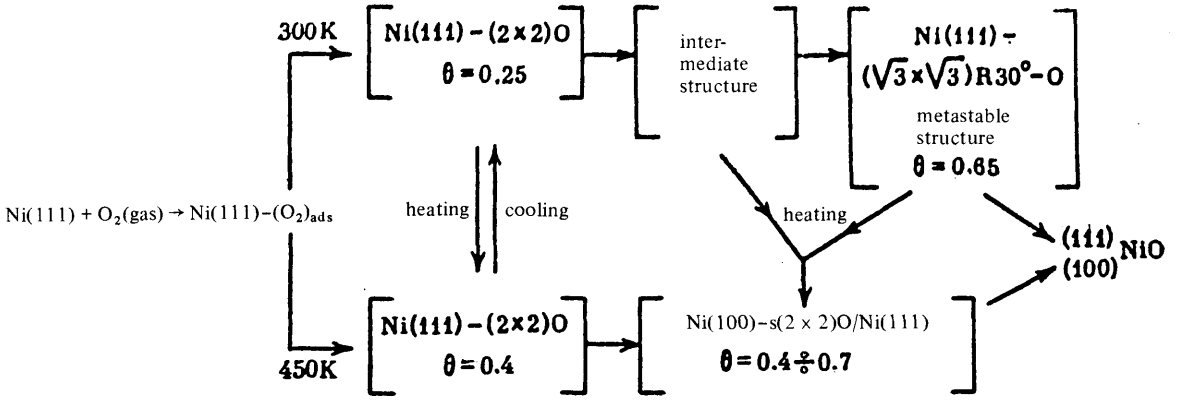


Figure 1. Structural transformations when O_2 is adsorbed on Ni(111).

surface region. With increase in the degree of covering ($\theta = 0.65$) at 300 K the structure ($\sqrt{3} \times \sqrt{3})R30°$–O appears. This structure is metastable, since on heating to 450 K it is transformed irreversibly into Ni(100)–c(2 × 2)O//Ni(111), that is for adsorption of type II, "reorientation" of the surface oxide into the most favourable configuration is possible, as a result of which the structure of the layer is the same, namely c(2 × 2)O on the (100) and (111) faces. A similar "reorientation" of the Ni(111) face was observed when sulphur is adsorbed.[25]

b) Adsorption on ruthenium

Oxygen adsorbed at 300 K on Ru(0001) is desorbed at T_{des} = 1200–1300 K; E_{des}/kJ mole^{-1} = 400 – 80 θ.[17,26] EAS has shown, however, that heating even at 400–600 K leads to an irreversible decrease in the magnitude of the Auger peak of oxygen. This can be attributed to the conversion of $O_{ads}(I)$ into the surface-oxide state (adsorption of type II) and the resulting shielding of the oxygen atoms by the ruthenium atoms and increase in the effective charge on the oxygen atom. The equation and kinetic constants were obtained for the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$. The activation energy of this transformation is ~20 kJ mole^{-1}. The formation of $O_{ads}(II)$ leads to a decrease in the subsequent adsorption of carbon monoxide in the layer.[26,27]

c) Adsorption on iridium

The principal adsorption properties of the (111) and (110) faces of Ir have been described.[28] A clean Ir(110) surface, which has the (1 × 2) structure, after several oxygen adsorption and thermal desorption cycles is rearranged to give a (1 × 3) structure, due to micro-facetting of the surface by (111) faces.[29]

When O_2 is adsorbed on Ir(111), a (2 × 2) diffraction pattern is observed, due to the existence of (2 × 1)O domains with three orientations, since $\theta = 0.5$.[30] EAS data and contact potential difference measurements indicate that the adsorption of oxygen on Ir(111) is of type I. The development of the (2 × 2) structure on the Ir(111) face is delayed relative to adsorption, indicating that adsorption takes place on any surface centres, after which ordering of the layer takes place as a result of lateral interaction between the O_{ads} atoms. Calculation of the energy of the lateral interaction from the temperature of the production of disorder in the (2 × 2)O layer (T_c = 480 K) in the Bragg–Williams approximation gave the value 4–8 kJ mole^{-1}.[30]

At $T \geqslant 450$ K on Ir(110), a non-stoichiometric surface oxide is formed,[14,28,29] and the (110)–(1 × 3) structure is converted into (110)–(1 × 1)O. The activation energy of the transformation is ~80 kJ mole^{-1}. As on Ni and Ru, on Ir the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ leads to a decrease in the heat of adsorption of carbon monoxide (by ~30 kJ mole^{-1} according to Ref. 31).

d) Adsorption on platinum

On Pt(111) and on a stepped surface Pt(s), oxygen is adsorbed in the (2 × 2)O structure. In the initial stage on Pt(s), the structure 2(1D)O is formed, that is the atoms are adsorbed on platinum steps with intervals of one atom. The activation energy of desorption E_{des} = 240 – 50 θ kJ mole^{-1}.[32]

The temperature dependence of the intensity of the (1/2, 1/2) reflections showed (curve *2* in Fig. 2*a*) that complete disordering of the (2 × 2)O layer on Pt(111) takes place even at 420 K.[33] For Pt(s), the graph consists of two regions (curve *3* in Fig. 2*a*): a region corresponding to a sharp decrease in the intensity of the reflections of the (2 × 2)O layer on terraces, similar to curve *2* for Pt(111), and a region corresponding to a relatively weak temperature dependence, associated with "bands" of the 2(1D)O structure, which pass through the positions of the (1/2, 1/2) reflections. Since the oxygen adsorbed on the steps in the 2(1D)O structure does not undergo disordering up to the desorption temperature, the adsorption on the steps is apparently reconstructive (type II).

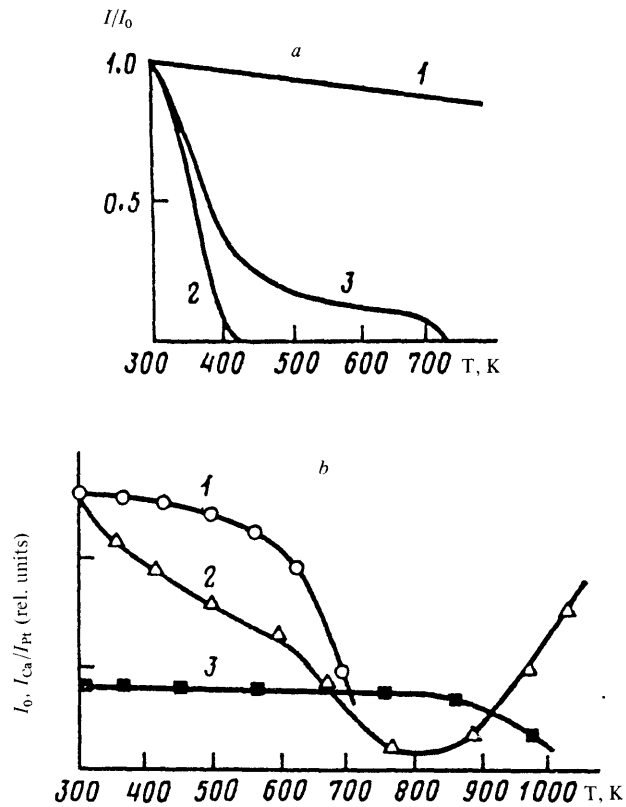


Figure 2. *a*) Temperature dependence of the intensity of the principal (1, 0) (*1*) and additional reflections of a layer of oxygen on Pt(111) (*2*) and Pt(s) (*3*); *b*) change in the magnitude of the Auger peak of oxygen on heating in a vacuum after the adsorption of O_2 on Pt at 300 K (*1*) and on heating in a flow of oxygen (*2*), and the temperature dependence of the concentration of calcium (*3*).

EAS has shown[34] (curve *1* in Fig. 2*b*) that when the (2 × 2)O layer on platinum is heated, no appreciable solution of oxygen takes place up to the desorption temperature, in contrast to the case of iridium[29] and rhodium.[35] If however platinum is heated in a stream of O_2 (curve *2*), then at high temperatures (800 K) the quantity of oxygen absorbed increases as a result of its solution in the surface layers of platinum. Thus the activation energy of the diffusion of oxygen in platinum is apparently greater than the activation energy of desorption. Thus in Ref. 36, the value given for the activation energy of the diffusion of oxygen in platinum is E_{diff} = 330 ± 100 kJ mole^{-1}. The formation and thermal stability of surface oxides of platinum may be influenced by impurities (Si, Ca).[37] Thus a calcium concentration corresponding to

1–2% of a monolayer at 300 K decreases when surface oxides are formed (curve *3*).

If a high concentration of oxygen is produced on a platinum surface, particularly on an "open" (321) face, the TD spectra, in addition to the usual broad O_{ads}(I) peak (second-order desorption), show a new narrow peak with T_{max} = 700 K, whose position remains unchanged with variation of the degree of covering, that is first-order desorption takes place.[38] The appearance of this peak may be related to the decomposition of surface (2D) oxides of platinum.

e) Adsorption on palladium

When O_2 is chemisorbed on Pd(111),[39] the (2 × 2)O structure is formed at 300 K, but disappears on heating in a vacuum to 600 K. Heating at $T \geqslant 600$ K in a stream of O_2 leads to saturation of the surface region with oxygen and to the reappearance of the (2 × 2)O structure, attributed[39] to the production of the surface oxide PdO. On thermal desorption, two oxygen peaks were observed: the first is due to the recombination of O_{ads} on the surface, and the second to the decomposition of the surface oxide.

In a PES study using synchrotron radiation,[40] the position of the O2*s* line indicated three states of oxygen, analogous to those found for platinum:[33] 1) O_{ads} on "smooth" regions of the Pd(111) surface; this is realised in "pure" form at 150 K; 2) oxygen inserted into the surface layer of the metal, apparently at points of structural breakdown (defects, etc.), this O_{ads} (type II, together with O_{ads} of type I) is observed on Pd(111) at 300 K; and 3) surface palladium oxides, formed at 600–700 K.

2. Properties of Adsorption Layers of Types I and II

The above data make it possible to put forward a general adsorption scheme. When oxygen reacts with metals, a succession of surface compounds is formed:[14]

$$M + O_2(gas) \rightarrow M{-}O_{2ads} \rightarrow M{-}O_{ads}(I) \rightarrow M{-}O_{ads}(II) \rightarrow MO(oxide)$$
$$O_{dissolved}$$

Several surface phases of types I and II may be formed. The data obtained make it possible to indicate the systems in which a given type of adsorption is realised. Oxygen is present in the non-reconstructive form at 300 K only on the most closely packed metal faces. As bulk analogues of the compounds formed it is possible to consider polynuclear complexes[41] for adsorption of type I, and metal oxides for adsorption of type II.

The "order–disorder" transformation in layers of type I is usually examined within the framework of the Ising model, for example in the Bragg–Williams approximation (an exact solution was found by Onsager only for $\theta = 0.5$)[42] or by modelling the situation on the surface by Monte Carlo methods.[43] The energy of the lateral interaction (the "direct" interaction via the metal atoms) for the layers of type I is 4–12 kJ mole^{-1}.[43]

Phase diagrams have been calculated.[44] It was assumed that the energy of repulsion is four times the energy of attraction ($\varepsilon_{nn} = 4\varepsilon_{nnn}$). Regions corresponding to p(2 × 2) and c(2 × 2) structures were distinguished on the phase diagram. The "order–disorder" transformation for the c(2 × 2) structures is smooth, that is with increase in temperature there is a gradual decrease in the degree of order in the adsorption layer.

The energy of disordering for the layers of type II is essentially the energy of the breakdown of the lattice of the surface oxide. It is apparently greater than 50 kJ mole^{-1}, so that disordering of these layers does not take place up to high temperatures (700–900 K). The conclusion[13] that adsorption in the W(100)–(2 × 1)O structure is reconstructive was recently confirmed[45] in a study of the production of this structure by SED, EAS, and contact potential difference (CPD) methods. At the same time, the sharp decrease in the intensity of the additional reflections with increase in temperature is not necessarily due to disordering of adsorption layers of type I. Thus the low temperature of disordering for the W(100)–c(2 × 2)H layer is related to the relative ease of the surface phase transformation (1 × 1) ⇌ c(2 × 2), since chemisorption with the formation of the c(2 × 2)H structure leads to the paired displacement of tungsten atoms relative to one another, that is it is reconstructive.[46,47]

The kinetics of adsorption in layers of type I with allowance for the interaction of the species in the quasi-chemical approximation and adsorption in the pre-adsorption state have been examined.[48] It was shown that the adhesion coefficient (s) is a maximum at $\theta = 0$, and that the subsequent course of the $s = f(\theta)$ curve depends on the energy of the interaction between O_{ads} and on the heat of adsorption in the pre-adsorption state. The kinetic curve for adsorption in layers of type II, if is is topochemical in character, may show an induction period, so that *s* at first increases with increase in the degree of covering.[15]

3. The Energy of the Bond Formed by Oxygen in States I and II with a Metal

Published data[1,49] and data obtained in a study of the adsorption of O_2 on metal single crystals have been used to obtain the dependence of the heats of adsorption of oxygen in the molecular form $\Delta H[(O_{2ads})]$, the non-reconstructive form $\Delta H[O_{ads}(I)]$, and the reconstructive form $\Delta H[O_{ads}(II)]$ on the heats of formation of the three-dimensional oxides ΔH_{oxide} of the corresponding metals.[50] Fig.3 shows that for most metals, the points corresponding to reconstructive adsorption lie on a straight line with a slope of 1. The fact that the heats of adsorption of O_{ads}(II) and the heats of formation of the oxides are approximately equal provides weighty evidence in support of chemisorption of type II.

The heats of adsorption of oxygen in the intermediate non-reconstructive form cannot be estimated by the TD method for metals lying to the right of iridium on the ΔH_{oxide} scale. To characterise the surface complexes $M{-}O_{ads}$(I) it is necessary to use methods which do not destroy the state of the species, for example infrared spectroscopy or low-energy electron characteristic loss spectroscopy. For the adsorption of oxygen on Pt(111),[51] Rh(111),[52] Ru(0001),[53] and Fe(110),[54] the following values of the vibration frequencies of the metal–oxygen bonds were obtained (at 300 K for low exposures): 490, 520, 516, and 500 cm^{-1} respectively. The reactivities of oxygen adsorbed non-reconstructively on the metals studied apparently do not differ greatly. The temperature ranges of the kinetic curves for the formation of CO_2, obtained by heating mixed layers (O_{ads} + CO_{ads}) on platinum, iridium, and ruthenium are fairly similar.[50] The activation energies of this reaction in the adsorption layer are E_a = 36–44 kJ mole^{-1}, whereas the pre-exponential factor k_a^0 varies from 10^{-9} cm^2 molecule^{-1} s^{-1} (Pt) to 10^{-12} cm^2 molecule^{-1} s^{-1} (Ru). The slight decrease in k_a^0 in the series Pt–Ru is apparently due simply to an increase in the rate of the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ when the crystals are heated.

Naturally, the vibrational frequencies and reactivity provide only an indirect characteristic of the $M{-}O_{ads}$ bond energy. In the series Ir–Ni, the heat of adsorption in the

non-reconstructive state $O_{ads}(I)$ possibly increases in the position of maximum coordination.

Adsorption of type I is thermodynamically more favourable in the series Ag–Ir. For Ru, Ni, Co, and other metals, the principal state is $O_{ads}(II)$, but at low degrees of covering on the most closely packed faces, the existence of reactive oxygen in the intermediate state $O_{ads}(I)$ is possible, and the oxygen atoms may not be in the position of maximum coordination.

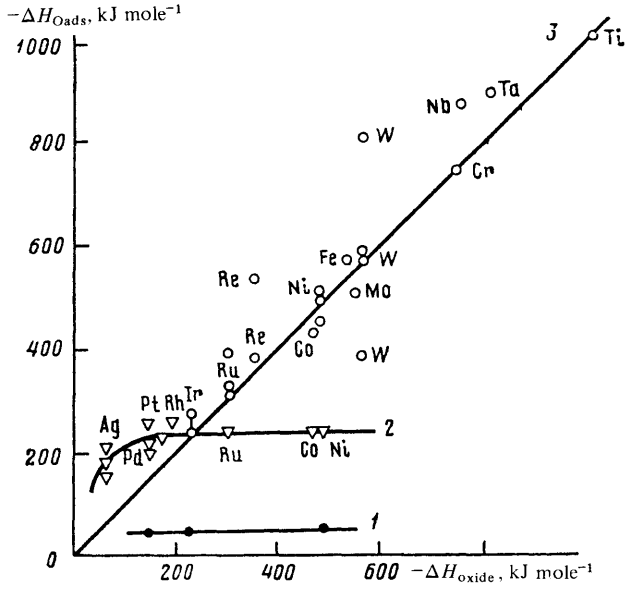


Figure 3. Plots of the heats of adsorption in the molecular (*1*), non-reconstructive (*2*), and reconstructive (*3*) forms against the heats of formation of the oxides of the corresponding metals.

The possibility of the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ depends on the energy of both the bonds being broken and the bonds being formed, and, in the general case, on the difference $\Delta H[O_{ads}(II)] - \Delta H[O_{ads}(I)]$. With decrease in the coordination number of the metal atoms in the series of structures: bulk (3D)–plane (2D)–step (1D), the heats of formation of the corresponding oxides apparently increase in the order:

$$|\Delta H[(1D)\text{oxide}]| > |\Delta H[(2D)\text{oxide}]| > |\Delta H[(3D)\text{oxide}]|$$

The insertion of an oxygen atom into a metal layer, that is the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$, is accompanied by an increase in the effective charge on the atom, and its state changes from the radical-like state $O^{\delta-}_{ads}$ [19,55] to the state of oxygen in the surface oxide O^{2-}_{ads}. [19,40]

III. THE OXIDATION OF CARBON MONOXIDE ON METALS

The investigation of the relationship between the kinetic and thermodynamic parameters of adsorption and heterogeneous-catalytic reactions is an important problem in the theory of heterogeneous catalysis.[56–58] The existence of a correlation between the heat of adsorption of oxygen and the catalytic activity of oxides in total oxidation reactions has been established.

The plot of the rate of the oxidation of CO against the energy of the bond formed by oxygen (Fig.4) is a curve with a maximum corresponding to the platinum group metals,[50] in agreement with the change in the rate of adsorption and the efficiency of the reaction in the same metal series.[59]

On metals for which the energy of the $M-O_{ads}$ bond is low (Ag, Au), the limiting stage is apparently the adsorption of oxygen. Thus a recent ESCA study[60] of the adsorption of oxygen on silver films (at an oxygen pressure up to 10 Pa) showed that the adsorption on the silver surface takes place with a low accommodation coefficient $s \cong 10^{-3}$ in a state characterised by a high reactivity towards CO (the efficiency of the reaction is close to 1). This agrees with published data.[61,62]

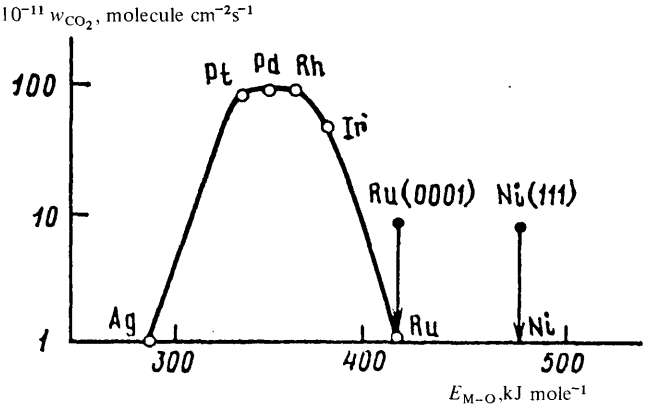


Figure 4. Plot of the rate of oxidation of carbon monoxide (520 K, $p(O_2) = p(CO) = 1 \times 10^{-5}$ Pa) against the energy of the bond formed by oxygen with metals; black points—catalytic activity of Ru(0001) and Ni(111) under non-stationary conditions.

For metals lying on the right-hand branch of the curve in Fig.4, the limiting stage is the reaction of CO with O_{ads}. Thus the adhesion coefficient of oxygen on Ru(0001) is 0.4, whereas the reaction rate at 520 K and $p(O_2) = p(CO) = 1 \times 10^{-5}$ Pa in the reaction mixture is only 2×10^{11} molecule cm^{-2} s^{-1}. [17] In Ref.63, the reaction rate on Ru(0001) under stationary conditions could not be measured at all ($w \leq 10^{11}$ molecule cm^{-2} s^{-1}). Under stationary reaction conditions at pressures of oxygen and carbon monoxide of 1.3×10^{-5} Pa on Ni(110), a layer of nickel oxide is formed.[64] Since it is highly endothermic ($\Delta H_p = 85$ kJ mole^{-1}), the reaction of CO_{ads} with O_{ads} on nickel takes place at a measurable rate only at temperatures above 600 K. The right-hand branch of the curve in Fig.4 agrees approximately with published data[65] which show that the rate of the oxidation of hydrogen decreases by a factor of 10^2 on going from platinum to nickel.

An interesting feature is that under certain conditions at low temperatures, Ru(0001) and Ni(111) show a high but unstable activity (Fig.4).

1. The Influence of the Transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ on the Activity of Ru, Ni, and Co

On the Ru(0001) face after a constant flux of the reaction mixture has been established ($p(O_2) = p(CO) = 1.3 \times 10^{-5}$ Pa)

with smooth increase in temperature (~1 K s^{-1}) from 300 K and above the formation of CO_2 is observed.[63,66] Fig. 5 shows that the reaction rate is a maximum at 470 K. The catalytic activity is not constant, however, since keeping the specimen at any temperature leads to a decrease in the reaction rate. As already noted, oxygen is adsorbed on Ru(0001) at 300 K in a reactive form (type I), which on heating is converted into a surface oxide (type II), leading to the suppression of the catalytic activity. The kinetics of oxidation of CO on Ru(0001) have been described using the observed rate constants for the stage of the adsorption of O_2 and CO, the reaction O_{ads} + CO_{ads}, and the stage corresponding to the irreversible transformation $O_{ads}(I) \rightarrow O_{ads}(II)$.[66]

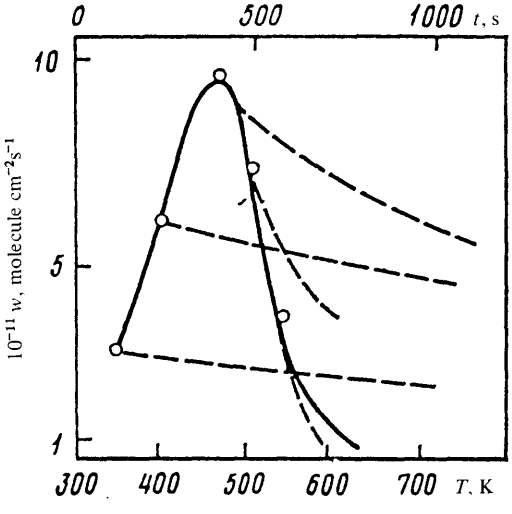


Figure 5. Temperature dependence of the rate w of formation of CO_2 on the Ru(0001) face for a specimen heated at a rate of 1 K s^{-1}. The points correspond to the specimen heated at the given temperature, and the broken lines correspond to the change in w with time.

When Ni(111) is cooled slowly from 800 K or kept under isothermal conditions at 450–500 K in the reaction mixture (5% O_2) a "burst" of catalytic activity is observed during the phase transformation Ni(111) → NiO.[14,67] In the case of Ni(100) under the same conditions, this "burst" is not observed. It is possible that on Ni(111) the reaction involves $O_{ads}(I)$, and that the surface region before the "burst" is gradually saturated with dissolved oxygen, preventing the diffusion of $O_{ads}(I)$ into the volume, so that the activity increases. The subsequent decrease in catalytic activity is due to the formation of a surface oxide. Essentially analogous data have been obtained[68] for the Co(0001) face.

Thus for metals such as Ru, Ni, Co, etc., the initial high catalytic activity associated with the production of $O_{ads}(I)$ gradually decreases as a result of the conversion of $O_{ads}(I)$ into the surface-oxide state (type II), in which the oxygen is unreactive under the given conditions.

2. The Oxidation of CO on Metals of the Platinum Sub-group

The oxidation of CO on metals of the platinum sub-group, which have a high catalytic activity under stationary conditions, can be considered.

a) Titration of the adsorbed oxygen with carbon monoxide

The (111) and (110) faces of a single crystal of Ir show a high specificity in the titration, that is the differences between the faces are extremely marked. Thus on Ir(111) the initial rate of the titration (w^0) is low at 300–400 K [69] and with increase in temperature it increases in proportion to the decrease in the intensity of the reflections of the (2 × 2)O structure, that is the degree of disorder in the (2 × 2)O layer. On an Ir(110)–(1 × 3) surface micro-faceted by (111) faces, the initial rate remains high ($w^0 \cong 10^{12}$ molecule cm^{-2} s^{-1}) at 300–400 K, that is at temperatures below the temperature at which disorder is produced in the (2 × 2)O layer. Thus on Ir(111) the reaction requires thermal disordering of the layer, whereas on Ir(110)–(1 × 3) the structure of the surface itself plays the role of the factor producing structural disorder. The high value of w^0 on Ir(110), from the viewpoint of formal kinetics, can be described in terms of the Eley–Rideal mechanism with E = 2–4 kJ $mole^{-1}$, although in fact the reaction takes place in the adsorption layer,[70–72] possibly with the participation of oxygen adsorbed on the edges of the micro-facets.

If the stream of CO is interrupted during the titration of O_{ads} on iridium and on a stepped platinum surface Pt(s), heating the specimen gives CO_2 as a result of the reaction O_{ads} + CO_{ads}.

For Ir(111), one "low-temperature" α-CO_2 peak is observed. Conversion of the temperature dependence of the rate of formation of CO_2 at this peak to a straight line in the coordinates $\lg w/[O][CO] = f(1/T)$ gives the values of the constants E_a = 44 kJ $mole^{-1}$, $k_a^0 = 10^{-10}$–10^{-11} cm^2 molecule^{-1} s^{-1}. For Ir(110)–(1 × 3), two peaks are observed: an α-CO_2 peak with constants close to those found for Ir(111), and a "high-temperature" β-CO_2 peak, which can probably be related to oxygen introduced into the metal in the "valleys" of the micro-facets.

For a stepped platinum surface,[73] the following values were obtained: for α-CO_2, E_a = 40 kJ $mole^{-1}$, $k_a^0 = 10^{-3}$ cm^2 molecule^{-1} s^{-1}; for β-CO_2, E_a = 80 kJ $mole^{-1}$, $k_a^0 = 10^{-6}$ cm^2 molecule^{-1} s^{-1}. The β-CO_2 peak can be assigned to the reaction of CO_{ads} with oxygen reconstructively adsorbed on the steps of the surface. Thus it has been shown[33] that the oxygen in the 2(1D)O structure on Pt(s) is less reactive than the $O_{ads}(I)$ on the terraces. Field-emission microscopy[74] previously showed that the reaction of CO with O_{ads} on platinum points, the surface of which consists chiefly of "open" faces and faces with a high density of steps, takes place at temperatures of 400–500 K, in agreement with the temperature range of β-CO_2 formation. In the region of the Pt(201) faces, the boundary of the reaction was gradually displaced.

b) The oxidation of CO under stationary conditions

The kinetics of the oxidation of CO on Ir(110) and platinum can be described by a two-path scheme (Langmuir–Hinshelwood and Eley–Rideal mechanisms) using the observed rate constants of the separate stages.[14,75] Agreement between the calculated (curve *1* in Fig. 6) and experimental temperature dependence of the reaction rate could be achieved only if it was assumed that the activation energy of the desorption of CO corresponds to the most firmly bound form β-CO_{ads}, indicating the importance of the presence of steps (defects) for the reaction on metals of the platinum group. It can be seen from Fig. 6 (curve *2*) that the increase in the rate over the range 480–525 K is effectively described by the Langmuir–Hinshelwood mechanism alone; the introduction of the Eley–Rideal mechanism is required to describe the reaction at

higher temperatures. It follows from the SED data at $T \geqslant 500$ K, however, that the Ir(110)–(1 × 3) surface is transformed into a surface oxide Ir(110)–(1 × 1)O, leading to a change in the constants for all the stages and to the appearance of hysteresis on going from the "forward" to the "reverse" change in temperature.

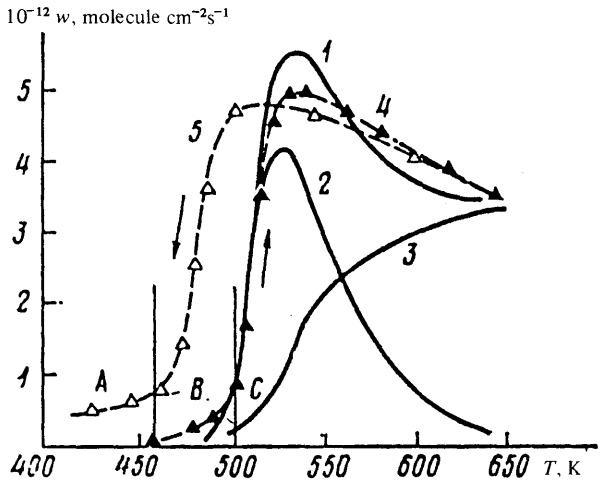


Figure 6. Temperature dependence of the rate of oxidation of CO on Ir(110) under stationary conditions (treatment for 5 min at each point; $p(O_2) = 1.6 \times 10^{-5}$ Pa, $p(CO) = 6.7 \times 10^{-6}$ Pa); *1–3*) calculated curves: *1*) overall rate, *2*) rate for the Langmuir–Hinshelwood mechanism, *3*) rate for the Eley–Rideal mechanism; *4, 5*) experimental curves: *4*) on heating, *5*) on cooling. The ranges of existence of the structures (1 × 3), 2(1D)O, and (1 × 1)O are denoted by the letters *A*, *B*, and *C* respectively.

On platinum in an excess of oxygen, for example at $p(O_2)/p(CO) = 5$, ($p(CO) = 2.6 \times 10^{-6}$ Pa), under stationary conditions (time of treatment at each point 5 min), hysteresis is also observed for the "forward" and "reverse" change in temperature (Fig. 7*a*).[73] This hysteresis is not truly kinetic in character, due to non-linearity of the stages involving the adsorption of O_2 and the reaction in the adsorption layer, as assumed in Ref. 76, since decrease in temperature from different initial points of the curve for the "forward" change in temperature gives different curves for the "reverse" change.[73] The hysteresis is evidently related to a change in the state of the oxygen on platinum.

Preliminary solution of oxygen at $T \approx 800$ K (see Fig. 2*c*) has no influence on the course of the $w = f(T)$ curves. Thus the hystersis is related to surface processes. Figs. 7*b* and 7*c* give the titration curves for oxygen adsorbed on platinum under stationary reaction conditions, obtained after the flow of oxygen had been stopped. Stopping the flow of O_2 at 430–460 K (Fig. 7*b*) leads to a sharp decrease in the rate, but at $T \geqslant 500$ K the curves are flat. The concentrations of O_{ads} obtained from the titration curves at 445 K are less than 10^{12} atom cm^{-2}, and at 600 K the value obtained was $\sim 5 \times 10^{13}$ atom cm^{-2}. The order of magnitude of the last value ($\theta = 0.05$) agrees with the density of steps. Under stationary reaction conditions at 500–600 K and during the titration (flat regions), the SED patterns show "bands" of the 2(1D)O structure. On cooling (see Fig. 7*c*), the proportion of flat regions on the titration curves, and the stationary concentration of inserted O_{ads}(II), are much greater than those for the "forward" change (Fig. 7*b*).

Thus at 300–400 K, the CO_{ads} molecules apparently block the Pt(s); at 400–460 K, the desorption of β-CO_{ads} liberates the steps on which O_2 dissociates, and the O_{ads}(I) form reacts immediately with CO_{ads}. At $T \geqslant 480$ K, as a result of the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$, the reaction no longer takes place on the steps (defects), but on the one-dimensional platinum oxide (1D)O.

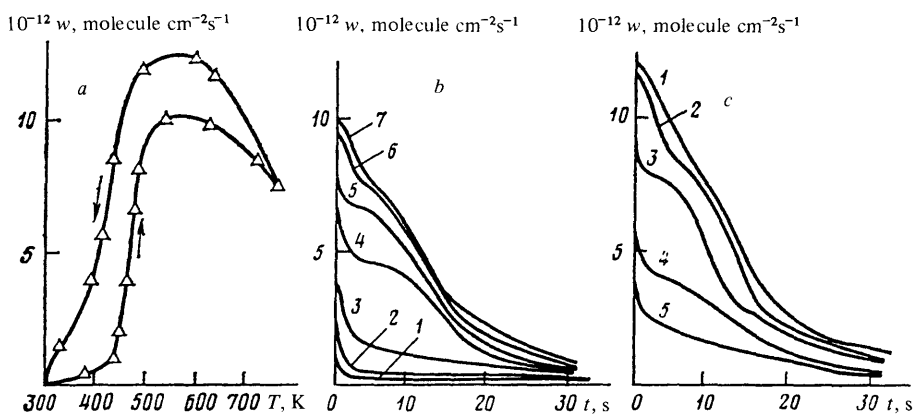


Figure 7. *a*) Temperature dependence of the rate of the oxidation of CO on platinum foil under stationary conditions ($p(O_2) = 1.3 \times 10^{-5}$ Pa, $p(CO) = 2.6 \times 10^{-6}$ Pa; *b*) titration curves for oxygen adsorbed under stationary reaction conditions (*a*), obtained after switching off the stream of O_2 during the "forward" change in temperature (heating). Temperatures of the titration, K: *1*) 430, *2*) 445, *3*) 460, *4*) 480, *5*) 495, *6*) 540, *7*) 600. *c*) The same for the "reverse" change in the temperature of the reaction (*a*). Temperatures of the titration, K: *1*) 535, *2*) 485, *3*) 450, *4*) 400, *5*) 340.

2. General Scheme for the Oxidation of CO on Metals

The equation for the reaction rate can be written in the following general form:[5]

$$w = k\mathrm{f}(c_i\theta_i)\,\varphi(c_i)\ .$$

The first term is determined by the stoichiometry of the active complex, and the second by the influence of the reaction medium on the properties of the catalyst. For the oxidation of CO, the set of stages determining the kinetics of the reaction on a non-changing surface (that is without allowance for the influence of the reaction medium) can be written as the four-stage scheme:[75-77]

$$O_2 + 2Z \xrightarrow{k_1} 2ZO \qquad (1)$$

$$CO + Z \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} ZCO \qquad (2)$$

$$ZO + ZCO \xrightarrow{k_3} CO_2 + 2Z \qquad (3)$$

$$ZO + CO \xrightarrow{k_4} CO_2 + Z \qquad (4)$$

Here, Z represents the adsorption centres on the metal surface. Stage (3) corresponds to the Langmuir–Hinshelwood mechanism, and stage (4) to the Eley–Rideal machanism. As already noted, the collision stage (4) in this model is introduced to describe the kinetics at high temperatures (see Fig.6), but oxidation of the metal already takes place under these conditions. In this scheme, ZO represents the radical-like[19,55] non-reconstructively adsorbed $O_{ads}(I)$.

The influence of the reaction medium ($\phi(c_i)$) is related to the oxidation of the metal in the stages:

$$ZO \xrightarrow{k_5} Z_{ox}O\,, \qquad (5)$$

$$Z_{ox}O + ZCO \xrightarrow{k_6} CO_2 + Z'_{ox} + Z\,. \qquad (6)$$

Here, Z_{ox} represents the centre of the surface oxide associated with $O_{ads}(II)$, and Z'_{ox} the same centre in the intermediate state after the removal of $O_{ads}(II)$ by reaction with CO_{ads} (stage (6)).

For metals such as Ru and Ni, the rate constants of stage (6) are low compared with k_3 and k_4, so that the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ (stage (5)) leads to the suppression of the catalytic activity.

For the platinum metals, the constants k_6 and k_3 do not differ so greatly.[73] Thus for Pt(s) the ratio of the rate constants for the reaction of CO_{ads} with $O_{ads}(I)$ and $O_{ads}(II)$ at 500 K is $k_3/k_6 = 10-10^2$, so that reaction is possible under stationary conditions. Oxidation of the metal naturally also changes the values of the constants of stages (1) and (2); the rates of the adsorption of O_2 and CO decrease slightly, and, which is more important, the heat of adsorption of CO_{ads} decreases; as a result, CO_{ads} blocks the surface at lower temperatures, and this is responsible for the hysteresis. Recently, a similar scheme (stages (1)–(6)) was used to obtain a quantitative description of the self-oscillations in the rate of the oxidation of carbon monoxide on platinum and iridium.[78,79]

Next, the displaced metal atoms (Z'_{ox}) formed in stage (6) apparently either return to their equilibrium position on the step (Z) or "roll out" on to a terrace, forming so-called adsorbed metal atoms Z_{ads}

$$Z'_{ox} \xrightarrow{k_7} Z\,, \qquad (7)$$

$$Z'_{ox} \xrightarrow{k_8} Z_{ads}\ . \qquad (8)$$

The appearance of thermodynamically unstable forms (Z_{ads}) under stationary conditions as a result of the heat of the reaction may have a significant influence on the catalytic properties of the metal.[80] The adsorbed atoms (or clusters) Z_{ads} can act as new "active centres" for the adsorption of O_2, bringing about a branched-chain process.[81] The heat of the reaction $O_{ads} + CO_{ads}$ on platinum is $\Delta H_p = -(30-50)$ kJ mole^{-1}, that is it is even lower than the energy of a single Pt–Pt bond (85 kJ mole^{-1}).[82] In view of the high rate of the dissipation of energy in the metal lattice, it is difficult to imagine that the reaction between CO_{ads} and $O_{ads}(I)$ can lead to the "ejection" of metal atoms, that is to the formation of Z_{ads}. In the case of reconstructive chemisorption, however, even at the stage of the insertion of oxygen into the layer of metal (stage (5)), displacement of platinum atoms (or at least a decrease in the strength of the Pt–Pt bond) takes place, so that the reaction stage (stage (6)) only facilitates the removal of platinum atoms. Thus the formation of $O_{ads}(II)$ is a necessary condition for the processes involved in the rearrangement of the surface.

Scanning microscopy has shown[83,84] that the oxidation of CO produces a marked change in the micro-relief of the surface of a platinum filament, although the adsorption of O_2 or CO alone has no significant influence on the surface. It is easy to imagine that if the rate of generation of Z_{ads} is high, and the rate of their diffusion over the terraces is low, then "loosening" of the surface will take place. If however the rate of diffusion is high, the Z_{ads} atoms will be able to migrate to the positions with minimum free energy, and completion of the most closely packed faces (facetting) will take place.

4. The Specific Features of the Faces in Catalysis and the Constancy of the Specific Catalytic Activity

The specific features of the faces and "active" centres in catalysis and the constancy of the specific catalytic activity have been examined.[5,14,59]

The rate of the reaction of H_2 with oxygen adsorbed in the Ni(111)–(2 × 2)O structure is 10–20 times the rate of the reaction with O_{ads} in the Ni(100)–c(2 × 2)O structure. The rearrangement of Ni(111) to the Ni(100)–c(2 × 2)O//Ni(111) structure, however, leads to approximately equal reactivities of oxygen on the two faces.[14,59]

The reaction of CO with O_{ads} on Ir(110) at 330 K is ten times that on Ir(111). In a reaction stream with relatively rapid heating of the specimens (~4 K s^{-1}), the Ir(110) to (1 × 3) face is 2.5 times more active than the Ir(111) face. Under stationary reaction conditions, surface oxides are formed, the Ir(110)–(1 × 3) surface at $T \geq 450$ K is rearranged to the (1 × 1)O structure, and the catalytic activities of the two faces become equal.[14,28,59]

Thus if under the reaction conditions (relative excess of CO, comparatively low temperatures) the oxygen on the surface is adsorbed as $O_{ads}(I)$, then the structure of the surface is important for the reaction, the steps act as "active" centres, and the actual reaction takes place via stages (1)–(4). At "high" temperatures with an "excess" of oxygen in the reaction mixture, $O_{ads}(II)$ is formed on the surface, stages (5)–(8) also take place, and rearrangement of the surface leads to the practical disappearance of the specific characteristics of the faces, that is the rule of approximate constancy of the specific catalytic activity is observed.

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Thus examination of the properties of the two most important types of adsorbed oxygen, namely the non-reconstructive (I) and the reconstructive (surface-oxide) (II) types, has made it possible to explain a number of phenomena of oxidative catalysis on metals in a single scheme.

This approach may be more general, since in addition to adsorption layers of type I (sulphur, nitrogen, carbon), surface sulphides, nitrides, and carbides are also known for metals.

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