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Review of the molar heats of chemisorption and chemabsorption by crystalline oxides and the surface "homogeneity versus heterogeneity" problem

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Abstract To obtain a solution of the surface "homogeneity versus heterogeneity" problem, the results of microcalorimetric measurements of the dependences of the molar heats of chemisorption and chemabsorption of different gases on the amounts of chemisorbed or chemabsorbed gases in more than 20 gas/metal-oxide systems, in which the molar chemisorption heats are coverage-independent over rather wide ranges of the surface coverages, are presented. In order to approach the states of the metal oxide samples to those in real catalytic processes catalyzed by these oxides, the coverage dependences of the heats of chemisorption of gases at the samples were measured for a number of gas/metal-oxide systems against the chemisorbed amounts of not only the gas under study but also of another gas chemisorbed previously. The calorimetric dataset is supplemented with data obtained by other methods capable of helping to solve the surface "homogeneity versus heterogeneity" problem. These data are discussed together with the data on chemisorption in more than 40 gas/metal systems for which homogeneity of the surfaces was stated in our previous review. The entire set of the measurements was published for several decades by about 40 different composite authors. The chemisorption and chemabsorption mechanisms are discussed. It is concluded that thermally stabilized powder metal and metal oxide surfaces are homogeneous relative to the chemical ability of their atoms in chemisorption and catalytic processes in line with Langmuir's opinion and the band theory of solids.

Keywords Catalyst-surface "homogeneity versus heterogeneity" problem · Chemisorption and chemabsorption mechanisms · Surface homogeneity of catalysts and chemisorbents

Introduction

The concept and origin of the surface "homogeneity versus heterogeneity" problem

The concept of the problem under consideration is as follows. In what way does a thermally stabilized surface of a solid of a definite chemical composition reveal itself in a stationary heterogeneous chemical process: as a homogeneous one, i.e., as a single whole or as a heterogeneous one, i.e., as a conglomerate of individual centers of different chemical activities? The homogeneity or heterogeneity is considered as a fundamental feature of crystalline solids rather than as an individual feature of some samples.

In the context of the science on chemisorption and catalysis, the following definitions can be formulated for the terms "surface homogeneity" and "surface heterogeneity".

The "surface homogeneity" term relates to the thermally stabilized crystal bodies, for which the differential heats of gas chemisorption are constant over a rather extended range of middle surface coverages. The "surface heterogeneity" term relates to the thermally stabilized crystal bodies, for which the differential heats (Q) of gas chemisorption decrease steadily over the range of middle surface coverages, this decreasing being associated with the proportional increasing in the activation energy (E) of chemisorption ($\Delta E = -\alpha \Delta Q$; $0 < \alpha < 1$). Therewith, gas chemisorption is considered as an individual process that is not associated with any other surface or body–surface

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processes. The values of the molar heats of chemisorption are considered as the indicator of the comparative reactivity of the surface centers in chemisorption and catalytic processes. It is important to accentuate that, from the viewpoint of description of the catalytic kinetics and chemisorption equilibriums and rates, the differential chemisorption heat behavior over the range of just middle surface coverages is especially important because, in the ranges $\theta \ll 1$ and $(1 - \theta) \ll 1$ (θ is the surface coverage), the available analytical equations deduced for heterogeneous surfaces transform to the corresponding equations deduced for homogeneous surfaces [1–3].

Langmuir postulated [4] that thermally stabilized surfaces of crystalline bodies are always homogeneous relative to their adsorption and catalytic ability; for multiphase catalysts, he left room for the occurrence of several types of homogeneous surface centers; therewith, he was the first to introduce the notion on heterogeneity (his term: amorphism) of surface centers, but he believed that the amorphism may be inherent in noncrystalline amorphous glasses only. The authors of work [5] believed that the geometric location of individual surface atoms influences their chemical activity, including their catalytic and chemisorption activity, and that the geometric heterogeneity of surface atoms, i.e., their locations at crystal tips, edges, or faces determines the degree of their chemical unsaturation, which, in its turn, determines their catalytic and chemisorption activity.

The importance and pendency of the problem

Solution of the surface "homogeneity versus heterogeneity" problem is important for: (1) revealing the common features in the nature of the catalytic and chemisorption actions of solids; understanding whether, under stationary catalysis, different crystal faces reveal their specificity or crystal surfaces are homogenized; (2) development of the catalyst preparation methods, analytical descriptions of the kinetics and equilibriums in gas/solid systems, and methods of industrial technological and reactor simulations; (3) practical needs of electronics; (4) understanding of a general physical and chemical problem relevant to crystals of a definite composition: whether the individual features of crystal atoms or the characteristics of the crystals as generalities determine the reactivity of the atoms at thermally stabilized surfaces.

In spite of the importance of this problem, it is not solved up to now by the following main reasons. First, as was shown in [6], the experimental data on the rates of chemisorption and on the equilibriums of chemisorption can be explained on the basis of the notion of either surface homogeneity or surface heterogeneity if data on the coverage dependences of the molar heats of chemisorption are absent. Second, the availability of questionable data on the chemisorption heats (along with the correct ones), which disorientates readers and initiates speculations. Third, deficiency in the number of critical reviews dedicated to the chemisorption heats and giving close attention to the technical and procedural problems inherent in the chemisorption and calorimetric measurements.

The occurrence in the literature of questionable data on the chemisorption heats is caused mainly by the smallness of the amounts of the heat (typically, no more than 0.2–0.5 J) and adsorbate (typically, 0.03–0.05 cm^3) to be measured in each experiment, by the possibility of side heat-evolving and heat-absorbing processes, such as surface–body diffusion of adsorbates and impurities, surface interaction between chemadsorbents and impurities, desorption of products of this interaction, sintering of the samples, chemisorption at glass and metal walls of adsorption apparatuses, and pressure dependence of the calorimetric sensitivity inherent in some calorimeters and difficulties in their elimination, and by poor standardization of the initial states of the solid samples (hereafter, the gas amounts are reduced to the normal conditions). In chemisorption studies at oxides, the possibility of specific interactions of adsorbed gases with surface oxygen and reduced metal atoms should be additionally considered. The side effects, which are possible in the course of the measurements of the molar heat effects of chemisorption and chemabsorption, and the methods for their elimination and consideration are analyzed in [7, 8]. The measurements of small heat effects in gas/solid systems under low gas pressures varying in time require a special undivided attention to calibration of calorimeters. Some specific features of calibration of microcalorimeters for chemisorption measurements are considered in [7]. In [9], it was shown that the calorimetric sensitivity of some purchasable microcalorimeters is the pressure-dependent in a field of low pressures. Such instruments are inapplicable for calorimetric measurements of chemisorption.

In this journal [10] and in [8], we recently considered the surface "homogeneity versus heterogeneity" problem as applied to the gas/metal systems and came to the conclusion that the thermally stabilized surfaces of metal powders, films, and supported metals are homogeneous; i.e., the molar heats of chemisorption are constant over a rather wide range of surface coverages. The list of available homogeneous gas/metal systems from [8] with the corresponding references is given below; it will be used for the general discussion.

Available gas/metal systems with the surfaces homogeneous in their chemisorption abilities.

H_2 at Fe [11–14], Fe/K_2O/Al_2O_3 [15, 16], Ni [17–19], Pt (black) [20], Pt/SiO_2 [21], Pt/W/SiO_2 [21], Pt [22], Pt (powder) [17], Ce, Dy, Lu, Er, Tm, and Yb [23], and W [24];

O_2 at Fe [25, 26], Ni [26], Pt/W/SiO_2 [21], Nb [26], W [26], Mn [26], Co [26, 27], Mo [26], Ta [26], Ti [26], Cu [28–31], Ag [32, 33], W/SiO_2 [21], and Au [34];
N_2 at Ni [35], Fe/Al_2O_3/K_2O [15, 36], and W [13, 37];
CO at Ni [19], Cu-component of ZnO/$Cu_4(OH_2)$/Al_2O_3 [38–40], Dy [41], and Ni, Ni/K, Ni/Cs, Pt, Pt/Rb, and Pt/Cs [42];
C_2H_2 at Pt [17, 43];
$H_3C–CCH$ at Pt [43];
$H_2C=CH_2$ at Pt (powder) [17].

Surface homogeneity is proved by many groups of authors for more than 40 gas/metal systems; for a number of the systems, surface homogeneity is shown repeatedly. In an absolute majority of these cases, the conclusions on the surface homogeneity are made on the basis of the direct calorimetric measurements performed at different constant temperatures, and several results are obtained by measurements of the chemisorption equilibriums and hydrogen thermodesorption.

The principal aim of this review consists in a solution of the surface "homogeneity versus heterogeneity" problem as applied to gas/metal-oxide systems. Some experimental data obtained by non-calorimetric methods and aimed at a solution of the surface "homogeneity versus heterogeneity" problem will be also considered. In conclusion of this review, the data presented in this review and in the review [10] published earlier in this journal and aimed at a solution of the surface "homogeneity versus heterogeneity" problem as applied to the thermally stabilized metal oxide and metal surfaces, respectively, will be discussed together.

The attendant aim of this review is that to demonstrate the not-popular unique and non-trivial results published in Russian and dedicated to calorimetric and chemisorption vacuum study of extremely slow multi-month reduction of oxides by successive very small H_2 (or other reducing gas) portions disjoint in time, with the control by the thermokinetic curves and the values of the molar heat effects and surface area and with measurements of desorbed water and chemabsorbed hydrogen in each experiment under conditions of continuous isothermal heating at regulated temperature levels and in such a way that the equilibrium within the solids is established in each experiment without formation of new phase and with measurements of the differential heats and rates of oxygen chemisorption in series of special experiments performed at different steps of reduction of oxides. These works were performed to approach the solid oxides to their states under different conditions of catalysis and to study these states and in order to clarify the mechanisms of reduction of oxides under conditions of very slow reduction.

Molar heats of chemisorption and chemabsorption of gases at crystalline oxides

General remarks

When the surface "homogeneity versus heterogeneity" problem as applied to the chemisorption and catalytic phenomena is being studied, the powder metal oxide samples should be carefully standardized. Namely, they should be freed completely of water, carbon dioxide, and other volatile components captured during the process of their preparation and the oxygen vacancies should be subjected after that to additional oxidation. The catalyst state after additional oxidation is termed by us "the standard state". The pellet size and the sample layer thickness should be minimized to exclude the non-uniformity in chemisorption along the pellet diameter and along the sample layer. Otherwise, the processes of body–surface diffusion of the impurities, their interaction with adsorbates, and desorption can cause side heat effects difficult-to-control and the big pellets and thick sample layers can cause a non-equal accessibility of the sample surfaces for gas chemisorption and, as a consequence, of the impossibility of obtaining of the correct information on the coverage dependences of the chemisorption heat. We consider the results obtained with small weights (usually, of about 1 g) of carefully standardized samples and under the conditions when not only chemisorption but also possible desorption of the products of the surface interactions in the course of the chemisorption experiments were carefully measured and taken into consideration in calculations of the molar heats of the processes under consideration.

Oxide catalysts and, on frequent occasions, chemadsorbents work under real conditions in the states of partial reduction of their surface layers and in the states when their surface layers contain chemisorbed or chemabsorbed particles of different chemical nature. For example, they can contain hydrogen, carbon, oxygen, and their chemically associated forms in chemisorbed states. Therefore, such measurements of the heats of chemisorption, in which surface and subsurface layers contain some known amounts of different chemical elements in chemisorbed and chemabsorbed states, are of special interest. Such states of chemadsorbents are achievable in experiments as a result of alternative measured chemisorption of different gases with careful analyzing and consideration of the possible products of desorption. The works in which the measurements of the heats of chemisorption were performed in such systems are rather rare, but they represent a special interest for understanding the catalyst states in the course of catalytic processes. We will see that calorimetric studies of such systems allow revealing of phenomena and mechanisms that are inaccessible by other techniques and obtaining principally new information relative to the mechanisms of chemisorption and to the "homogeneity versus heterogeneity" problem. The methods, including the apparatuses, techniques, and procedures, are detailed in [7, 8, 10, 28].

To take into consideration the contents of different chemical elements in catalysts during alternative chemisorption experiments and to study the chemisorption heats under the conditions when the contents of two or three chemadsorbates at catalysts are variable, we take that the oxygen, hydrogen, and carbon contents in the catalysts pretreated to their standard states are equal to zero. In the course of the subsequent chemisorption and desorption experiments, the samples chemisorbed H_2, O_2, H_2O, and CO_2 and desorbed H_2O and CO_2; therewith, the contents of the elements in the samples varied. During any experiment, the H_2 and C (gas) contents might be zero or positive ($\Delta H_2 \geq 0$ and $\Delta C \geq 0$) and the O_2 content might be zero, negative, or positive ($\Delta O_2 > 0$, $\Delta O_2 < 0$, or $\Delta O_2 = 0$), because the occurrence of chemabsorbed hydrogen in the samples increases the possible oxygen content in them over that characteristic for the standard state of the samples.

Pretreatment of each of the samples considered in this review is described in the corresponding papers (the corresponding references are given in the above list). Most of the samples were pretreated to the standard state. As an example, we present the Cr_2O_3 pretreatment procedure applied in [44–47]: (1) tableting of a Cr_2O_3 reagent weight of about 1 g; (2) calcination for 6 h in the air flow at 700 K and breaking; (3) heating of the 1–2 mm flakes in a Pyrex glass ampoule soldered with a vacuum apparatus (for 10 h at 773 K and 8 h at about 860 K) with a trap cooled to 77 K up to full cleaning of the biographic H_2O and CO_2 from the sample; (4) slow decreasing of the temperature for 4 h to about 620 K; (5) filling of the oxygen defects by O_2 at 4 hPa for 8 h at 620 K; (6) gentle deoxygenation of the volume over the sample through its repeated adjunction to degassed glass volumes; (7) soldering of the ampoule with the standardized sample without its contact with air to an adsorption-calorimetric vacuum apparatus.

At present, surface homogeneity is stated over wide ranges of surface coverage, at least, for the gas/metal-oxide systems listed below. The catalysts studied in the works under consideration represent either individual oxides or composed oxide systems; all they are applicable as catalysts or components of catalysts for corresponding chemical processes. For multicomponent systems, two or more levels of chemisorption heats are possible in the context of Langmuir's opinion [4] written back more than 90 years. All systems considered in this section were studied on the basis of adsorption-calorimetric techniques under isothermal conditions.

Available gas/metal-oxide systems with the surfaces homogeneous in their chemisorption abilities.

O_2 at Cr_2O_3 [44, 45] and CuO [48];
$H_2C{=}CHCOOH$ at V/Mo, V/Mo/Cu, V/Mo/P, and V/Mo/Cs oxides [49];
C_2H_4 at Co/Mg/Mo, Ni/Mg/Mo, Cu/Al_2O_3, Ti, and Ag oxides [50];
C_3H_8 at Co/Mg/Mo, Ni/Mg/Mo, Cu/Al_2O_3, Ti, and Ag oxides [50];
CO_2 at Cr_2O_3 [46, 47], $CuCr_2O_4$ [51, 52], and ZnO-component of $ZnO/Cu_4(OH_2)/Al_2O_3$ [38];
H_2O at Cr_2O_3 [44] and $CuCr_2O_4$ [51, 52];
H_2 at Cr_2O_3 [44–47], ZnO-component of $ZnO/Cu_4(OH_2)/Al_2O_3$ [38, 53] and NiO [54].

Below, the results of studies of concrete systems are shortly considered.

Chemisorption and chemabsorption of different gases by different oxides

Oxidized copper-containing systems as chemisorbents and chemabsorbents

We consider here the results of extensive studies of the chemisorption characteristics inherent in the oxidized and partially reduced forms of the finely dispersed $ZnO/2CuO/0.16Al_2O_3$ catalyst (the SNM-1 catalyst useable in its reduced form for the industrial processes of CH_3OH synthesis and shift reaction), CuO catalyst, and $CuCr_2O_4$ spinel catalyst [30, 31, 38, 40, 48, 51, 53–60].

First, we consider the partially reduced forms of the SNM-1 catalyst. The reduction was performed by small H_2 or CH_3OH vapor portions at a pressure of no more than several tens of Pascal and at temperatures no higher than 550 K for many months on a 24-h basis within a thermostat, with inter-experiment many-hour intervals necessary for establishing the surface/body equilibriums in the solids. As a result of such a treatment, different forms of partially reduced copper oxide were obtained (as three-dimensional intermediate phases) according to the equations [6, 30] (Fig. 1).

The water content in $Cu_4(OH_2)$ corresponds to the SNM-1 catalyst water content measured after its reduction under the conditions of the usual fore-exploitation treatment in an industrial reactor intended for the methanol synthesis [40, 61]. This correspondence evidently means that the Cu-component of the catalyst has the form of $Cu_4(OH_2)$ under industrial conditions of CH_3OH synthesis.

$$4CuO \xrightarrow{+1.25H_2-H_2O} Cu_4O_3\cdot 0.25(OH_2) \xrightarrow{+1.25H_2-H_2O} Cu_4O_2\cdot 0.5(OH_2) \rightarrow$$
$$\xrightarrow{+1.25H_2-H_2O} Cu_4O\cdot 0.75(OH_2) \xrightarrow{+1.25H_2-H_2O} Cu_4\cdot(OH_2)$$

Fig. 1 Mechanism of copper oxide reduction

Note that this is the unique case [30, 39, 40, 53], when the process of reduction for any oxide is studied up to almost metal state in such a way that the equilibrium states were achieved over the entire period of reduction; the process proceeded for many months to provide the equilibrium in the course of the reduction process. It was proved that the Cu-sublattice of CuO did not change over the course of the experiments; i.e., that the processes proceeded as H_2 chemabsorption and H_2O desorption from the chemabsored state, the H_2 chemabsorbed amount being higher than the H_2O desorbed amount. The experimental series on reduction with H_2 or CO alternated repeatedly with experimental series on oxidation by O_2. Each intermediate phase was identified through the constancy of the molar heats of O_2 chemisorption measured by direct experiments with O_2 and through the constancy of the molar heats of O_2 chemisorption calculated from the measured heats of reduction of the samples by H_2 with H_2O-vapor formation; the absence of phase transformations in the course of the treatment was also confirmed by the constancy of the internal surface area of the Cu-component (30 m^2/g) of the sample and by the absence of any dramatic changes in the rates of chemisorption of gases.

In [6, 30] the intermediates $Cu_4O_3{\cdot}0.25(OH_2)$, $Cu_4O_2{\cdot}0.5(OH_2)$, $Cu_4O{\cdot}0.75(OH_2)$ are termed the δ-, ε-, and ζ-oxyhydrates of copper, respectively, and the product $Cu_4{\cdot}(OH_2)$ is termed copper crystalline hydrate.

Neither H_2 nor CO are capable to reduce ZnO and Al_2O_3 under the conditions of these experiments. In [6, 30, 40], the initial oxidized state of the catalyst just before the experiments was termed "the S-state" (standard state), and the terminal reduced state of the catalyst, when its Cu-component was transformed to $Cu_4(OH_2)$, was termed "R-state" (reduced state). The copper crystalline hydrate has the Cu-substructure inherent in CuO, it is stable in vacuum of about 10^{-3} hPa at about 550 K. In the process of CH_3OH synthesis, catalyst "works" just in this state; this is proved in [38, 40, 60]. The copper hydrate has chemisorption characteristics inherent in metal copper; they are considered in [38, 40], and we only mention here that the $Cu_4(OH_2)$ surface is homogeneous. The chemisorption characteristics of the copper oxyhydrates are considered below.

It was stated that the chemisorption parameters for the process of O_2 chemisorption depend not only on the O-content but also on the H-content in the solid. The chemisorption heat and rate and the chemisorption capacity do not represent definite functions of the O-content in oxides but depend also on the H-content in them. The parameter that unambiguously determines the chemisorption characteristics of a solid is termed oxygen deficiency (*D*) [30, 62]. For the system under consideration, $D = 0.5\Delta H_2 - \Delta O_2$ (μmol/m^2), where ΔH_2 and ΔO_2 are the H_2 and O_2 contents in the catalyst relative to its S-state, respectively. This relation means that chemisorption or chemabsorption of two H_2 molecules by the catalyst, as compared to its S-state, gives, after leveling of the solid-state equilibrium, two centers for chemisorption of one O_2 molecule in the form of atoms in addition to those oxygen defects which were formed as a result of oxygen withdrawal from the S-state by CO or H_2 with CO_2 or H_2O formation, respectively.

It was stated that measurements of the molar heats of O_2 chemisorption at any chosen state of the cupper oxide component of the catalyst under consideration at 473 K by three procedure, namely, by direct chemisorption of O_2 and by CO and H_2 interaction with the oxide and CO_2 and H_2O formation, respectively, lead to different values of the molar heats of O_2 chemisorption ($(Q_{O_2(a)})$, $(Q_{O_2(b)})$, and $(Q_{O_2(c)})$, respectively). Therewith, the approximate relation

$$Q_{O_2(c)} = 0.5\left(Q_{O_2(a)} + Q_{O_2(b)}\right) \tag{1}$$

was stated [30, 62]. This result was explained on the basis of the notion on the occurrence of the particles Z^{2+}, $Z^{2+}O^{2-}$, and $Z^{+}{O_2}^{-}$ (for this oxide, Z denotes Cu atoms) at the catalyst surface in different ratios under different conditions. A similar conclusion was made for other oxides [59, 63–66]. It was taken that different molar heat effects of O_2 chemisorption relate to the following processes:

$$O_2 + 2Z^{2+} + 4e^- = 2\,Z^{2+}O^{2-} + Q_{O_2(a)}, \tag{2}$$

$$O_2 + \ 2Z^{2+}O^{2-} = 2\,Z^{+}O_2^{-} + Q_{O_2(b)}, \tag{3}$$

$$O_2 + Z^{2+} + 2e^- = Z^{+}O_2^{-} + Q_{O_2(c)}. \tag{4}$$

Subtraction of (2) from (4) duplicated gives (1).

It was stated that, at 473 K, the equilibrium is shifted to the atomic body O^{2-} form, that the surface under the equilibrium conditions is oxygen-depleted, and that the surface–body equilibriums after O_2 chemisorption and after surface reduction by H_2 or CO level slowly, for many hours; meanwhile, the surface quasi-equilibriums level rather fast. Therefore, the different forms of surface oxygen at the oxide are identifiable if the experiments intended for this aim follow one by one with no longtime intervals.

On this basis and for explaining the experimental relation (1), it was taken that H_2 interacts with $Z^{2+}O^{2-}$ with formation of $Z^{+}{O_2}^{-}$, the consumption of $Z^{2+}O^{2-}$ initiates destruction of $Z^{+}{O_2}^{-}$ with formation of new $Z^{2+}O^{2-}$ forms, and thus, the gross equation for the process of the catalyst reduction by hydrogen is as follows:

$$2H_2 + Z^{+}O_2^{-} = \ 2\,H_2O + 2e^- + Z^{2+} + q_{H_2}. \tag{5}$$

Carbon monoxide reduces the catalyst by the equation

$$CO \ + \ Z^{+}O_2^{-} \ = \ CO_2 + \ Z^{2+}O^{2-} + q_{CO}. \tag{6}$$

Such interpretation is, apparently, necessary to explain the extensive file of experimental data published in [30, 59].

The occurrence of different forms of chemisorbed and chemabsorbed oxygen does not mean that she surfaces are heterogeneous: at any chosen state of the catalyst, all surface particles of any specified sort have the same heat of O_2 chemisorption or desorption and the same reaction ability. Figure 2 gives unique data on the heats of O_2 chemisorption at different steps of reduction of the copper oxide, beginning from the state S up to the state R.

According to the calculation, the $D(Cu_4OH_2)_R$ value, measured for the R-state of the catalyst, responds to the stoichiometry of $Cu_4(OH_2)$. In this scale, the S- and R-states are degenerated into A and R points, respectively. In the figure, the segment 1, 2, or 3 presents the results of the measurements of differential molar heats of the direct O_2 chemisorption ($Q_{O_{2}(c)}$) at 473 K in the form of δ-, ε-, or ζ-oxyhydrate of copper, respectively. It was said above that the series of reduction and of oxidation were performed alternately. Thus, after some reduction of the sample, in the course of which the state of the sample changed from left to right along the abscissa of Fig. 2, the series of O_2 chemisorption were performed and thus the segments 1, 2, and 3 in this figure were obtained, each in the direction from right to left along the abscissa. The segments are connected to each other by the narrow fields with transition heat effects. For comparison with other copper-containing systems, the segments 4 and 5 give the heats of O_2 chemisorption for pure Cu (at $\Delta H_2 = 0$) at 373–403 K and different ΔO_2 [29, 31] and the segment 6 gives the heats of O_2 chemisorption for $CuCr_2O_4$ at 393–463 K and at $6.25 < \Delta H_2$ (µmol/m^2) < 39. Each of the linear dotted segments is obtained as a result of a great number of successive calorimetric experiments on O_2 chemisorption.

In Fig. 2, the solid line is plotted through the midpoints of the segments, and the horizontal dashed line is plotted through the solid line midpoint and between the vertical lines that respond to the S-state (point A) and the R-state (point R). It allows determination of the integral molar heat of oxygen interaction with the sample and determination of the molar heat of oxygen desorption from the copper hydrate $Cu_4(OH_2)$, i.e., the energy of H_2O binding in $Cu_4(OH_2)$. This energy is about 75 kJ/mol.

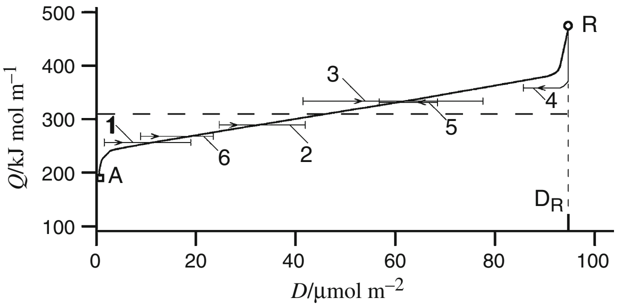

Fig. 2 Molar heats of O_2 chemisorption ($Q_{O_{2(c)}}$) at the sample reduced gradually from the S- to the R-state

It is seen that the surfaces of the fully oxidized oxide in its S-state and of each of its intermediate reduced forms are homogeneous relative to the molar heats of oxygen chemisorption.

Thus, we see that the molar heat of oxygen chemabsorption for each oxyhydrate is constant; at least, there are no grounds to say about their heterogeneity. Apparently, this phenomenon is somewhat similar to hydrogen chemabsorption by some metals, for example, by Pd. Possibly, in different processes and under different conditions, the Cu-component in this or any other catalyst may work in the forms of these oxyhydrates. We see that the heats of oxygen chemisorption at the surfaces of these oxyhydrates are constant; i.e., their surfaces are homogeneous. It is possible to say about two surfaces at each of the oxyhydrates: the O^{2-} and O_2^{-} ones; however, each of them is homogeneous. Maybe, this case is not typical; however, just therefore, we consider necessary to draw attention of the community to it. Below, we will consider more traditional chemisorbing oxide systems.

Consider now a somewhat simpler copper oxide system, namely, the Cu(II) spinel, $CuCr_2O_4$. The “homogeneity versus heterogeneity” problem as applied to the surface of this catalyst will be considered on the basis of works [51, 52].

Figure 3 presents the molar heats of O_2 chemisorption measured at 463 K at the $CuCr_2O_4$ surface, which contented hydrogen chemisorbed preliminary. Two series of the experiments were performed. At the beginning of the former and of the latter, the sample contained about 0.6 and 0.8 cm^3 H_2/m^2, respectively.

Two principal results follow from these experiments. First, the $CuCr_2O_4$ surface reveals itself as homogeneous; i.e., the molar heats of oxygen chemisorption depend neither on the oxygen content nor on the hydrogen content in the catalyst. Second, the occurrence of hydrogen in the catalyst leads to an additional oxygen chemisorption as compared to the oxygen content occurring in the standard completely oxidized catalyst. We see here the phenomenon similar to that described above as applied to the SNM-1 catalyst. Namely, hydrogen interacts with oxygen of the oxide structure, form particles located in the structural cavities, and thus creates the sites (i.e., oxygen defects) for additional oxygen chemisorption. Although just the first effect is the subject of our consideration, let us note that $D(CuCr_2O_4) = \Delta H_2 - \Delta O_2$ (µmol/m^2), contrary to $D(Cu_4OH_2) = 0.5\Delta H_2 - \Delta O_2$ (µmol/m^2) inherent in the Cu-component of the SNM-1 catalyst. This means that OH^--groups form in $CuCr_2O_4$, contrary to OH_2-groups that form in the SNM-1 catalyst.

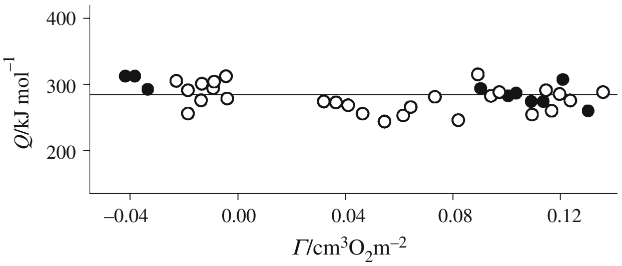

Fig. 3 Molar heats of O_2 chemisorption at $CuCr_2O_4$ in two series that differ the hydrogen content in the sample, 463 K; series 1: *light circles*; series 2: *black circles*

Table 1 contains the data on the molar heats of CO_2 chemisorption and desorption measured at the catalyst under consideration at different oxygen and hydrogen contents in the sample. The mean value $Q_{CO_2} = 107$ kJ/mol ± 5.6%. Note that each experiment on CO_2 desorption was performed just after an experiment on CO_2 chemisorption.

Thus, we see that the $CuCr_2O_4$ surface is homogeneous.

Direct determination of the differential heats of O_2 chemisorption at any completely oxidized oxide is impossible, because such oxides are not capable of chemisorbing oxygen. However, such an aim can be attained on the basis of measurements of the differential heat effects of water formation from gaseous H_2 and surface oxygen of the oxide under study with attraction of the tabulated data on water formation from the elements.

Figure 3 gives the differential heat effects of water formation from H_2 and the surface oxygen of a standardized CuO sample. The experiments were performed at 383 K [48]. The horizontal line allows for calculating the molar heats of chemisorption of the oxygen removed in these experiments. The molar heat of O_2 chemisorption near the S-state of CuO is equal to 194 kJ/mol. The leftmost point in Fig. 3 responds to a lowered molar heat of O_2 chemisorption; the total oxygen amount that reacted with H_2 during this experiment corresponds to a surface coverage of no more than $\theta = 0.009$. Apparently, it is influenced by a contribution to the reaction with H_2 of a small amount of the excessive oxygen that was physically adsorbed during the preliminary re-oxidation of the sample.

We see again that the CuO surface is homogeneous relative to the heats of O_2 chemisorption.

As was mentioned above, $D(CuCr_2O_4) = \Delta H_2 - \Delta O_2$ (μmol/m^2); the same expression for the oxygen deficiency is characteristic for CuO. It does not reveal itself in Figs. 3 and 4, because the molar heats of oxygen chemisorption are constant in these figures. The performance of this expression is shown in [51, 52, 56, 57] and is illustrated, for example by Figs. 3 and 4 in [57], where it is seen that O_2 chemisorption at CuO (at 473 K) terminates when $D(CuO) = \Delta H_2 - \Delta O_2 = 0$; i.e., when the usual oxygen defects and the oxygen defects created by H_2 chemabsorption are exhausted.

We accentuate that all the phenomena considered above relate directly to the heterogeneous catalysis. As a rule, researchers do not know the degree of reduction for a catalyst that works in a catalytic process. Meanwhile, some oxide systems, including the copper ones, are capable of catalyzing different reactions that proceed in the mediums characterized by different redox potentials. It is reasonable to think that the metal oxide systems that can exist in different stable forms of oxidation are capable of realizing and keeping any one of these forms, depending on the redox potential of the medium. On the other hand, the possibility of the above-described phenomena of the step-by-step reduction with H_2 of the oxide systems in which the metal–metal distances in the metal and metal oxide lattices differ by no more than 15–17%, like in CuO and Cu, was predicted. Fifty years ago, such a possibility was noted by Delmon [67] for the mechanisms of phase transitions that proceed so slowly that the equilibrium within solids keeps in time as reduction proceeds. The occurrence in nature of such stones as the noble opals favors such a phenomenon. Apparently, formation of such solid systems as a result of pretreatment of the industrial catalysts under mild conditions necessary for preventing the sintering is quite possible. Noted that, according to [61], the water content in the industrial $Cu/Zn/Al_2O_3$ catalysts responds to $Cu_4(OH_2)$ formation. Under other conditions, the δ-, ε-, and ζ-oxyhydrates of copper are also possible. Therefore, the demonstration of the surface homogeneity for these copper oxyhydrates, likely to that for CuO and $CuCr_2O_4$, is, in our

Table 1 Differential molar heat of CO_2 chemisorption at $CuCr_2O_4$ [51, 52]

Temperature/K	Excessive O_2 content in catalyst/cm^3 m^{-2}	H_2 content in catalyst/cm^3 m^{-2}	C (gas) content in catalyst/cm^3 m^{-2}	Heat of CO_2 chemisorption/kJ mol^{-1}	Heat of CO_2 desorption/kJ mol^{-1}
383	+0.234	0.957	0.0222	99.2	118
383	+0.227	0.957	0.0400	107	107
383	+0.202	0.957	0.0344	107	108
383	+0.137	0.967	0.00785	113	–
423	+0.212	0.957	0.0323	98.7	105

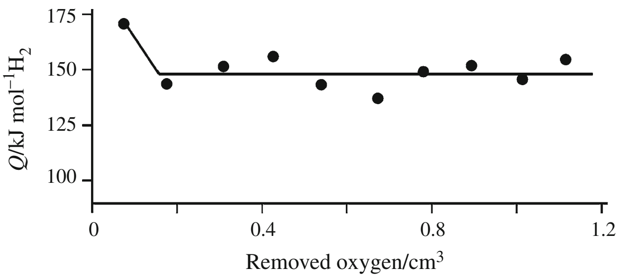

Fig. 4 Differential molar heats of surface reduction of CuO by H_2 with H_2O-vapor formation measured at 383 K, beginning from the CuO standard state

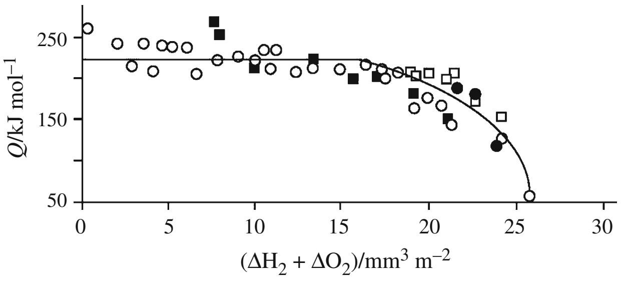

Fig. 5 Differential heats of H_2 chemisorption measured at 463 K at a sample of NiO in series A (*light circles*), B (*black circles*), C (*black squares*), and D (*light squares*)

Table 2 Oxygen and hydrogen amounts in the NiO sample just before and after each of four series of experiments on H_2 chemisorption

Series	Amounts/mm^3 m^{-2}			
	Before the series		After the series	
	O_2	H_2	O_2	H_2
A	0.0	0.0	−8.3	−33
B	−1.6	−23.5	−3.9	+26.5
C	+7.8	0.0	+1.2	+20.5
D	+9.0	+10.0	+5.3	+20.0

(−) and (+) mean that the amount is less or more, respectively, than that in the standard state of the sample before series A

opinion, important for understanding the nature of the catalysis as of one of the natural phenomena.

Now, after the rather detailed consideration of the original approaches, techniques, and procedures as applied to the copper oxide systems, we will consider, in less detail, the results of application of similar methods to solution of the “homogeneity versus heterogeneity” problem by the examples of other oxide systems.

Chemisorption of H_2 at nickel oxide

Figure 5 presents data on four series (A, B, C, and D) of experiments on H_2 chemisorption at sample 5 of NiO at 463 K [7, 54, 68]. Between the A and B, B and C, and C and D series, controlled O_2 chemisorption was performed with no contact of the sample with the atmosphere, and, thus, some controlled water amounts were desorbed. Thus, before each of the series, the sample contained different amounts of chemisorbed hydrogen and different amounts of oxygen at its surface. The ΔH_2 and ΔO_2 values at the beginning and at the end of each series relative to the standard oxidized state of the sample are given in Table 2.

In each experiment, a part of H_2 transformed to water; the H_2 amounts consumed and the H_2O amounts desorbed were measured, and the H_2 amounts chemisorbed were calculated. The molar heats of H_2O desorption were measured, and the heat effects of side water desorption in the course of each experiment were taken into consideration. The experiments in each series were performed portion by portion and continued up to termination of H_2 chemisorption. The maximum hydrogen amounts that were retained by the sample in different series were different.

In Fig. 5, the molar heats of H_2 chemisorption are plotted versus the D value, $D(\mathrm{NiO}) = (\Delta H_2 + \Delta O_2)$ mm^3/m^2. It is seen that the results obtained in four series can be described by one curve and the saturation of the sample with hydrogen proceeds in all the series at the same D(NiO) value. This result means that the oxygen and hydrogen atoms occupy the centers of the same nature. For any definite state of the catalyst surface, the higher is the oxygen content at the surface, the less is the number of the centers capable of hydrogen chemisorption. The data on the molar heat of H_2 chemisorption can be approximated by a horizontal line over a wide range of surface coverage; i.e., the NiO surface reveals itself as homogeneous.

In [68], the measurements of the heats of H_2 chemisorption at NiO were accompanied with the measurements of the chemisorption rates. Such measurements were performed for one of the experimental series at 463 K. In this series, the rates of H_2 pressure decreasing were measured for each H_2 portion. It was stated that the equation $-\mathrm{d}P/\mathrm{d}\tau = kP(1-\theta)$ is fulfilled; therewith, $k = 3.1 \cdot 10^{11}$ molecule s^{-1} cm^{-2} hPa^{-1} (± 6.7%). Thus, the data on the rate of H_2 chemisorption can be described on the basis of the simple Langmuir’s model. They do not contradict the notion on surface homogeneity.

The fact that the oxygen and hydrogen atoms occupy the centers of the same nature is non-trivial and requires a special explanation.

It is known that the $d^8s^2 \rightarrow d^9s$ transition in Ni-atoms requires about 2.5 kJ/mol only [69]. At the temperature of the experiments (463 K), this value is less than the thermal energy (3.84 kJ/mol). Obviously, in the NiO matrix, the reduced Ni-atoms are capable of interacting with O-atoms in the d^8s^2-state or with H-atoms in the d^9s-state, as these states are easily interconvertible. Just therefore, the Ni-atoms are capable of chemisorbing H_2 or O_2.

Two NiO samples were capable of chemisorbing 0.0310 or 0.0330 cm^3 H_2/m^2 at 463 K from their oxidized standard states up to termination of chemisorption. This means that, under the conditions of the maximum surface coverage by hydrogen, two chemisorbed H-atoms occupy, on the average, an area of 11.5 nm^2. Hydrogen does not absorb, and no additional centers for its chemisorption arise at 460 K. This conclusion followed from a special experiment: one of the samples, which was saturated completely with H_2 at 460 K, was aged at this temperature for 720 h, and, after that, it obtained no capability for additional chemisorption of hydrogen. This result means that all above-described experiments on H_2 chemisorption at NiO relate to the surface monolayer.

We see that the data on H_2 chemisorption at NiO can be explained on the basis of notions on surface homogeneity.

Chemisorption of gases at zinc oxide

Consider now two more examples: H_2 and CO chemisorption at the ZnO-component of the $Zn/Cu/Al_2O_3$ catalyst (SNM-1) for CH_3OH synthesis and shift reaction.

The catalyst was slowly degassed, and its CuO-component was reduced at 550 K [8, 10, 30, 38, 39, 53, 61] up to the R-state as was described above. Therewith, ZnO-component of the catalyst was cleaned of absorbed H_2O and CO_2 but was not reduced. After such a pretreatment, neither the Cu-component nor the Al_2O_3-component chemisorbed H_2 under the experimental conditions. At the catalyst thus obtained, the molar heats of H_2 and CO_2 chemisorption (Table 3) were measured.

Table 3 Molar heats of H_2 and CO_2 chemisorption at ZnO-component of the $Zn/Cu/Al_2O_3$ catalyst

System	Exp. no.	Temperature/ K	H_2 (ads)/ µmol g^{-1}	Q/kJ mol^{-1}
H_2 at ZnO [38, 39]	1	298	16	41
	2	298	12	46
	3	303	15	40
	4	303	13	49
	5	303	13	43
	6	293	14	49
	7	323	14	51
	8	353	12	50
	9	323	125	49
CO_2 at ZnO [38]	1	293	13	57
	2	293	15	62
	3	323	18	59
	4	323	27	59

When the H_2 amounts in the portions varied by a factor of more than 10, from 12 to 125 µmol/g, and the CO_2 amounts in the portions varied by a factor of more than two, from 12 to 125 and from 13.3 to 27.4 µmol/g, respectively, their molar heats of chemisorption varied beyond the limits of experimental errors. These results mean that the ZnO surface is homogeneous.

These examples of chemisorption at the ZnO-containing catalysts confirm the concept of surface homogeneity.

Chemisorption of acrylic acid at W/Mo oxide catalysts

Figure 6 contains the results of studies of the heats of acrylic acid chemisorption at 373 K at complex oxide systems of different nature. The molar heats of chemisorption of this organic chemadsorbent at surfaces of four complicated oxide systems are constant over wide ranges of surface coverages [49].

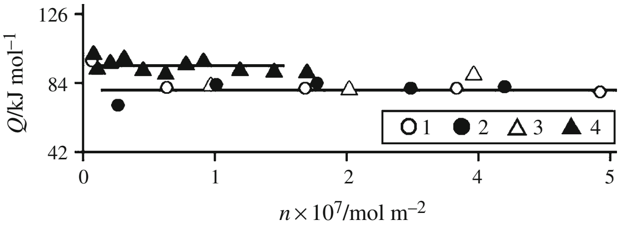

Fig. 6 Molar heats of chemisorption of acrylic acid at promoted oxide V/Mo catalysts: *1* V/Mo, *2* V/Mo/Cu, *3* V/Mo/P, *4* V/Mo/Cs [49]

Chemisorption of C_2H_4 and C_3H_8 at some complicated oxide catalysts and at titanium oxide

Figure 7 relates to chemisorption of C_2H_4 and C_3H_8 at different complicated oxide catalysts at 373 K [50]. It is seen that the molar heat of chemisorption for each of the catalysts is coverage-independent over wide ranges of variations in chemisorbed amounts either for C_2H_4 or C_3H_8; i.e., the surfaces are homogeneous. Meanwhile, for each adsorbate/adsorbent pair, the first point that corresponds to small surface coverage is somewhat higher that all other points. The information given in [50] is insufficient for unambiguous explanation of this peculiarity. Most likely, a side process reveals itself. The fact is that, the side processes reveal themselves to the largest degree, as a rule, at small surface coverages, when chemisorption starts. There is no ground to specify it because side processes can be of different nature. There are no grounds even to curve in such a form as it is made by the author of [50]. For multicomponent catalysts, different molar heat effects could be characteristic for the surfaces of different components of such catalysts and the specificity of the molar

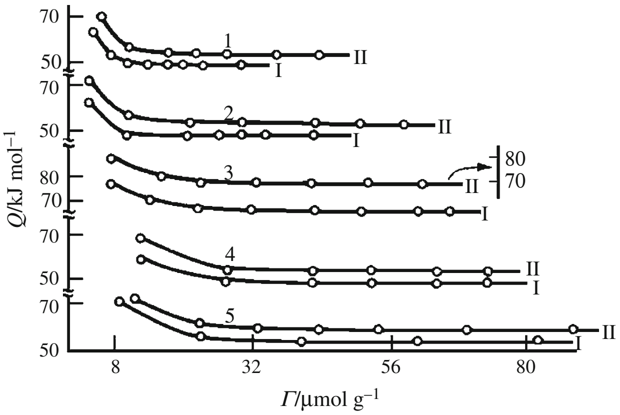

Fig. 7 Molar heats of chemisorption of C_2H_4 (curves I) and C_3H_8 (curves II) at oxides: *1* $CoO/MgO/MoO_3$, *2* $NiO/MgO/MoO_3$, *3* Cu_2O/Al_2O_3, *4* TiO_2, *5* Ag_2O/Al_2O_3 [50]

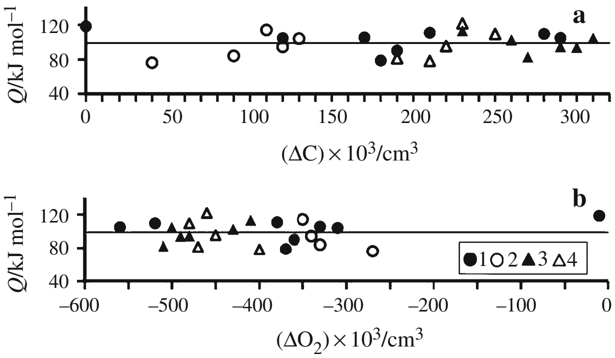

Fig. 8 Molar heats of CO_2 chemisorption and desorption at Cr_2O_3 versus the content of excessive **a** oxygen (ΔC) and **b** carbon (ΔO_2) in the sample; *1* chemisorption, 473 K, *2* desorption, 473 K; *3* chemisorption, 423 K, *4* desorption, 423 K [47]

heat effects measured in the first portion of any adsorbate could mean not heterogeneity of any surface but the occurrence of surfaces of two chemical natures with different molar heats of chemisorption**.** It is quite possible that these heat–coverage dependences are in fact step-wise with transition curves between two their coverage-independent portions. Anyhow, it is obvious that, even for the multicomponent catalysts, for which the occurrence of surfaces with different chemisorption properties is quite possible, rather wide ranges of surface coverage characterized by coverage-independent heats of chemisorption occur.

Chemisorption of different gases at chromic oxide

In conclusion of this paragraph, we demonstrate some results of studies of chemisorption of gases at chromic oxide.

The first calorimetric study of H_2 chemisorption at powder Cr_2O_3 was performed more than 70 years ago [70, 71]. Up to 1960, the methods of calorimetric studies of chemisorption at elevated temperatures were not developed. The chemisorption heats were measured at room temperature after uncontrolled pretreatment with O_2 or H_2 with subsequent degassing.

In [44–47], improved chemisorption and calorimetric techniques and procedures were applied. They allowed studies of chemisorption of different gases at the samples containing the hydrogen, oxygen, and carbon amounts varied from one experiment to another and carefully controlled. Owing to these improvements, the states of the samples were approached to the catalyst states occurring in the course of the real catalytic processes.

Before the experiments that are considered below, the samples were degassed, freed of the biographic CO_2 and water, reoxidized, and thermally stabilized up to the standard state as it was described in "General remarks" section. All subsequent experiments were performed at temperatures significantly lower than the temperatures of the preliminary treatment of the samples.

In Figs. 8a, b, the molar heats of CO_2 chemisorption measured at 473 and 423 K at one of the studied samples are presented as a function of the oxygen content in the sample (calculated relative to its standard state) and as a function of the carbon content in the sample, respectively [46]; the experiment on CO_2 chemisorption was followed by the experiment on CO_2 desorption. The Cr_2O_3 sample (6.3 m^2; 0.89 g) contained about 0.70 cm^3 of hydrogen in its subsurface layers. The heat of chemisorption is constant and depends on neither C nor O_2 content in the sample; it is equal to 99 kJ/mol (± 13.5%). At another sample [47], which contained 0.585 cm^3 of H_2, a value of 107.3 kJ/mol (± 5.0%) was obtained.

It is seen that the surface of Cr_2O_3 is homogeneous. This conclusion was confirmed by CO_2 chemisorption at two samples [47].

Figure 9 presents the molar heats of H_2 chemisorption at Cr_2O_3 [46]. It demonstrates the occurrence of the effect of diffusion of chemisorbed hydrogen (chemabsorption) into the subsurface layers and the independence of the molar heats of H_2 chemisorption at the surface from the hydrogen content in the subsurface layers after the full saturation of the subsurface layers with hydrogen. In the course of the series, the oxygen and hydrogen contents in the sample changed in the following limits: $0 < \Delta H_2\ (cm^3) < 0.50$ and $-0.060 < \Delta O_2\ (cm^3) < 0$. The experiments were performed portion by portion at 473 K; this temperature was constant for the entire experimental series on a 24-h basis. The H_2 amount in each portion was less than the monolayer amount of physically adsorbed Kr by a factor of several tens. Nevertheless, the molar heat effect of H_2 chemisorption decreased significantly after the first morning

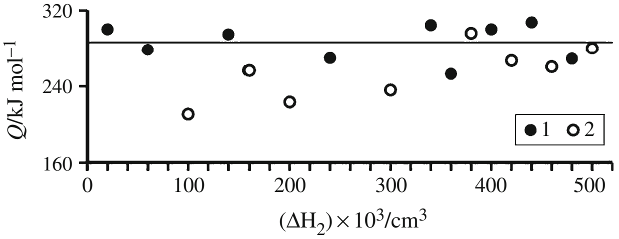

Fig. 9 Molar heats of H_2 portion-by-portion chemisorption versus the hydrogen content in the thermostabilized Cr_2O_3 (0.89 g, 6.3 m^2) with an excessive O_2 contents in the sample of $-0.060 < \Delta O_2$ (cm^3) < 0; *1* molar heats of H_2 chemisorption measured in the first morning experiments performed after no less than 15-h warming of the sample in vacuum at 473 K; *2* molar heats of H_2 chemisorption measured in the second and third experiments after night intervals; the *solid line* is a result of averaging of the results measured in the first morning chemisorption experiments [46]

experiment; namely, in the second experiment, it was lower than in the first one and, in the third experiment, it was lower than in the second one. The solid line in the figure is a result of averaging of the results measured in the first morning chemisorption experiments. It is seen that, for each of the first several days, the molar heat effect of chemisorption repeatedly increased after each prolonged nighttime warming. For these days, the morning rate of chemisorption decreased by a factor of about two. For the experiments performed in subsequent days, after saturation of the subsurface layers with hydrogen, the molar heat effects and the rates of chemisorption did not decrease from one experiment to another.

We presented Fig. 9 with the aim to show once more that the chemisorption processes at oxides are much more complicated than it is generally believed. There are a lot of phenomena that can be taken, after their superficial study, as an effect of surface heterogeneity. Meanwhile, they are unrelated to this notion that was introduced as a voluntary assumption and was not supported for almost the entire century.

Figure 10 demonstrates the results of studies of O_2 chemisorption at a sample of Cr_2O_3 of the same mass and the same surface area as the sample used for the measurements of CO_2 chemisorption [44]. The hydrogen content in the sample varied during these experiments from 0.50 to 0.70 cm^3. In the figure, the abscissa gives the oxygen content in the sample relative to its standard state and the ordinates give the value proportional to the rate of O_2 chemisorption (left) and the value of the molar heat of O_2 chemisorption (right).

Before the experiments on O_2 chemisorption, the O_2 content in the sample was decreased by 0.27 cm^3 relative to its standard state as a result of experiments on H_2 chemisorption and H_2O desorption. As O_2 chemisorption proceeded, the sample approached to its standard state. It is

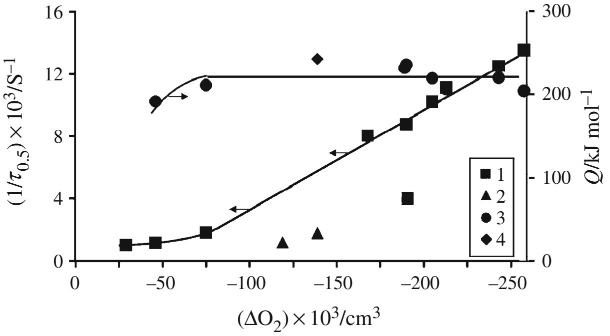

Fig. 10 Chemisorption of O_2 at a sample of Cr_2O_3: *1* rates at 473 K; *2* rates at 423 K; *3* molar heats of chemisorption at 473 K; *4* molar heats of chemisorption at 423 K

seen that, over a wide range of surface coverages, the molar heat of O_2 chemisorption is constant and that the rate of chemisorption decreases linearly as the degree of saturation of the sample by oxygen increases.

Apparently, it is seen that the study of O_2, H_2, and CO_2 chemisorption at Cr_2O_3 shows that the chromic oxide surface is homogeneous relative to the chemisorption ability of its centers of chemisorption ([44], water chemisorption was also studied with the same result; depending on the degree of oxidation, water chemisorbs in the form of water or hydroxyls, each with a constant molar heat of chemisorption); moreover, the molar heats of O_2 and H_2O chemisorption are constant over a wide range of variations in the oxygen surface concentration. This conclusion relates to an oxide whose surface, similarly to the surface of any catalyst under conditions of reactions of hydrogenation, is defective relative to the O-content and contains chemisorbed hydrogen.

It is also seen that chemical transformation of Cr_2O_3 under studied conditions and, consequently, under conditions of catalytic hydrogenation, is not limited by the surface monolayer. Chemabsorption of some gaseous components from reacting mixtures is peculiar not only to copper oxide systems. An analysis of the data on all studied adsorbates shows that the conclusion that the adsorbate remains in the surface monolayer could be made only about CO_2. However, even this conclusion can be made with the proviso that CO_2 dissociation and subsequent diffusion of the O-ions into the sample body cannot be excluded.

As was mentioned above, up to works [44–47], there was no available information on the molar heats of chemisorption of gases at Cr_2O_3 at elevated temperatures and under conditions of the controlled composition of the adsorbent. The results obtained in these works can be compared only with the initial molar heats of H_2 chemisorption measured in [71] at room temperature after uncontrolled treatment of the oxide sample by H_2 and its degassing (151 kJ/mol) and after uncontrolled treatment of the oxide sample by O_2 and its degassing (302 kJ/mol). These values are close to the values obtained in [44–46] for the molar heats of H_2 chemabsorption (170 kJ/mol) and chemisorption (309 kJ/mol), respectively. Evidently, in the experiments of [71], the surface of the "reduced" sample was covered with hydrogen and, therefore, the additional adsorbed hydrogen diffused into the crystal body and the "oxidized" sample contained no hydrogen and, therefore, the first H_2 portion chemisorbed at the surface and did not diffuse into the crystal body. Thus, the results obtained in [44–46] allow for understanding the mechanism of H_2 interaction with Cr_2O_3 under elevated temperatures and the results obtained earlier under room temperature.

Note that the surface homogeneity of the thermally stabilized surfaces in catalytic processes or chemisorption equilibriums by no means contradicts the observable differences in the catalytic and chemisorption activity of different well-defined crystal faces at rather low temperatures. The matter is that the chemisorption and catalytic processes at elevated temperatures reconstruct surfaces of solids; in the course of such processes, the surfaces become disordered and approached in their forms to the densest crystal faces. Such conclusion was first made as a result of generalization of electron microscopic studies [72] and was then repeatedly confirmed (e.g., in [73]). Apparently, in the thermally stabilized solids, the valence electrons of surface and body atoms form a common valence zone. All surface atoms are practically of the same chemical activity, because their quantity is usually much less than the quantity of the body atoms. Therefore, the chemical interactions between the surface atoms of a crystal and chemadatoms vary the Fermi level of the electrons for the entire crystal almost not at all, independently of the surface coverage, and, thus, the chemisorption heat is almost independent of the surface coverage.

Confirmation of surface homogeneity of metal oxides by measurements of some parameters other than chemisorption heats

Below, we present some not popular results of measurements of the specific catalytic activity of different oxide catalysts with the crystal sizes down to 3 nm in different reactions.

Table 4 shows that the specific catalytic activity (calculated per 1 m^2) of silica gel samples in chlorbenzene hydrolysis is almost constant [74, 75] independently of the temperature of their pretreatment although their specific surfaces varied by a factor of more than seven.

The constancy of the specific catalytic activity in C_2H_5OH dehydration was observed for Al_2O_3 samples that were obtained from different source reagents and calcined at different temperatures and, therefore, had different specific surface areas (Table 5) [74, 76].

Similar results were obtained for the catalytic activity of MgO in ethanol decomposition at 673–72 K [74]. The catalyst samples prepared by different methods and calcined at different temperatures had almost the same specific catalytic activity.

We will discuss these data somewhat below in the context of the surface "homogeneity versus heterogeneity" problem.

As is written above, the notion on a continuous increase in the activation energy of chemisorption with a continuous decrease in the heat of chemisorption with the surface coverage is the necessary component of the hypothesis on surface heterogeneity. In this connection, we together with A. Kuznetsov studied hydrogen chemisorption rates at a sample of standardized and thermally stabilized ZnO/Cr_2O_3 catalyst of high-temperature methanol synthesis. The experiments were performed portion by portion; each portion was dozed to the catalyst at an initial pressure of 10–26 Pa. The rate of chemisorption for each portion was characterized by the $1/\tau$ value, were τ is the period the pressure decreasing from 2.66 to 1.32 Pa. Up to 490 K, the chemisorption rate was too small for accurate measurements. The chemisorption rates were measured over the

Table 4 Catalytic activity of silica gel in chlorbenzene hydrolysis

Silica gel calcination temperature/K	Surface area/$m^2\ g^{-1}$	Relative catalytic activity of 1 g of Pt	Relative specific catalytic activity of 1 m^2 of Pt
798	500	1.0	1.0
873	480	0.83	0.79
973	280	0.67	1.1
1073	225	0.43	0.89
1173	70	0.18	1.2

Table 5 Catalytic activity of alumina in ethanol dehydration

Preparation method for alumina samples	Sample surface area/$m^2\ g^{-1}$	Catalytic activity of 1 m^2 of alumina
From nitrate	330	47
From aluminate	300	41
From amalgam	225	43
From commercial hydroxide (washed)	195	34
From nitrate after heating at 723 K	330	32
At 873 K	300	28
At 1,073 K	180	35
At 1,273 K	135	43

temperature range 490–635 K. The experiments were performed in such a way that the temperature varied from one experiment to another and several experiments were performed at each temperature. The total amount of the chemisorbed hydrogen in the experiments presented in Fig. 11 is about 40 µmol/g. The numerals in the figure field respond to the sequence in the performance of the experiments. At low pressures, further chemisorption is influenced by the equilibrium between chemisorbed and gaseous states of hydrogen and, therefore, the rates of H_2 chemisorption cannot be measured at higher surface coverages. The figure shows that the activation energy is about 50.5 kJ/mol and is constant over the entire studied range of the surface coverage by hydrogen. It is important that the rates of chemisorption were measured at each temperature at different surface coverages. Therefore, it is possible to certify that the activation energy does not depend on the surface coverage. The constancy in the activation energy of chemisorption corresponds to homogeneity of the surface.

Final discussion of the surface “homogeneity versus heterogeneity” problem as applied to metals and oxides

In the previous section we showed by the examples of more than 20 systems that the thermally stabilized surfaces of different oxides reveal themselves as homogeneous relative to the chemisorption heats and some other parameters. In [10] and also in [6], we came to an analogous conclusion relative to gas/metal systems on the basis of consideration of more than 40 gas/metal systems listed in “The importance and pendency of the problem” section. This conclusion was made, in the main, on the basis of direct calorimetric and chemisorption measurements of the heats of chemisorption. Besides, data obtained by several other methods were also attracted.

In particular, measurements of catalytic activities inherent in catalysts of the same chemical nature but prepared on the basis of different procedures, are of importance for solution of the surface “homogeneity versus heterogeneity” problem. In the mid-twentieth century, when the techniques of the measurements of the chemisorption heats were at the early stage of their development and no data on the chemisorption heats at elevated temperatures were available, Boreskov [74] concluded that “…the specific catalytic activity that is inherent in catalysts of a definite chemical composition is approximately constant and just the chemical composition and the chemical structure of a catalyst are the main factors that determine the specific catalytic activity”. There is no telling that the surfaces of the catalysts prepared by principally different methods have the same character of their heterogeneity. Therefore, the independence of the specific activity of catalysts from the method of their preparation means that the surfaces are homogeneous.

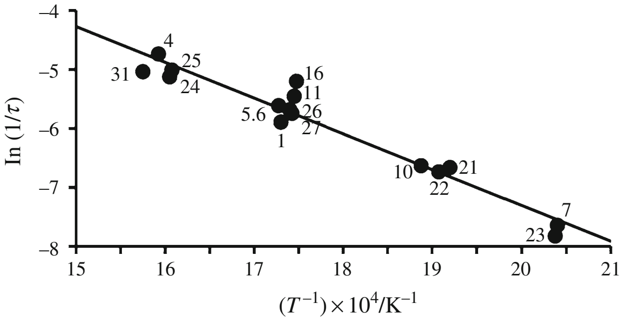

Fig. 11 Activation energy for H_2 chemisorption at the ZnO/Cr_2O_3 system

Boreskov rested upon the data obtained not only with metal oxide catalysts, but also upon very informative data obtained with metal catalysts. Two following examples [74] are especially illustrative. First, the specific catalytic activities of samples of Pt-foil, Pt-wire, and Pt supported at silica gel in the reaction of H_2 oxidation were found to be almost the same, although the specific surface areas of these catalysts varied by a factor of about 43,000. Second, the specific catalytic activities of samples of Pt-grid, Pt-foil, Pt-wire, Pt-black, and Pt supported at silica gel (0.2 and 0.5% of Pt) in SO_2 oxidation were of the same order of magnitude, although the specific surface areas varied by a factor of about 100,000. The variations in the catalytic activities, with the exception of the Pt-foil, are completely explainable by the imperfections of the methods and procedures used for measurements of the platinum surface area and catalytic activity and by the effects of the impurities in the metal [74, 77].

The data on approximate constancy of the specific catalytic activities of oxide and metal catalysts of any definite chemical composition were obtained a long time ago. However, the techniques and procedures for the measurements of the catalytic activity and surface area were rather good in these works and did not undergo principal changes since then. Therefore, there are no grounds for any doubts in these results.

Apparently, it is difficult to imagine that the samples of different aggregate states, or prepared by different modes from different source materials, or calcined at different temperatures could have the same character of surface heterogeneity and, therefore, this collection of the data confirms surface homogeneity of oxides and metals relative to their catalytic ability.

Consider now another issue in the context of our discussion.

It is well-known that the process of NH_3 synthesis and the iron catalysts at which it proceeds are the objects mostly used as the model ones for solution of general problems of heterogeneous catalysis. In particular, homogeneity of the surfaces of iron catalysts was proved in a greater number of the available works than homogeneity of the surfaces of catalysts of any other chemical nature was.

The following results of chemisorption and desorption studies testify that the iron surfaces reveal themselves as homogeneous. (1) The molar heat of N_2 chemisorption at $Fe/K_2O/Al_2O_3$ catalysts is constant over a wide range of surface coverages and decreases only near the saturation [15, 36]. (2) The rate of N_2 desorption from individual iron crystal faces is proportional to the surface coverage [78, 79]. (3) The iron surface is homogeneous relative to the activation energy of H_2 desorption [11]. (4) The iron surface is homogeneous relative to the heat of O_2 chemisorption [25, 26]. (5) The molar heat of H_2 desorption from the nitrogen/hydrogen radicals chemisorbed at the surface of the $Fe/K_2O/Al_2O_3$ catalyst depends on the surface concentrations of neither H_2 nor N_2 [6, 16]. (6) The activation energy of N_2 desorption from iron crystal faces depends on the surface coverage almost not at all [78, 79]. (7) Surface homogeneity of the $Fe/K_2O/Al_2O_3$-catalyst was unambiguously proved by measurements of the dependence of catalytic activity from the degree of surface coverage by sulfur, which is the poison for this catalyst [80, 81]. The radioactive isotope ^{35}S was used as the marker. This Russian work was cited seldom in international journals and remains little-known. It was shown that the catalytic activity is proportional to the degree of surface coverage by sulfur. Figure 12 is taken from [80]. If the surface were heterogeneous, the first portions of sulfur should poison the most active catalytic centers and decreased dramatically the catalytic activity. The plot presented in Fig. 1 is characteristic for homogeneous surfaces, and, of course, it requires no more complicated notions.

It is important that the surface homogeneity of iron catalysts was stated in different works on the basis of the measurements of chemisorption of different gases not only at powders but also at metal films under conditions when no diffusion phenomena in solid could control the results. As it was said above, homogeneity of the $Fe/Al_2O_3/K_2O$ catalyst is stated on the basis of not only chemisorption and calorimetric methods but also is unambiguously confirmed by the fact that the catalytic activity is proportional to the degree of surface covering by sulfur.

Meanwhile, iron catalysts are under study for about a hundred years, and many works that were performed on the basis of the techniques or procedures proved to be incorrect and to contain questionable and mistaken results are available. Deficiency of critical reviews dedicated to analyzing of the methods and procedures of chemisorption and calorimetric measurements lead to the situation when the users not experienced in these techniques apply available incorrect results to defend erroneous hypotheses. Thus, in [82], an attempt to advocate and restore the notion on surface heterogeneity was undertaken.

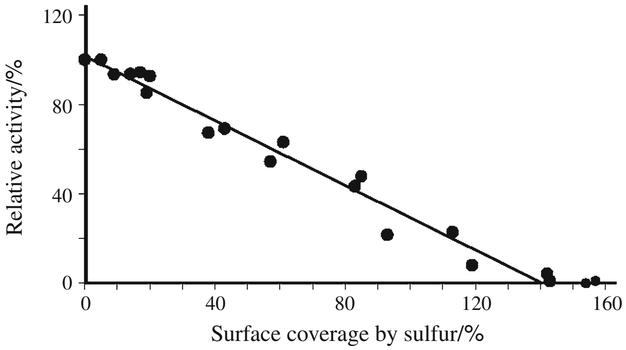

Fig. 12 Relative activity of the $Fe/K_2O/Al_2O_3$ catalyst in the reaction of NH_3 synthesis against the surface coverage by sulfur [80]

Authors of [82] wrote that the data on N_2 chemisorption published in [83–85] confirm surface heterogeneity of iron catalyst and that the results of the measurements of the N_2 chemisorption heats [15, 16, 86] used in [6, 86, 87] as a proof of surface homogeneity are incorrect because they are allegedly weighed down by diffusion control of chemisorption and opposes to them the coverage-dependent heats of N_2 chemisorption obtained in [88]. This criticism forces me to stay at the techniques and procedures applied in [83–88].

In [83], the degree of the preliminary reduction of the powder iron catalyst was inadequate, the catalyst contained iron oxide, and this defect influenced the results. This defect of this work was noted in 1959 [84, 85]. However, the reduction procedure applied by Scholten was also insufficient (see below).

In [84, 85], the results of the measurements of the rates of N_2 chemisorption are rather dubious. The matter is that, in these works, the Fe-catalyst weight was 87 g, the catalyst layer thickness was about 10 cm, and the N_2 pressures were as high as 100 hPa and more. Under such conditions, the entire catalyst layer was under inadequate conditions in the course of the chemisorption process, and, apparently, nitrogen covered the catalyst layer-by-layer, similarly to the harmful gas that flows through the gas-mask canister adsorbent but not uniformly over the entire catalyst layer, and the chemisorption rate was diffusion-controlled. (This criticism was earlier given in [86].). In addition, works [84, 85] contain no proofs that the samples were completely reduced and freed of sorbed hydrogen. On the contrary, in our works [15, 16] where the N_2 and H_2 chemisorption heats were measured, the samples of the catalyst were completely reduced and fried of sorbed hydrogen as it described below, the catalyst weight was about 1 g only, the granule sizes were 1–3 mm, the pressure was about 0.1 hPa and less, and the surface and surface/gas equilibriums after each experiment were controlled by returning of the thermokinetic curve to the pre-experiment zero line. Therefore, no diffusion phenomena distorted the results of [15, 16]. It should be mentioned that the heats of N_2 chemisorption were obtained in [15, 16] from the measurements of the heat effects of NH_3 decomposition to chemisorbed nitrogen and gaseous H_2 on the basis of preliminary experiments on the measurements of the heats of H_2 desorption from chemisorbed nitrogen–hydrogen radicals [15].

In [88], the source iron oxide sample was under-reduced and hydrogen that was sorbed in the course of reduction of the sample was desorbed then incompletely before subsequent N_2 chemisorption. Namely, the iron oxide sample was treated with H_2 at 723 K in flowing hydrogen for several hours, purged with helium for 2 h to remove adsorbed hydrogen, cooled to room temperature in flowing helium, and evacuated to 5×10^{-4} Pa. Such a pretreatment is inadequate.

A complete reduction and complete desorption of H_2 are necessary for obtaining adequate data on the heats of N_2 chemisorption at powder iron samples in subsequent experiments. Otherwise, N_2 chemisorption is accompanied with different side processes and their contribution is coverage-dependent. In [16, 89], it was shown that 200-h reduction at 823 K (about 1.5 g of oxide catalyst, 10% H_2–He mixture, and 15,000 h^{-1} volume velocity of flowing gas mixture) and subsequent 55-h degassing at 823 K (below 1×10^{-5} Pa) are necessary to have sufficiently pure samples of industrial promoted catalysts applicable for subsequent rather correct measurements of the heats of chemisorption. The 50-h reduction is necessary if 100% hydrogen is used. The necessity of such regimes was stated as a result of special experiments with three samples [90]. After 100-h reduction by the 10% H_2–He mixture, the rate of water desorption to the flowing gas was equal to 0.10 mg H_2O/h g. The necessity of the prolonged degassing of H_2 from reduced catalysts is seen from the following experiments. The catalyst sample reduced for 200 h (reduced mass was about 1.2 g) was degassed at 823 K to less than 1×10^{-5} Pa. After 15-min degassing, the rate of H_2 desorption into a degassed closed volume for 10 min was equal to 0.06 cm^3 (ntp)/g. (Hereafter, the gas amounts are reduced to the normal (ntp) conditions.) Then, the sample was degassed at 823 K for 9 h. After that 0.027 $cm^3 H_2/g$ was desorbed for 1 h into the same degassed closed volume. The H_2 desorption from the catalyst was observed after even 39-h degassing of the catalyst (for 1 h, 0.003 cm^3 H_2/g).

The conditions of reduction and degassing of the samples in [83–85, 88] were very far from these requirements.

There is no doubt that the many-hour hydrogen treatment and many-hour after-reduction degassing are necessary for cleaning oxygen and hydrogen from industrial iron catalysts. It is well-known that the residual oxide and residual hydrogen influence N_2 chemisorption as a result of diffusion of the residual gases to the surface and their reacting at the surface with nitrogen. On the basis of the extensive studies of the promoted iron catalysts [15, 16, 89, 90], we conclude that the authors of [88] measured not the molar heats of N_2 chemisorption but a sum of several reactions among which the nitrogen–hydrogen chemisorbed radical formation apparently prevailed. Unfortunately, the authors of [88] had in their adsorption apparatus no instruments for quantitative measurements of small amounts of desorbed H_2, H_2O, and NH_3 in the course of catalyst reduction and H_2 degassing and in the course of the process of the catalyst treatment by N_2 and, therefore, no quantitative understanding of their calorimetric data is possible.

We answer to the authors of [82] so thoroughly by two reasons. The first one is as follows. As was said above, the system under consideration represents a model one for studies of principal catalytic problems, which are common for metal and metal oxide catalysts. Meanwhile, according to our opinion, the present state of studies of chemisorption and catalytic phenomena allows for the conclusion that the thermally stabilized surfaces of all crystal bodies, metals and metal oxides, except very small crystals of 3–5 nm and less in size, reveal themselves under stationary conditions as the homogeneous ones in their catalytic and chemisorption activity; this is a principal common feature of crystal bodies, which is caused by the zone character of their electron structure (this conclusion in no way means that each catalyst has the surface of only one sort; for example, the well-known $Zn/Cu/Al_2O_3$ catalysts have surfaces of three sorts, each of them revealing itself as the homogeneous one [40]). This idea runs through the entire set of our reviews [6–8, 10] of the last decade, and we formulate it in the general form in this review, which is considered by us as the conclusive one for this set. In our opinion, there is no ground to open a door to the assumption that this feature of solids is selective for some systems. In the mentioned reviews, analyzing a number of the works whose authors reported that the surfaces are heterogeneous, we concluded that all these works were performed on the basis of inadequate methods or inadequate techniques and procedures. It is seen that the data on iron catalysts do not represent an exception to this generalization. The second reason is that we wish to demonstrate the necessity of an advertency to the technical and procedural features of experiments from the direction of not only producers but also users of chemisorption and calorimetric data.

Consider now the following question. Are not the data on the heats of chemisorption and other parameters considered above the direct contrary of the possibility of description of a number of data on chemisorption equilibriums and rates and on catalytic kinetics by the equations deduced analytically from the notions on surface heterogeneity?

In order to answer this question, we will concentrate mainly on the data published earlier in the literature and will add some new considerations.

In [91], to justify the use of the notion on surface heterogeneity for description of the kinetics of NH_3 synthesis near the equilibrium conditions, it was contended that the observed kinetics cannot be understood in the framework of Langmuir's notions on surface homogeneity.

Meanwhile, it was later shown [6, 86, 87, 92] that this opinion was mistaken. For the reaction

$$3H_2 + N_2 \leftrightarrow 2NH_3, \tag{7}$$

the kinetic equation which follows unambiguously from the empiric kinetic equations given in [93] and [94] for the reactions of NH_3 decomposition and synthesis, respectively, and which was deduced in [91] on the basis of the notion on surface heterogeneity, was also deduced in [86, 87, 92] (see also [6]) on the basis of the notion on surface homogeneity. The following mechanism

$$N_2 + Z \leftrightarrow ZN_2 \tag{8}$$

$$2ZN + 3H_2 \equiv 2NH_3 + 2Z \tag{9}$$

$$ZN_2 + Z \equiv\!\rightarrow 2ZN \tag{10}$$

was used. Symbol $\equiv\!\rightarrow$ means that the equilibrium is shifted to the right; i.e., in the course of the process, the surface is covered with ZN almost entirely. The rate of NH_3 synthesis is controlled by partially reversible N_2 chemisorption (partial reversibility is marked by the symbol $\leftrightarrow$), and the rest portion of the reaction is always in equilibrium with the gas mixture; i.e., the gas–solid chemisorption–desorption equilibrium establishes much quicker than the reaction proceeds. Thus, the reaction is considered as the one-step one. Just such a mechanism corresponds to the present views.

If the degree of surface coverage by ZN is so high that $\theta_{ZN}^2 \cong 1$, we have $K_9 = \theta_Z^2 P_{NH_3}^2/P_{H_2}^3$ and $K_{10} = 1/\theta_Z\theta_{ZN}$, where K_9 and K_{10} are the constants of equilibriums (9) and (10), respectively, θ_Z is the degree of surface coverage by the free centers Z, and P_{NH_3} and P_{H_2} are the NH_3 and H_2 pressures, respectively. The reaction rate

$$\begin{aligned} r &= k_{+8}\theta_Z P_{N_2} - k_{-8}\theta_{ZN_2} \\ &= \left(k_{+8}K_9^{1/2}P_{N_2}P_{H_2}^{3/2}/P_{NH_3}\right) - \left(k_{-8}P_{NH_3}/K_{10}K_9^{1/2}P_{H_2}^{3/2}\right), \end{aligned} \tag{11}$$

k_{+8} and k_{-8} are the real rate constants for the rate-determining reaction (8) in the direct and inverse directions, respectively. The observable (effective) rate constants for the reaction (7) in the direct and inverse directions are k_{+7} and k_{-7}.

We accentuate that the observable rate constants for the direct ($k_{+7} = k_{+8}K_9^{1/2}$) and inverse ($k_{-7} = k_{-8}/K_{10}K_9^{1/2}$) reactions that are detectable from the kinetic experiments represent products of the real rate constants and some equilibrium constants in some powers. We will term this feature of the measurable rate constants multi-pithiness. In [92], kinetic equations for a number of reactions have such a feature, and, thus, it is inherent in different available kinetic equations. The multi-pithiness of the measurable effective rate constants of catalytic reactions is their important feature. It means that the temperature coefficients of such reactions can not be a priori considered as the temperature coefficients for reaction steps. We intend to consider the importance of this feature for understanding catalytic mechanisms in another paper.

Thus, we showed that the kinetic equation which responds to Winter's and Benton's results can be deduced in the framework of Langmuir's notions on surface homogeneity. As was noted, (11) was first deduced on the basis of the scheme (8)–(10) in 1989 [86, 87].

Equations similar in their form to (11) were obtained on the basis of the notion on surface heterogeneity for the reactions of SO_2 oxidation to SO_3 at Pt [95], shift reaction [96] and oxygen exchange between CO_2 and CO [97] at ferric oxide, and methanol synthesis from CO and H_2 at zinc–chromium oxide [98].

We considered the kinetics of each of these reactions on the basis of the notion that the surfaces of the corresponding catalysts are homogeneous and deduced the same kinetic equations as those obtained on the basis of the notion on surface heterogeneity [6, 92]. For all these reactions, the multi-pithiness of the effective rate constants was confirmed.

We accentuate that we do not discuss here the field of applicability of kinetic equation (11). We only demonstrate that the kinetic equations of the same form can be deduced on the basis of the notion on either surface heterogeneity or surface homogeneity (the physical essences of the constants in these equations are different). This means that the forms of the kinetic equations proposed earlier by the advocates of the surface heterogeneity in no way prove the heterogeneity of the catalyzing surfaces. Corma et al. [99] studied 19 catalytic reactions and found that the notion on surface heterogeneity is not necessary for description of their kinetics. Meanwhile, the surface heterogeneity of thermally stabilized surfaces of crystalline bodies, if it were in the reality, should be their fundamental feature and should be inherent in all catalysts. In [100], it was stated that no kinetic study of a stationary catalytic reaction is capable of solving the "homogeneity versus heterogeneity" problem.

Thus, the possibility of description of the kinetics of any catalytic reaction by an equation deduced from the notion on surface heterogeneity does not contradict the real homogeneity of the catalyst surface.

Consider the following question: are not the data on the heats of chemisorption considered above the direct contrary of the possibility of description of a number of data on chemisorption equilibriums by the equations deduced from the notions on surface heterogeneity?

The possibility of description of data on chemisorption equilibriums by the logarithmic isotherm (12), which is usually applied in the form

$$\theta = (1/f)\ln(a_0 P), \tag{12}$$

or by the Freundlich isotherm (13)

$$\theta = Cp^{1/n} \tag{13}$$

is usually considered by the advocates of the concept of surface heterogeneity as the proof that the surfaces are really heterogeneous. The isotherms similar to (12) and (13) were proposed as empiric formulas in [101, 102], respectively, and later were approximately deduced in [2] and [103, 104] on the basis of assumptions that the molar heat of chemisorption decreases linearly or exponentially, respectively, with the surface coverage.

Note the following: The procedures of deductions of these equations are based on the assumption that the variations in the heats of chemisorption with the θ value are describable by a definite function with a constant derivative over the entire field $0 < \theta < 1$, the resulted equations relating to a conventional field of the so-called middle surface coverages. The term "field of middle coverages" relates to a field of the surface coverages for which the conditions $a_0P \gg 1$ and $a_1P \ll 1$ should be fulfilled. Here, P is the equilibrium pressure and a_0 and a_1 are the equilibrium constants of chemisorption at a surface free of chemadsorbate particles and at a surface entirely filled by them, respectively. Meanwhile, for 70 years, none work that proves the occurrence of such chemadsorbent/chemadsorbate system is available. Therefore, there are no grounds to think that the θ ranges, for description of which these equations are intended, occur in reality.

According to the procedures of deduction of these isotherms [105], the values of the constants in (12) and (13) are determined by the initial chemisorption heats, by the characters of their coverage dependences, and by the values of the equilibrium constants of chemisorption. However, there are no available works, in which it would be stated that these equations with the constants predetermined by independent procedures are applicable for description of experimental data on chemisorption equilibriums. In all works, in which the applicability of the isotherm (12) or (13) was declared, the authors examined only the possibility of linearization of experimental data in the coordinates θ against $\ln P$ or $\lg \theta$ against p, respectively. They took that experimental data obtained for a field of middle surface coverages are describable by the isotherm under testing and that the surface of the chemosorbent is, therefore, heterogeneous if they managed to obtain linear dependences in the corresponding coordinates. However, such a procedure is not sufficient to conclude, whether the data are describable by the model that was used as the basis for deduction of these chemisorption isotherms.

Thus, there are no convincing proofs that could show that (12) or (13) describes any experiment data on chemisorption equilibriums.

Graphic data that show that the surface "homogeneity versus heterogeneity" problem principally can not be solved on the basis of analyzing of the form of the equations for chemisorption equilibriums are available. Trapnell ([106], Chap. 5) showed graphically that the constants in the Freundlich isotherm can be chosen in such a way that its graphic form becomes practically indistinguishable from the graphic form of the simple Langmuir isotherm. In our paper ([6], Fig. 3), it is shown that the experiments on the equilibrium of N_2 chemisorption at five samples of industrial iron catalysts that earlier were described in [107, 108] by logarithmic isotherm are also describable on the basis of the isotherm deduced in [3, 109] (and presented in [6]) for chemisorption at homogeneous surface when adsorbate molecules chemisorb with dissociation and each chemisorbed atom occupies two surface centers. In Fig. 13, the plot reproduced from [110] is given. Curve 1 is the logarithmic isotherm, and curve 2 is the isotherm of multi-centered chemisorption at homogeneous surfaces. The set of experimental data obtained by authors of [110] can be described by the logarithmic isotherm and by the isotherm of multi-centered chemisorption at definite chosen parameters that enter the equations of these isotherms. Unfortunately, [110] contains no used values of the parameters.

Thus, we can conclude that the possibility of formal description of chemisorption equilibriums by the isotherms deduced from the notion on surface heterogeneity does not contradict the real homogeneity of catalyst surfaces. The surface "homogeneity versus heterogeneity" problem principally can not be solved on the basis of analyzing of the form of isotherms.

The data on the heats of chemisorption considered above and in [10] show that the thermally stabilized surfaces of crystal bodies are homogeneous relative to the chemisorption and catalytic activity of their surface centers. This conclusion contradicts the available data on neither the chemisorption equilibriums nor the rates of catalytic processes. The point is that the authors who applied the notion on surface heterogeneity to analytical descriptions of such processes never used independent heat measurements for

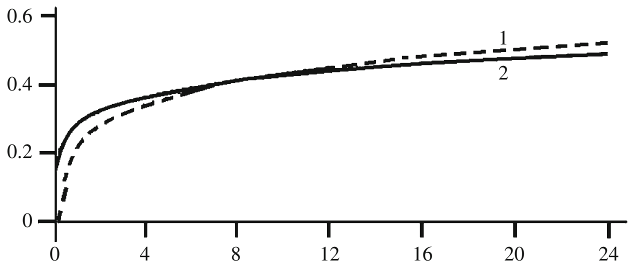

Fig. 13 Comparison between the isotherm 2 for multi-centered chemisorption at homogeneous surfaces and the logarithmic isotherm 1 (reproduced from [110])

specification of the values of the constants in their equations and used the equations that follow from the hypothesis on surface heterogeneity only formally on the basis of the optional choosing of the constants; therefore, these formal analytical descriptions do not allow for distinguishing between homogeneous and heterogeneous surfaces.

Thus, we stated that the concept of surface heterogeneity of the thermally stabilized surfaces of crystal bodies has no experimental grounds and its main conclusions expressed in the form of the equations and the procedures for description of the rates and equilibriums of catalytic and chemisorption processes are not necessary for this aim because the inter-parametric connections describable by them can be described by the corresponding equations deduced on the basis of the concept of surface homogeneity.

Conclusions

Finishing this paper, I terminate the study of the surface "homogeneity versus heterogeneity" problem, which took us several decades. When starting this work half a century ago, I heard around me solid opinions that the surfaces are heterogeneous in the heats of chemisorption at their atoms and that this heterogeneity reveals itself in the catalytic and chemisorption ability. I had faith in this idea. It was widely distributed, and even the classical works performed by Boreskov [74–77] and his colleagues did not ruin this faith, because the so-called "induced heterogeneity" (mutual repulsion) was in reserve. I understood that the problem is rather important because the understanding of the nature of the catalysis as a natural phenomenon and the relation between the physicochemical grounds of catalysis and the notions that underlie the zone theory of solids depend on its solution. Our works were aimed at studies of powder catalysts as the most approached to the actual industrial catalytic processes. When we began these works, no microcalorimeters applicable for chemisorption studies were on sale. Together with my colleagues and assistants, we constructed calorimeters, accessory instrumentation (electrical calibrators, temperature regulators, etc.), and vacuum chemisorption apparatuses on the basis of available descriptions and, mainly, by using original technical ideas and solutions. The first measurements gave us the coverage-dependent heats of chemisorption [111], and they caused joy and gave hope to us and our colleagues. Meanwhile, the first chemisorption calorimetric measurements allowed us to reveal the defects in the instruments and chemisorption and calorimetric procedures. We constructed new calorimetric equipments and new chemisorption apparatuses and step-by-step approved the chemisorption and calorimetric methods and procedures and learned to eliminate or take into consideration the side processes. The more religiously we improved the techniques and procedures, the more homogeneous became the surfaces. Along with the FOSKA and DMK calorimeters of our own construction, we used Calvet calorimeters from DAM (pioneering Calvet's company) and from Setaram. The calorimetric and chemisorption instruments, techniques and procedures, including the specific equipment and techniques for calibration of the chemisorption heat effects, developed by us are described in English in reviews [7, 8, 28] and in Russian in a number of papers, some of which are cited in these reviews.

Some our theoretical works in the field of analytical description of catalytic kinetics and chemisorption equilibriums and rates, which relate to the topic of this paper and the results of which are used in this paper and in [8], are reviewed in [6].

This paper and [10], as a complete unit, represent a review of the available data of the most principal and most reliable chemisoption heat studies selected on the basis of analysis of the degree of fulfillment of the principal requirements, which can be reduced to four main points: (1) standardization of the initial state of the samples; (2) maximal isolation of chemisorption processes under study from the side processes, including the surface reactions, surface-to-body and body-to-surface diffusion of the adsorbed substances and impurities, desorption of the products of surface reactions, and the processes at the walls of chemisorption apparatuses; (3) availability of the means and procedures for controlling, elimination, and consideration of the side processes; and (4) adequate calibration and consideration of the related questions and corrections. The results, to which the non-compliance with these requirements can lead, are shown, for example, in [6, 7].

On the basis of chemisorption heat measurements, surface homogeneity was stated for more than 40 gas/metal systems by about 30 composite authors and for more than 20 gas/metal-oxide systems by about 10 composite authors. This conclusion is confirmed in this paper and in [10] by a number of measurements performed on the basis of other methods, from which, in my opinion, the results by Boreskov et al. [74–77] and the results relative to contamination of iron catalyst by sulfur [80, 81] are the most convincing.

In addition, here and in [6], it was shown that the equations deduced on the basis of the notion on surface homogeneity for analytical descriptions of chemisorption equilibriums and rates can be successfully applied instead of the equations deduced for this aim earlier on the basis of the notion on surface heterogeneity and that the kinetic equations for the catalytic NH_3 synthesis and for a number of other reactions deduced by us on the basis of the notion on surface homogeneity can be successfully used instead of the corresponding equations deduced earlier from the notion on surface heterogeneity. Thus, it was shown that the principal equations deduced for description of the equilibriums and rates of chemisorption and catalytic processes on the basis of the notion on surface heterogeneity are not necessary for description of these processes and can be successfully replaced by the equations deduced on the basis of the notion on surface homogeneity.

Therefore, this collection of results allows solid solution of the surface “homogeneity versus heterogeneity” problem and gives a possibility to state that the thermally stabilized surfaces of crystal solids are homogeneous relative to the catalytic and chemisorption abilities of their atoms.

This conclusion relates to the metal and metal oxides with particles larger than 3–5 nm when the ratio of the numbers of their body and surface atoms is significantly greater than unity by the order of magnitude. This conclusion is in line with Langmuir’s opinion and the band theory of solids.

The fact is that chemisorption and catalytic reactions are associated with electron interactions between gas molecules or atoms and surface atoms of solid crystals. Meanwhile, according to the band theory, the surface electron gas in crystals together with the infinite reservoir of a three-dimensional electron gas form a continuous equilibrium distribution and the surface valence electrons constitute a small portion in this distribution. Therefore, variations in the surface coverage in the course of catalytic and chemisorption processes are incapable of significant changing the energy of electrons that provide the chemical adsorbent–adsorbate bonds. When the crystal sizes are less than 3–5 nm, the numbers of their valence surface and body electrons can become of the same order of magnitude and it is possible to expect that the heat of chemisorption can become coverage-dependent. However, as a result of sintering, such small crystals can not exist under stationary conditions in the ordinary present catalytic processes. May be, when the fine-crystalline catalysts subjected neither to sintering nor to volatilization are produced and when their chemisorption characteristics are studied rather well, the necessity of returning to the problem considered in this review will appear again.

Apparently, establishment of surface/gas equilibrium over each very thin catalyst layer in the course of any stationary catalytic process levels the crystal surfaces in this layer and the free exchange by electrons between the surface and body of each crystal completes this leveling. In the multicomponent catalysts, the surface of each component is characterized by individual characteristics. As for the boundary inter-crystalline fields, it is possible that they have some peculiarities but their significance is, apparently, rather small and that the common catalytic activity is limited not by them.

It is possible to establish with certainty that the notion on surface homogeneity is quite sufficient for simulations of real chemisorption and catalytic processes and technological regimes. This does not mean that the equations deduced from the notion on surface heterogeneity cannot be used as empirical formulas, because, in respect to practical requirements, they are capable of satisfactory translating the inter-parametric dependences within some limits of variations in the industrial conditions. By the way, all above-considered principal equations deduced on the basis of the hypothesis on surface heterogeneity, the Freundlich and logarithmic isotherms and Elovich equation, were given initially just as the empiric formulas. As for the widely known kinetic equation for the NH_3 synthesis near the equilibrium conditions, it was obtained initially from the empirical equations given for the NH_3 synthesis and decomposition by Benton [94] and Winter [93], respectively, through equating the rates of the direct and inverse reactions and searching the missing dependence of the direct reaction rate from the NH_3 concentration on the basis of the equilibrium constant formula.

Consideration of the problem of surface “homogeneity versus heterogeneity” is, in our opinion, rather topical. Let us consider the grounds for such an opinion.

The deductions of different equations for chemisorption and catalysis on the basis of the hypothesis on surface heterogeneity enter largely into the composition of many catalytic textbooks. This fact produces the illusion of the reality of heterogeneity of thermally stabilized surfaces relative to the catalytic and chemisorption activity of their atoms. However, none of those textbooks gives sufficient experimental grounds for such deductions because no ground exists. Apparently, these deductions have been transmitted from one generation of researchers to the next one because those who were the first to make them hoped that the grounds will be found in the future and those who came in the stead of them believe that the grounds for these deductions are found long ago. Just the notions on surface heterogeneity gave birth to the notion on catalytically active surface centers of specific configuration, and this notion has propagated among some researchers. If catalyzing surfaces are homogeneous, the uncertainty of such a concept increases. Moreover, taking into account the concept on surface homogeneity, on island chemisorption [112–117], and on significant excesses in the rates of chemisorption as compared with the rates of catalysis [118, 119], we recently proposed a new understanding of the phenomenon of heterogeneous catalysis [8, 40] and described the kinetics of a number of catalytic reactions on this basis [6, 40, 120]. It was also mentioned above on the possibilities of different practical applications of the solution of this problem. We hope that these points are sufficient in order to consider that the solution of the surface "homogeneity versus heterogeneity" problem is topical.

Meanwhile, measurements of the coverage dependences of chemisorption heats are the best tool for reliable solving the problem under consideration. However, such measurements are rather difficult because of the necessity of cleaning the possible contributions of a number of side processes from the chemisorbed amounts and heats. To reveal and eliminate or take into consideration these side effects, the experience and knowledge not only in chemisorption processes as such but also in different related fields, such as heating engineering, thermophysical behavior of solids and gases, metrology, diffusion, etc., are necessary. Meanwhile, the professional calorimetrists who work in the field of chemisorption and use microcalorimeters of their own design are rare in our days. The reviews of the measurements of the chemisorption heats are rare and consider limited groups of chemisorbents and chemisorbates. As examples, the reviews by Beeck [13], Gravel [121], and Černý [122] can be mentioned. The review series that includes works [6–8, 10, 28, 40] and this paper represents the most comprehensive critical consideration of the available data obtained since the 1960s for the chemisorption heats of gases at metals [8, 10] and metal oxides (this paper) and includes consideration of the principal requirements to the chemisorption [7, 8] and calorimetric [28] techniques and procedures; we are among the first to demonstrate the direct transition from the chemisorption and calorimetric measurements to the mechanisms and kinetics of complicated catalytic processes [6, 40].

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