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Review Paper

REVIEW OF THE HEATS OF CHEMISORPTION OF GASES AT METALS IN THE CONTEXT OF THE PROBLEM OF ‘HETEROGENEOUS’ *vs.* ‘HOMOGENEOUS’ CATALYTIC SURFACES

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A critical review of available data on the heats of chemisorption of gases at metals is given. The effect of upward technical and procedural trends on measured results is demonstrated. The results for surfaces approached to their states occurring in catalytic processes are accentuated. Several tens of chemisorbent/gas systems are considered; a number of the results are confirmed by several independent measurements. The coverage-independence of heats of chemisorption for powders, supported catalysts, components of multi-component catalysts, and films is demonstrated; the better the techniques and procedures, the closer to zero the angle between the heat–coverage function and the abscissa. The principal conclusion on surface homogeneity of stabilized surfaces is made.

Keywords: *adsorption calorimetry, calorimetry in catalysis and chemisorption, catalyzing-surface homogeneity, chemisorption heats at metals, heat effects of chemisorption, surface homogeneity*

Introduction: formulation of the problem

The problem of ‘heterogeneous’ *vs.* ‘homogeneous’ surfaces of catalysts during stationary catalytic processes is of grave importance for the theory and practice of chemisorption and catalysis. It is also important for the general solid-state theory in view of the question: is the reactive ability of a thermally stabilized crystal surface controlled by the structural characteristics of its individual atoms or by the characteristics of the surface as a whole, i.e. as an integral part of this crystal?

Chemisorption (CHS) and catalysis are chemical phenomena, and, according to a widespread notion, the chemical ability of individual centers of a surface should be practically uniform because, according to the band theory of solids, their reactivity is determined by a continuous equilibrium distribution of the crystal electron gas within an ‘effective infinite reservoir’ from which the electron levels of surface atoms can be filled up [1–4]. This notion relates to the crystals whose sizes are so large that the number of their body atoms is far beyond that of their surface atoms. Usually, actual today catalysts functioning under stationary conditions answer this requirement.

Meanwhile, a number of catalytists advocate the concept on surface heterogeneity.

Authors of [5, 6] were the first to conclude that studies of the kinetics of heterogeneous reactions are not capable of solving the problem whether the catalyst surfaces are homogeneous or heterogeneous. We showed [7–11] that neither the form of kinetic equations of stationary processes nor the form of equations of CHS isotherms or rates of CHS allows for solid solution of this problem.

Numerous data on the kinetics of isotopic exchange between surface and gaseous oxygen showed that the exchange rate is rather high and that it can be described with the equations peculiar to homogeneous surfaces [12]. Authors of [13, 14] concluded that ’… differential isotopic method based on the use of H_2, N_2, and their isotopes shows that all active centers formed by the surface atoms of crystal faces of porous platinum and graphite have the same CHS activity with respect to each of the studied gases, i.e., the surfaces of these adsorbents and catalysts are uniform’ [13].

However, some authors have so perfect confidence in the concept of surface heterogeneity that they are ready to depreciate their own experimental

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data in order not to come into conflict with this concept. One of such examples of the birth of a myth about surface heterogeneity will be considered below by the example of O_2 and H_2 uptake by iridium supported at alumina.

The results given below demonstrate the general effect of the upward technical and procedural trends on the available values of the molar heats of CHS and on the fundamental conclusion about the distribution of surface centers of the thermally stabilized metals by their affinity to CHS of gases.

We accentuate that it is unlikely that coverage-dependent molar heats could be transformed by overlooked side processes to the coverage-independent ones; meanwhile, different side processes (such as body–surface diffusion of an impurity or surface interaction of the adsorbate with an impurity) can decay as CHS proceeds and can produce an illusion that the heat of CHS decreases with the coverage. Therefore, the coverage-independent molar heats of CHS provoke less technical questions and look more convincing than the coverage-dependent ones.

Correct measuring of the heats of CHS or desorption of small portions of gases is a rather complicated problem, and the quality of its solution depends not only on the skill of experts in calorimetry but also on the current state of the adsorption techniques and procedures. The matter is that the heat effects should be related to the amounts of individual substances reacting in a strictly determined process. Meanwhile, CHS may be accompanied by different side processes; among them, interaction of the adsorbate with substances chemisorbed previously and formation of surface or gaseous products; interaction of the chemisorbed grease vapor with the adsorbate; adsorbate diffusion into the solid body; interaction of the adsorbate with impurities or with solid components diffusing from the body to the surface; adsorbate adsorption on the walls of the adsorption apparatus; chemical interaction between the adsorbate and the walls of the adsorption apparatus, metal taps, and balances; sintering of the samples; and so on. In the course of CHS experiments, each of these processes may influence the values of the heat effects, gas amounts actually chemisorbed or desorbed, and adsorbate surface/body distribution. Therefore, all side phenomena should be precluded or taken into consideration. The difficulties are redoubled by the fact that the observed signal from which the heat effects of side processes should be cleaned is usually very small.

Therefore, available heats of CHS should be analyzed in respect to the degree of overcoming these difficulties. The acceptance of any available unconfirmed data on molar heats of CHS without their critical analysis would be superficial.

Just below, we list a number of the systems in which coverage-independent or almost coverage-independent molar heats of CHS are obtained for rather wide ranges of surface coverages. The results of another kind are also available. However, we will give a number of examples demonstrating that the more recent is the study and the more attention is given to the adsorption and calorimetric techniques and procedures, the smaller is the angle between the abscissa and the heat–coverage function. We consider the CHS freed from side processes as the two-dimensional phase transition. In the general case, it includes three successive chemical steps of formation of crystallization centers, of two-dimensional phase I, and of two-dimensional phase II (e.g., M_2A and MA, or MA and MA_2, respectively; M is a surface metal-atom and A is an adsorbate atom); therewith, each step is characterized by a definite heat effect and the heat effect for phase II formation is smaller than that for phase I formation. In practice, the first step may manifest itself not at all, because the calorimetric sensitivity is limited, and the third step may be absent or may be so slow that its heat effect cannot be measured. (Notice that we say about the heat effects of CHS not influenced by sintering of the samples; to avoid sintering, the samples should be heated before calorimetric measurements.)

H_2 at Fe [15, 16], Ni [17, 18], Pt (black) [19], Pt/SiO_2 [20], Pt/W/SiO_2 [20], Pt [21], Pt (powder) [22], Ce, Dy, Lu, Er, Tm and Yb [23];

O_2 at Fe [24], Ni [24], Pt/W/SiO_2 [20], Nb [24], W [24], Mn [24], Co [24, 25], Mo [24], Ta [24], Ti [24], Cu [25–27], Ag [28, 29], W/SiO_2 [20], Ir(5%)/SiO_2 and Ir(0.5%)/SiO_2 [30];

N_2 at Ni [31] and Fe/Al_2O_3/K_2O [32, 33];

CO at Ni [18], Cu-component of ZnO/$Cu_4(OH_2)$/Al_2O_3 [34, 35], Dy [36], Ni (powder) [37], Ni/K (powder) [37], Ni/Cs (powder) [37], Pt (powder) [37], Pt/Rb (powder) [37], and Pt/Cs (powder) [37];

$CH_2{=}CHCOOH$ at V/Mo, V/Mo/Cu, V/Mo/P, and V/Mo/Cs [38];

$HC{\equiv}CH$ at Pt [22, 39];

$H_3C{-}C{\equiv}CH$ at Pt [39];

$H_2C{=}CH_2$ at Pt (powder) [22]; etc.

The calendar-year effect on the measured results

In 1966, Bröcker and Wedler published the results of measurements of the molar heats of H_2 CHS at Ni-films in an ultra-vacuum apparatus [17]. It was shown that the heat of CHS is coverage-independent up to almost full coverage of the surface. These authors presented a figure (Fig. 1), in which they plotted their own data and the data obtained for the same pro-

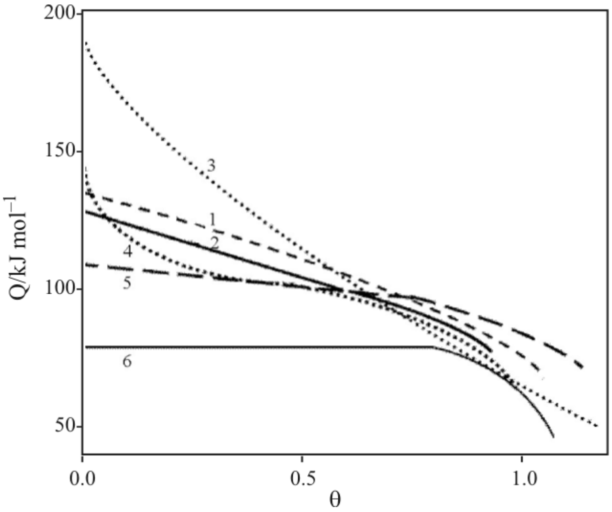

Fig. 1 Heats of H_2 chemisorption at Ni-films at 273 and 298 K: 1 – 1950 [40], 2 – 1953 [41], 3 – 1957 [42], 4 – 1960 [43], 5 – 1964 [44] and 6 – 1966 [17]; at monolayer chemisorption, θ=1

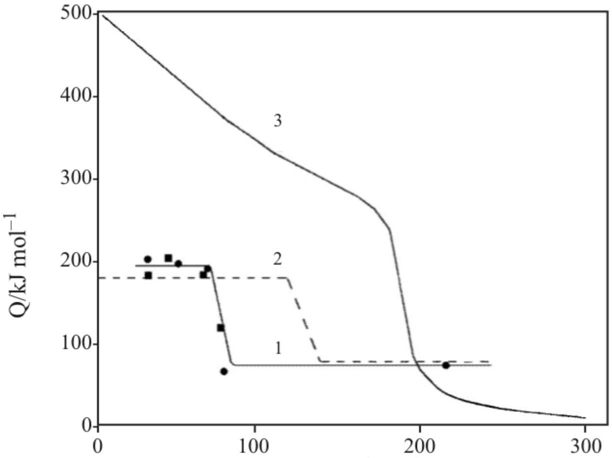

Fig. 2 Heats of oxygen chemisorption at Ag-powders: 3 – 1966, 373 K [45]; 2 – 1977, from isotherms, 450–615 K [29]; 1 – 1979, 465 and 496 K [28]

cess by other authors [40–44] in 1950, 1953, 1957, 1960 and 1964. It turned out that, the fresher are the data, the smaller is the angle between the measured dependence and the abscissa; only one curve falls out of this regularity. It is obvious that this effect results from progressive improvements of the adsorption and calorimetric techniques and procedures.

The analogous conclusion can be made for some other adsorbent/adsorbate systems. In 1966, we published the molar heats of O_2 CHS at silver powder [45]. It was our first calorimetric work and the first adsorption-calorimetric work performed at heightened temperatures. The measurements were made on the basis of adsorption procedures characteristic for the early 1960s. We obtained the heats of CHS decreasing with the surface coverage. After improvement of the methods and procedures of CHS measurements, we repeated the work and obtained a two-level curve consisting of two coverage-independent sections of about 200 and 70 kJ mol^{-1} connected by a transition curve [28] (Fig. 2).

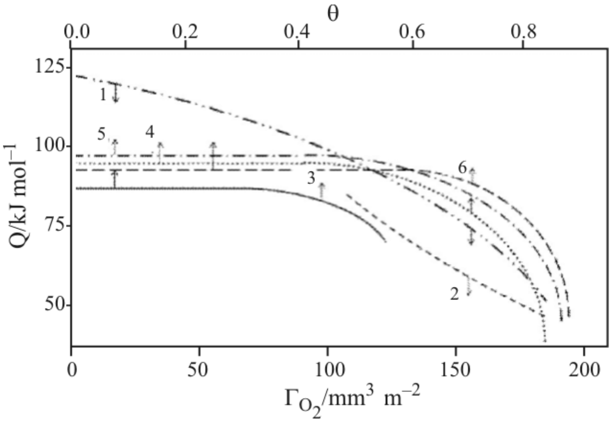

Fig. 3 Heats of H_2 chemisorption at Fe-films at 273 and 298 K: 1 – 1950 [47], 2 – 1953 [48], 3 – 1972 [15], 4 and 5 – 1978 [49], and 6 – 1990 [16]

Similar heat–coverage dependence was obtained for this system by Czanderna [29] on the basis of his measurements of the CHS isosters in ultra-vacuum apparatus. These two works shows that Ag surfaces are really homogeneous and that O_2 chemisorbs in two forms (apparently, O^{2-} and O_2^-); therewith, the latter arises when the surface is covered with the former. The details are given in [28, 46], where the reaction of H_2 with chemisorbed oxygen and the heats of H_2 CHS at oxidized surface are also considered.

One more example of such a kind is the history of measurements of the molar heats of H_2 CHS at iron films (Fig. 3). In the 1950s, coverage-dependent molar heats of H_2 CHS were obtained [47, 48]; however, beginning from 1972, it was repeatedly shown that the heats of CHS at about room temperature do not depend on the surface coverage over a wide range of its variation [15, 16, 49].

Heats of chemisorption at surfaces approached to their states in the course of catalytic processes

The works considered below are important for our consideration because the solids studied in them represent samples of the real composite catalysts that are useable for large-tonnage industrial processes and because these samples are approached maximally to those chemical states which are characteristic for the catalysts working in these processes.

The matters in enquiry are the industrial SA-1 catalyst of the NH_3 synthesis (Fe/0.083 K_2O/0.033

Al_2O_3/0.038 CaO) [50] and SNM-1 catalyst of the CH_3OH synthesis (ZnO/0.50 $Cu_4(OH_2)$/0.14 Al_2O_3) [51]. These compositions correspond, according to our studies, to the catalyst compositions occurring during stationary processes of the NH_3 and CH_3OH syntheses, respectively. The methods, techniques, and procedures used for preliminary treatment of the catalysts and for performance of the experiments are detailed in the reviews [27, 46, 51–53] and original works [32, 34, 50, 54–58].

The experimental apparatuses and procedures are detailed in [46, 51]. Principal features of the pretreatment of the $Fe_2O_3/K_2O/Al_2O_3$/CaO or ZnO/CuO/Al_2O_3 catalyst consist in the following. Each of the catalysts was reduced under soft conditions by small H_2 amounts dosed portion by portion into the volume with one of the catalysts under low pressures. From time to time, small NH_3 or CH_3OH portions were introduced into the volumes with each of the catalysts. Hydrogen reduction was performed until the complete decomposition of NH_3 or CH_3OH portions changed into their partial decomposition, and the states approached to the equilibriums were established in each of the systems. Thus, the catalyst surfaces before sorption experiments were in equilibrium or almost in equilibrium with the reaction mixtures. These studies had also the following important features: from the start of the pretreatment and to the end of the experiments, each of the samples had no contact with the atmosphere; during the pretreatment, each sample was completely degassed (from H_2O, CO_2, etc.) by their thermo-vacuum treatment; and, after that, the content of different adsorbates in the samples was controlled rather carefully during several subsequent series of adsorption–desorption experiments. When studying CHS or desorption of any one gas, we often had to measure the changes in the gas pressures of more than one gas and to consider the corresponding side heat effects. Each serial experiment with one catalyst sample continued for many months, up to one year. Apparently, these features made these experiments unique; they were performed by E. Igranova (with the $Fe_2O_3/K_2O/Al_2O_3$/CaO catalyst) and by A. Dyatlov (with the ZnO/CuO/Al_2O_3 catalyst).

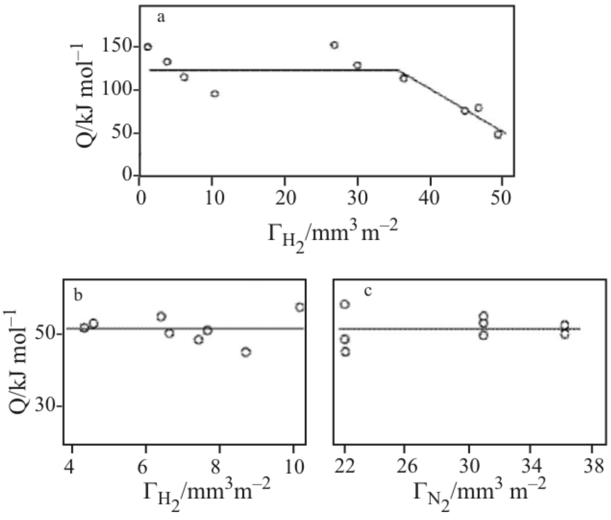

Fig. 4 Heats of chemisorption at a Fe/K_2O/Al_2O_3 catalyst at 470 K: a – of N_2 *vs.* coverage by nitrogen and b – of H_2 *vs.* coverages by hydrogen and c – nitrogen [33, 50, 52, 54]

Table 1 Molar heats of H_2 CHS at the ZnO-component and of CO CHS at the $Cu_4(OH_2)$-component of the ZnO/$Cu_4(OH_2)/Al_2O_3$ catalyst

No.	Tempature/ K	H_2 adsorbed/ μmol g^{-1}	Molar heat Q/ kJ mol^{-1}
		H_2/ZnO-component	
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/$Cu_4(OH_2)$-component	
1	303	13	60
2	353	33	67
3	303	12	67
4	303	2.4	67
5	303	5.8	73
6	303	9.2	61

With the Fe/K_2O/Al_2O_3/CaO catalyst, we measured the molar heats of N_2 CHS against the nitrogen surface coverage (under conditions when the surface was free of hydrogen) and the heats of H_2 desorption from the surface containing both nitrogen and hydrogen (namely, the particles containing nitrogen and hydrogen in an associated form) against the hydrogen and nitrogen surface coverages. The molar heats of N_2 CHS are coverage-independent and the molar heats of H_2 CHS are independent of the coverages by both hydrogen and nitrogen [33, 7] (Fig. 4).

Table 1 contains the results of measurements of the molar heats of H_2 CHS at the ZnO-component and of CO CHS at the $Cu_4(OH_2)$-component of the ZnO/$Cu_4(OH_2)/Al_2O_3$ catalyst. The molar heats of H_2 and CO CHS are coverage-independent and are equal to 46.44±4.13 and 65.83±4.75 kJ mol^{-1}, respectively.

Before each of these experiments, the catalyst surface did not contain the adsorbate under study. It is seen that the variation in the amount of chemisorbed hydrogen by a factor of 12.5 (from 12 to 125 μmol per 1 g of the catalyst) does not change the molar heat of H_2 CHS at the ZnO-component and the variation in the amount of chemisorbed carbon monoxide by a factor of 13.7 (from 2.4 to 33 μmol per 1 g of the catalyst) does not change the molar heat of CO CHS at the $Cu_4(OH_2)$-component of this catalyst.

In addition, it was stated that the kinetics of O_2 and CO_2 CHS at the $Cu_4(OH_2)$- and ZnO-components, respectively, obeys the equation

$$r=kp[1-(\Gamma/\Gamma_\infty)]^2\{z/[z-(\Gamma/\Gamma_\infty)]\} \qquad (1)$$

(r is the CHS rate, p is the pressure, Γ is the chemisorbed amount, Γ_∞ is the monolayer CHS). This equation is a particular case of our theory considering the rates and equilibriums of CHS of the substances, each molecule of which occupies several surface center at homogeneous surfaces [59–61]; Eq. (1) corresponds to the CHS of each molecule at two surface centers of the /100/ crystal face.

Figure 5 gives the heats of O_2 CHS at the $Cu_4(OH_2)$-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst (the grounds allowing us to specify the Cu-component composition of the catalyst as $Cu_4(OH_2)$ and to relate the O_2 CHS to just this catalyst component are given in [27, 51]).

Note that the initial O_2 portion (up to a degree of coverage of 5.7%; it is not shown in the figure) chemisorbs with a molar heat effect of about 485 kJ mol^{-1}. The heat of O_2 CHS at higher coverages (O_2 portions 1–4 in Fig. 5a) is constant up to the region of saturation of the surface (the procedure of CHS of portion 6 is described below). Closely equal results were obtained earlier for O_2 CHS by us [62] and by the authors of [26] for powder Cu and for Cu-film, respectively [52]. It is seen that the real $Cu_4(OH_2)$ surface of this composite catalyst is homogeneous.

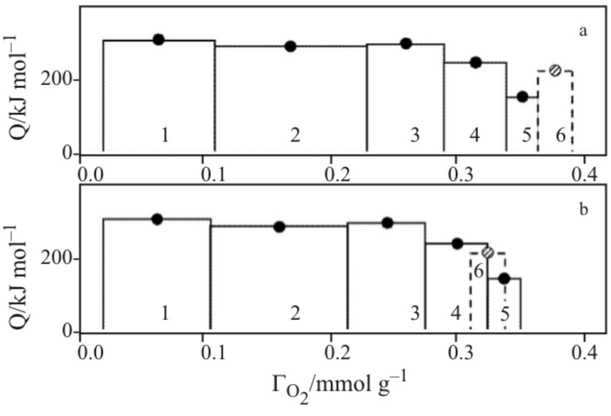

Fig. 5 Molar heats of O_2 chemisorption at $Cu_4(OH_2)$-component of $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst *vs.* chemisorbed amount (293 K); a – without consideration of O_2 diffusion into the sample body for the time interval of 90 h between the experiments 5 and 6; b – with consideration of O_2 diffusion into the sample body

As for the initial O_2 CHS (up to 5–6% of the total coverage), it represents, most likely, the process of origination of the nuclei of the oxygen chemadphase (chemisorbed surface phase; detailing in [51]). The high molar heat effect observed at the start of CHS can not be explained by any side process because the similar effect was repeatedly observed not only by us in different Cu-systems [8, 26, 52, 62]. This heat effect can not be explained either by the hypothesis on surface-Cu_2O formation forerunning surface-CuO formation. Indeed, the difference between the initial (about 485 kJ mol^{-1}) and most abundant (about 305 kJ mol^{-1}) molar heat effects is very high and, therefore, if these two processes occurred, the first of them would be much more preferable thermodynamically and, if it began, it would proceed up to full coverage of the surface.

Thus, the surface homogeneity of the $Fe/K_2O/Al_2O_3/CaO$ catalyst is proved twice, by the measurements of the heats of N_2 and H_2 CHS at the surfaces containing both nitrogen and hydrogen, and the surface homogeneity of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst is proved five times, by the measurements of the heat of O_2, H_2, and CO CHS and of the rates of O_2 and CO_2 CHS.

We see that the surface of industrial Fe-containing catalysts is homogeneous likely to the surface of Fe-films (Fig. 3). Note that the homogeneity of Fe-containing catalysts was repeatedly proved by different other measurements: the isosteric molar heats of N_2 CHS at the $Fe/K_2O/Al_2O_3/CaO$ catalyst [32], calorimetric molar heats of O_2 CHS at Fe-films [24, 63], and activation energy for N_2 [64, 65] desorption from Fe-films are coverage-independent and the rate of N_2 desorption from individual Fe crystal planes is proportional to the coverage [64, 65].

This subsection shows that the measurements of the CHS heats and rates not influenced by side processes testify that real surfaces of different catalysts are homogeneous in their CHS ability; at least, there are no grounds to say that any heterogeneity reveals itself in the heats or rates of CHS.

Heats of chemisorption of some gases

Oxygen chemisorption

Figure 6 presents the results of one of the first ultra-vacuum measurements [24] of the heats of O_2

CHS at metal films at 273 K, when the oxygen surface–body diffusion is hardly significant.

It is seen that the molar heats of O_2 CHS at eight metals are constant over wide ranges of surface coverages; thus, these surfaces reveal themselves as the homogeneous ones.

Later [25] (see also [52]), we measured the heats of O_2 CHS at Co-powder at 298 K and confirmed the results of [24].

Figure 7 presents the molar heats of O_2 CHS at Cu-powder (373 and 383 K) [62], Cu-component of the reduced powder $CuO/ZnO/Al_2O_3$ catalyst (293 K) [34], and Cu-film (298 K) [26]. For the densest crystal face /111/, monolayer CHS in the form of Cu–O(ads) corresponds to about 130 mm^3 O^2/m^2. It is seen that dependences of the same form are obtained for these three copper systems. They correspond to formation of the centers of two-dimensional crystallization with an enhanced molar heat effect in a rather narrow range of surface coverages and to CHS with a constant molar heat effect up to CHS of, at least, 70% of one monolayer. It is also seen that the horizontal levels of the curves differ not very significantly from the level characteristic for Cu_2O formation.

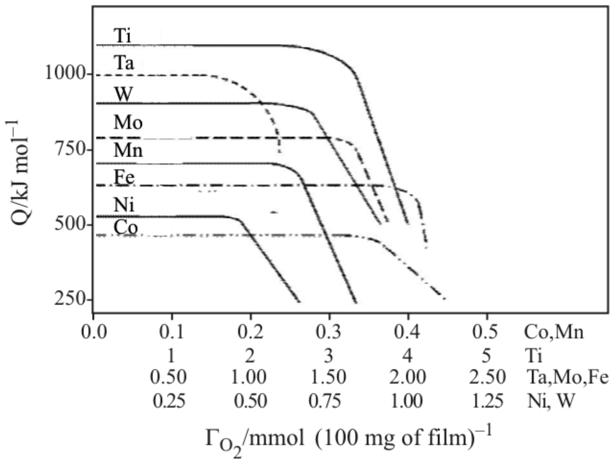

Fig. 6 Molar heats of O_2 chemisorption at evaporated metal films *vs*. chemisorbed amounts, 273 K [24]

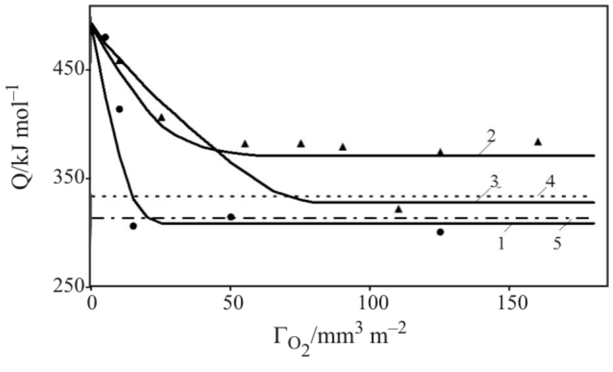

Fig. 7 Molar heats of O_2 chemisorption at Cu *vs*. chemisorbed amounts: 1 and circles – CHS at the reduced Cu-component of the $CuO/ZnO/Al_2O_3$ catalyst (a FOSKA calorimeter is used); 2 and triangles – CHS at the reduced Cu-powder (a FOSKA calorimeter is used); 3 – CHS at the Cu-film formed at the CuO-surface (ultra-vacuum [26]); 4 and 5 – ΔH^0_{298} for the reactions $O_2+4Cu=2Cu_2O$ and $O_2+2Cu=2CuO$, respectively

Analogous results were published in [66, 67] a little while since. The authors of [67] studied the $CuO/ZnO/Al_2O_3$ catalyst similar to that studied in [34]. The main difference between these works consisted in the procedures of preliminary treatments of the samples. In [34], we aimed at approaching the catalyst state characteristic for the process of methanol synthesis. We reduced the catalyst samples very slowly for more than 100 h with successive small portions of H_2 and CH_3OH vapors and continuously controlled the catalyst composition [46, 51]. The reduction continued up to the catalyst state at which the admission of CH_3OH vapor portion resulted not in its full oxidation by the Cu-component of the catalyst to CO_2 and H_2O but in production of a gas mixture of CO, H_2, CO_2, and residual CH_3OH. Under these conditions, the copper component had the $Cu_4(OH_2)$ composition. We term this substance copper hydrate [27]; its chemical characteristics can be approximated by the characteristics of metal copper, and curve 2 in Fig. 7 gives the molar heats of O_2 CHS just at such a copper hydrate. Unlike this technique of reduction, authors of [67] reduced their samples for 12 h by H_2 (2%)/He mixture at 448 K without controlling the degree of reduction and degassed them for 30 min. Our studies show that such a procedure does not lead to the catalyst state characteristic for the process of methanol production but produces a poly-crystal powder consisting of copper with an admixture of copper oxide and some amount of intracrystalline water. Nevertheless, the surface layer of the copper oxide was apparently reduced and the authors of [67] measured the heats of O_2 CHS at almost pure copper surface. They obtained two levels (about 380 and 270 kJ mol^{-1}) of the constant molar heats of oxygen uptake and a transition curve between them; they attribute the levels of 380 and 270 kJ mol^{-1} to the surface oxidation and bulk oxidation, respectively. The level of 380 kJ mol^{-1} corresponds well to the level 2 in Fig. 7. In [67], there is no drooping branch in the Q_O–Γ_O curve over the range of small surface coverages; apparently, this peculiarity is caused by the incomplete reduction of the sample in [67], i.e. by the occurrence of copper oxide germs at the surface.

We see that constant levels for the molar heats of O_2 CHS were obtained for different systems based on metal copper in a number of works performed in different decades; the heats of CHS depend on the history of the samples and on their composition, but they

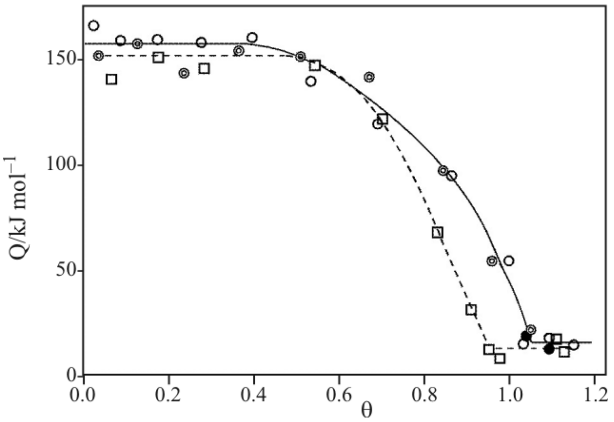

Fig. 8 Molar heats of O_2 chemisorption at Ir/SiO_2: 5% Ir, crystal size 2.8 nm (circles); 0.5% Ir, crystal size 3.5 nm (squares) *vs.* surface coverage (315 K) [30]

are leveled in all measurements under consideration. Note that different characteristics of Cu-containing systems are given in [68].

Figure 8 relates to O_2 CHS at the Ir/SiO_2 and Ir/Al_2O_3 systems [30]. For each of these systems, two-level curves were obtained. These results show that the surfaces of the systems under study are homogeneous relative to their CHS abilities. As was said above, two-level curves with transition drooping branches between them are characteristic for CHS of adsorbates in two forms. The notion on the occurrence of O^{2-} and O_2^- is universally recognized (e.g., [27, 69]).

The authors of [70], when discussing coverage-independent molar heats of O_2 CHS and coverage-dependent heats of H_2 CHS at the Ir/Al_2O_3 system at 315 K [30], declare with no proof that the surface heterogeneity ‘is present beyond doubt’ and that the cause of the constancy of the O_2 CHS heat is the immobilization of the surface O-atoms, which leads to their random arrangement at the surface and to leveling of the molar heats of CHS. Giving such an explanation, these authors ignore well-established facts that the Pt-group metals are capable of absorbing H_2 at somewhat heightened temperatures, that the so-called spillover-effect is characteristic for H_2 CHS at supported metals of Pt-group, that the equilibrium arrangement of surface O-atoms is achievable as a result of not only surface migration but also as a result of exchange with gas molecules (the homomolecular oxygen exchange proceeds at Ir at 315 K with a rather high rate [71]), etc. These authors ignore even their own result showing that H_2 CHS reaches 2.5 hydrogen atoms per one surface Ir atom and consider the H_2 uptake as CHS at the Ir surface. In addition, the papers [30, 70] take no notice of a number of technical questions without which the correctness of the calorimetric and adsorption measurements as such can not be estimated; for example, they write nothing about the mode of measuring of the residual pressure and about the form of the thermokinetic curves (whether they had endothermic ‘tails’), do not indicate whether the adsorption apparatus has a cold trap in the volume with the catalyst and whether adsorbate portions come into two calorimetric cells simultaneously, and do not mention about a number of other technical features of primary importance for calorimetric measurements in their specific system. We showed [30, 46, 50, 60] that H_2 absorption is capable of falsifying molar heats of H_2 CHS even at Fe, although Fe has a weaker affinity to H_2 than Ir has.

Figure 9 relates to O_2 CHS at gold powders. The calorimetric results (Fig. 9a) are obtained in two series of experiments performed with two samples at 413 and 393 K; they testify unambiguously that the real gold surface after a prolonged reduction by H_2 and thermo-vacuum treatment is homogeneous (the details are given in [46, 61, 72, 73]).

For some adsorbent/adsorbate systems, the rate of CHS decreases with surface coverage quicker than (1–θ) (θ is the degree of surface coverage). Advocates of surface heterogeneity consider such experimental

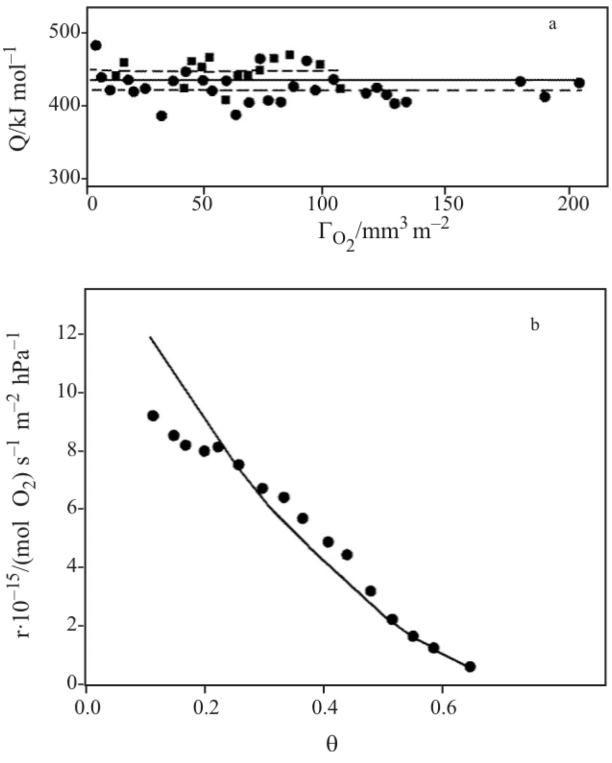

Fig. 9 a – Molar heats of O_2 chemisorption at powdery Au *vs.* chemisorbed amount [46, 72]: sample 1 (413 K), circles; sample 2 (393 K), squares; lower and upper dashed lines give the mean *Q* for samples 1 and 2, respectively; solid line gives the overall mean *Q*; b – rate of O_2 chemisorption at powdery Au *vs.* surface coverage [61, 74], sample 1 (413 K): points are experimental values, curve is calculated by Eq. (2) (n=4, z=6)

data as a support for the concept of surface heterogeneity. Work [61] was used to show that the rates of CHS should decrease much quicker than (1–θ) at homogeneous surfaces if each adsorbate molecule occupies several adsorption centers. It was shown that the rate (r_+) of CHS proceeding with formation of mobile films consisting of nondissociated admolecules or of dissociated ones and migrating as a single whole is described by the equation [7, 61, 73, 75, 76]

$$r_+ = \alpha'(n,z)\alpha'_0 p(1-\theta)^{n}\{z/[z-(n-1)\theta]\}^{n-1} \quad (2)$$

here, α'_0 and α' are constants, the last being a function of n and z; p is the pressure; n is the number of the surface CHS centers covered with a chemisorbed molecule; and z is the number of the CHS centers that would be covered with a chemisorbed molecule when we mentally rotate it by 360° in the surface plane around any CHS center at which this molecule is mentally fixed. For example: n=6 for the /111/ face of a face-centered cubic lattice and n=4 for the /100/ face of a simple cubic lattice; and z=18 for CHS of benzene (at seven CHS centers) at the /111/ face of a face-centered cubic lattice and z=8 for CHS of two paired O-atoms (at four CHS centers arranged as a square) at the /100/ face of a simple cubic lattice.

In Fig. 9b, the points are the experimental CHS rates and the solid curve is calculated for the case of CHS of each O_2-molecule at four surface centers of the /111/ face of a face-centered cubic lattice (n=4, z=8) in the form of O-atoms, each of which occupies two surface centers. It is seen that the curve corresponds to experimental data and describes the r_+ decrease by a factor of about 15 when the (1–θ) value decreases by a factor of about 3 (from 0.9 to 0.3).

The molar heats of O_2 CHS at Ag and Cu are considered in 'The calendar-year effect on the measured results' and in 'Heats of chemisorption at surfaces approached to their states in the course of catalytic processes', respectively.

Carbon monoxide chemisorption

We showed (Table 1) that the molar heat of CO CHS at $Cu_4(OH_2)$-component of the methanol-synthesis and shift-reaction catalyst is coverage-independent and is equal to 65.83±4.75 kJ mol^{-1}.

This result was confirmed in [67]; according to this work, the molar heat of CO CHS at the reduced Cu-component of the catalyst is coverage-independent and is equal to 60 kJ mol^{-1}.

We mentioned above that the experimental samples in this work were reduced incompletely and contained absorbed water; this statement follows from the results published in [46, 51] and relevant to the catalyst of the same nature. The adsorption apparatus had no means allowing controlling the sufficiency of reduction of the samples and of their dehydration before experiments. Therefore, some of the measured results are questionable and, without independent data, it is difficult to filter out the incorrect results.

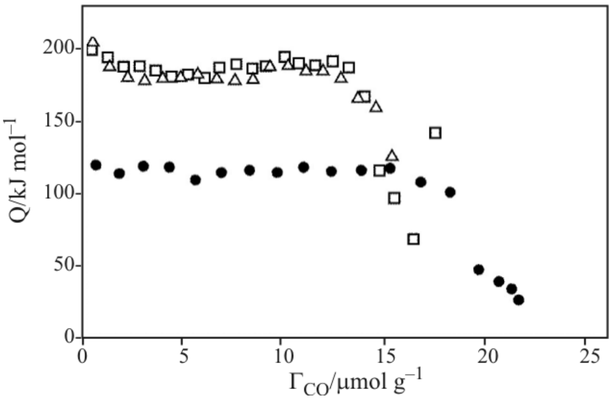

Fig. 10 Molar heats of CO chemisorption at powders (308 K): Ni (circles), Ni/K (squares), and Ni/Cs (triangles) *vs.* chemisorbed amounts [37]

Consider other examples.

Figure 10 demonstrates the results by Dumesic and Spiewak [37] on CO CHS at 308 K at three powder samples prepared on the basis of nickel. For each of the samples, the molar heats of CO CHS are coverage-independent (within the possible experimental deviations) over a wide range of surface coverages, and thus the surfaces of the samples are homogeneous. Molar heats of CO CHS at bimetallic Ni–Pt and Ni–Pd catalysts supported on alumina nano-fibre are considered in [77].

Work [37] also contains no less demonstrative data on CO CHS at 403 K at surfaces of platinum and of Cs-promoted and Rb-promoted platinum samples calcined in O_2 and then reduced in H_2 and degassed. The surface of each of these samples is homogeneous, and the molar heats of CHS and the CHS capacities per unit mass are approximately the same.

The list given in 'Introduction Formulation of the problem' contains also other examples of CO CHS.

Note the following. Two-level curves with transition branches lying between two heat levels are typical for CHS proceeding in two forms, one of which is thermodynamically preferable and originates at the first step up to full or almost full surface coverage. Therewith, the second, weakly-bound adsorbed form can be associated with absorption or surface transformation of chemisorbed particles with compacting of the chemisorbed layer. Besides, different side processes reveal themselves most clearly at the initial or final steps of CHS processes; therefore, CHS proceeding just over middle coverages is most informative for conclusions on the degree of homogeneity of surfaces.

Hydrogen chemisorption

We presented the results showing that surfaces of Ni (Fig. 1), Fe (Figs 3 and 4), and ZnO-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst (Table 1, ‘Heats of chemisorption at surfaces approached to their states in the course of catalytic processes’) are homogeneous relative to H_2 CHS. Several other works demonstrating coverage-independence of the molar heats of H_2 CHS at metals over wide ranges of surface coverages are listed at the end of ‘Introduction Formulation of the problem’ [18–23]; the results obtained in one of these works (H_2 CHS at Pt-powder [22]) will be shown below in ‘Chemisorption of hydrocarbons’.

The data of [23] on H_2 CHS and sorption by Ce, Dy, Lu, Er, Tm, and Yb are of special interest for the theory of catalysis. We will present (Fig. 11) the heats of H_2 CHS and sorption by Ce and Dy. The molar heat effect does not vary with the H/M (M is a metal) atomic ratio. The character of the data obtained for other rare-earth metals is similar. To understand the importance of these data, an excursion into the historical domain is necessary.

To explain the NH_3-synthesis kinetics that follows from the works by Winter [78] and Benton [79], Temkin assumed [80] that the surfaces of $Fe/K_2O/Al_2O_3$ catalysts and of a number of other catalysts are linearly heterogeneous. Factually, this hypothesis includes the assumption that the CHS heats decrease linearly with the surface coverage. Meanwhile, nobody proved experimentally surface heterogeneity of catalysts working in stationary catalytic processes. Temkin understood that, even if the catalyzing surfaces would be heterogeneous relative to the heats of CHS and relative to the reaction ability of their centers, ‘…physical grounds making heterogeneity of the surfaces to be linear could hardly be seen’ [81]. To explain the possibility of the uniform heterogeneity, he took [81, 82] that the surface electrons are as if located in an infinitely deep potential well giving a ‘surface electron gas’ and that CHS influences the electron concentration and the kinetic energy of the near-surface electron layer and thus decreases the molar heats of CHS with the coverage. This assumption supplemented with several other hypotheses led him to an equation giving linear decreasing in the heats of CHS with the surface coverage. This concept was criticized in [1–5, 7, 83]. It was noted that, if the assumption on the surface electron gas would be correct, the heat of H_2 dissolution in metals would be coverage-dependent as a result of a similar effect of the three-dimensional gas. Works [2, 3] give examples when the heat of H_2 sorption was found to be constant.

The extensive measurements performed in [23] with many metals did not confirm the coverage dependence in the heats of H_2 dissolution and, thus, refuted the hypothesis proposed in [81, 82].

Chemisorption of hydrocarbons

Coverage-independent heats of CHS were obtained even for CHS of some hydrocarbons, i.e., of the substances that, according to some opinions, can chemically interact with metal surfaces at about 300 K. Figure 12 gives the heats of C_2H_2 and CH_3C_2H CHS at Pt-films [39].

Works [22, 37] contain no proofs for the completeness of reduction of the samples and for the absence of CO_2 and H_2O desorption in the course of each experiment and between them. However, the side processes associated with surface–body diffusion, surface reactions, and desorption of the side products didn't reveal themselves under rather low temperatures at which these studies were performed.

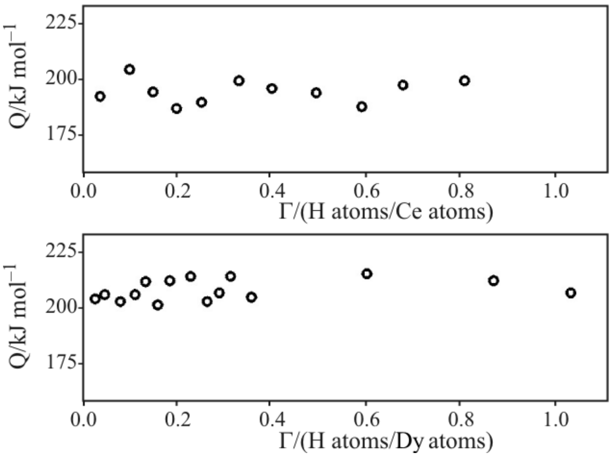

Fig. 11 Molar heats of H_2 chemisorption by lanthanides *vs.* relative H-content (295 K) [23]

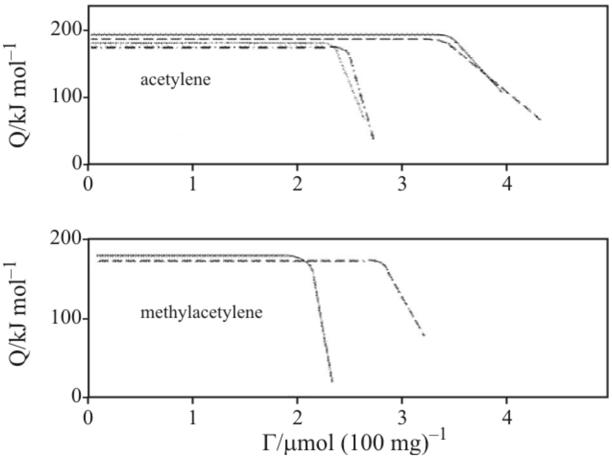

Fig. 12 Molar heats of C_2H_2 and HC_2CH_3 chemisorption at Pt films *vs.* chemisorbed amounts (room temperature, measurements with different samples) [39]

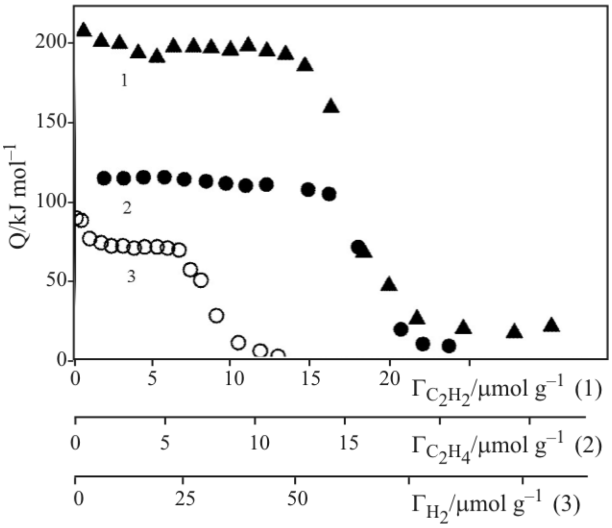

Fig. 13 Molar heats of 1 – C_2H_2, 2 – C_2H_4 and 3 – H_2 chemisorption at Pt-powder (173 K) *vs.* chemisorbed amounts [22]

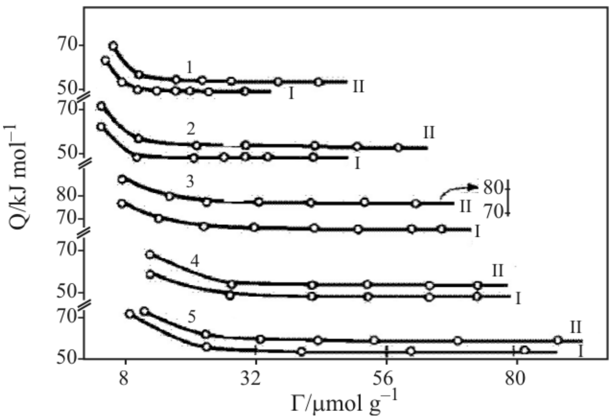

Fig. 14 Chemisorption of I – C_2H_4 and II – C_3H_8 at 1 – Co/Mg/Mo, 2 – Ni/Mg/Mo, 3 – Cu/Al_2O_3, 4 – Ti and 5 – Ag [84]

The results of these works are quite sufficient for the surfaces of the studied adsorbents to be considered as homogeneous, because the molar heats of CHS over rather wide ranges of surface coverages are constant within the experimental errors (Fig. 13).

Several examples of ethylene and propylene CHS at different catalysts are given in Fig. 14 [84]. These examples are rather demonstrative.

Conclusions

Surface homogeneity is a fundamental feature of the solids subjected to the stationary action of chemical reactions in which these solids participate as catalysts or chemisorbents. This statement relates to powders, films, wires, etc.

Some researchers believe that certain of surfaces are homogeneous and the rest ones are heterogeneous relative to their catalytic and CHS characteristics under stationary conditions. Meanwhile, there is no reliable confirmation for such a position relative to catalysts or adsorbents of specified chemical compositions located in any medium where a stationary catalytic or CHS process proceeds. Extended data obtained in [85] showed that catalytic reactions are capable of transforming crystal faces, decreasing their crystal indexes, and making them to be randomly distributed. In other words, in stationary states, the conditions of any catalytic reaction dictate some equilibrium arrangement to the surface CHS centers. It in no way follows that such surfaces reveal themselves as heterogeneous relative to the reaction ability of their active centers; and this review shows that the critical consideration of data on the molar heats of CHS allows the conclusion that surfaces are homogeneous.

Note that most data on the molar heats of CHS presented in this review were obtained by calorimetric methods with the instruments and adsorption and calorimetric techniques and procedures described in [46, 52, 86–89] and also by methods of CHS equilibriums and thermodesorption.

We wrote in Introduction that, according to the authors of a number of papers (e.g., [1–4, 7]), the notion on the so-called ‘induced heterogeneity’ (sometimes, it is termed ‘the effect of mutual influence of chemisorbed particles’) contradicts the band theory of solids.

The notion on the so-called biographic surface heterogeneity contradicts Boreskov’s rule on the approximate constancy of the specific (per surface unit) stationary catalytic activity of different catalysts of any specified chemical composition. It is clear that, if a surface heterogeneity existed, its character could not be the same for powders, supported crystals, foils, evaporated films, and wires of any definite chemical composition. On the other hand, if the stationary catalytic activity were determined by the surface heterogeneity, different aggregate states of a chemical substance would be characterized by different specific catalytic activities. Meanwhile, Boreskov stated unambiguously that they are approximately the same. Table 2 contains some of the data presented in [90]. The first two examples in Table 2 demonstrate that the variation in the specific surface of Pt catalysts by a factor of 43500 changes the specific catalytic activity for Pt wires, foils, grids, blacks, and SiO_2-deposited crystals in the reactions of H_2 oxidation and SO_2 oxidation almost not at all. For different catalysts of other chemical natures, variations in the crystal size, mode of preparation, and calcination temperature also don’t change the specific catalytic activity in different

Table 2 Experimental results underlying Boreskov’s rule

No.	Catalyst and reaction	Number of samples	Content of the study	Factor of the specific-surface variation	Specific catalytic activity/cm^{-2}	Refs
1	Pt wire, foil, and SiO_2-deposited; (H_2+O_2)	3	Variation of the form and mode of preparation of Pt-catalysts	43500	9.5±45%	[90]
2	Pt wire, foil, grid, black and SiO_2-deposited (0.2 and 0.5%); (SO_2+O_2)	6	Variation of the form of Pt-catalysts	43500	0.58±99%	[90]
3	γ-Al_2O_3; C_2H_5OH dehydration	8	Preparation-mode and calcination-temperature variation (723–1273 K)	2.5	37.9±17%	[91]
4	SiO_2; C_6H_5Cl hydrolysis	5	Calcination-temperature variation (798–1173 K)	7.15	16.5±13%	[92]
5	Soots; cracking of paraffins	3	Preparation-mode variation	6.7	4.8±20%	[93]
6	Graphite; (Br+H_2)		Variation of sizes of graphite crystals (3–300 nm)		Almost constant	[94]

reactions. These results were obtained by different authors and in different laboratories.

This outstanding generalization was first published in 1955 [90] (in English, [95]). It forestalled the time, and its fundamental importance was underestimated because, in the 1950s, the techniques and procedures for calorimetric measurements of the heats of CHS were imperfect, data on the heats of CHS at elevated temperatures were not available, and the notions on surface heterogeneity generated on the basis of speculative models were widely distributed in spite of the fact that a number of experts in surface sciences, such as Langmuir, De Boer, Tompkins, and others, did not support them. The generalized data presented in Table 2, apparently, were not published in English journals, and they are little-known over the world. Meanwhile, the experiments described by Boreskov are performed with rather simple and clear techniques, and their processing includes no questionable or closed procedures; therefore, they can not be disproved and belong to eternity.

One more fundamental result was obtained by Boreskov together with Karnaukhov: the specific CHS capacity of any massive or supported metal is approximately the same (if the crystal size is no more than 2 nm) [96, 97]. This result is well-known and is extensively applied to calculate the specific surface areas of metals from CHS data. The applicability of this method means that the CHS ability does not depend on the mode of preparation and, essentially, confirms that the surfaces are homogeneous because it is difficult to imagine that surfaces obtained on the basis of different procedures are equally heterogeneous.

Forty five years ago, we were the first over the world to begin the calorimetric studies of chemisorption at elevated temperatures [98]. We were sure that catalyst surfaces are heterogeneous, and we hoped that our measurements would dispel those doubts which appeared with respect to the surface heterogeneity after the works published in 1950–1960 by Boreskov [90] and by Brennan [24] (see above Fig. 6). The first our measurements instilled optimism into us: at elevated temperatures, we obtained the molar heats of O_2 CHS at silver powder (see above, Fig. 2 [45]) that decreased with the surface coverage. However, after improvement of the adsorption techniques and procedures that were widely distributed at that time, we ascertained that the thermally stabilized surfaces of different catalysts are homogeneous, that work [90] has trivial explanation, and that the results obtained in [24] and in subsequent works of this group (e.g., [99]) are not accidental.

This review is primarily oriented towards CHS at metals. However, the data on the kinetics and heats of CHS of gases at oxides, such as Cr_2O_3 [100–102], NiO [103], and ZnO [34, 51], also can be explained on the basis of notions on surface homogeneity.

As was noted in Introduction, the problem of ‘heterogeneity’ *vs.* ‘homogeneity’ of thermally stabilized surfaces is important not only for catalysis and CHS but also for the solid-state physics. The point is that both the CHS and catalysis are chemical phenomena and each surface act is associated with the full or partial electron transition to or from the corresponding solid body. The question is whether these electrons are localized and transit between the chemisorbed particles and electron shells of individual surface atoms affected only by the neighboring surface atoms or between the chemisorbed particles and the so-called Fermi level characteristic for the crystal as a whole and representing the upper energy level for the collectivized crystal electrons.

We showed [7–11] that a number of the kinetic equations derived earlier on the basis of notions on surface heterogeneity can be derived on the basis of surface homogeneity and that the so-called logarithmic isotherm and Elovich's equation translate the dependences which can be derived for homogeneous surfaces if the occupation of more than one surface center by each chemisorbed molecule is taken into account. Boreskov's rule and works [96, 97] count in favor of surface homogeneity. A number of the data on isotopic exchange between gaseous and chemisorbed particles do not confirm surface heterogeneity. At last, this review shows that the molar heats of chemisorption at thermally stabilized samples are constant over wide ranges of surface coverages. The results that are similar not only in the form of the heat–coverage function but also in the molar-heat levels are obtained for O_2 chemisorption at cobalt films and powders, for copper films and powders, for silver powders from calorimetric measurements and isotherms, for H_2 CHS at Fe-films in four different works, for CO CHS at copper powders in two works, for N_2 CHS at Fe-catalyst in two works, etc. When the side processes within solid bodies and at their surfaces are eliminated or are taken into consideration and when other principal requirements to the calorimeters and adsorption and calorimetric methods and procedures are fulfilled, the molar heat levels are as reproducible as it is possible for the works performed by different authors with different techniques and procedures at different samples and under different conditions.

From the results presented in this review, in the reviews [7, 46, 51, 52], and in the technical, experimental, and theoretical reviews and regular papers cited in these reviews, it follows that the surfaces of thermally stabilized catalysts and chemisorbents consisting of crystals of the same chemical composition reveal themselves as the homogeneous ones in stationary catalytic processes and in CHS processes. Meanwhile, there are researchers who continue to advocate the concept of surface heterogeneity. It is the author's opinion that the causes of this discrepancy are housed in imperfect studies, a portion of which is considered in 'The calendar-year effect on the measured results' of this review and in references [7] and [46].

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