ON THE DEPENDENCE OF THE CHEMISORPTION PROPERTIES OF METALS ON THE STRUCTURE OF THEIR SAMPLES

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Abstract

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ON THE DEPENDENCE OF THE CHEMISORPTION PROPERTIES OF METALS ON THE STRUCTURE OF THEIR SAMPLES

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In connection with the growing number of facts indicating a profound relationship between the catalytic activity of metals and their chemisorption capacity, and also in connection with the establishment (^{8}) of an approximately constant specific catalytic activity of bodies with identical chemical composition, it became necessary to provide an experimental basis for the constancy of the specific chemisorption capacity of substances (i.e., the magnitude of adsorption per unit surface area) when the composition is constant. From the standpoint of the modern understanding of the nature of catalysis and taking into account the law of mass action, the constancy of the specific catalytic activity of bodies may occur if there is constancy of their specific chemisorption capacity.

The available experimental data ($^{1-4}$) make it possible to assert that in a number of cases the specific chemisorption capacity of bodies, in particular metals, is constant and does not depend on their geometrical structure.

As is known, the structure of metal layers changes as their vapors condense (^{5,6}): at first there arises a certain number of embryonic particles—islands of clearly or latently crystalline granules, separated by free intervals. The particles of Ag, Au, Cu have a spherical form, while Zn and Cd have a regular crystalline form and larger dimensions (up to 200 Å). An increase in the amount of metal in the layer leads to development of the layer through the growth and coalescence of the initially formed particles (new crystallization centers are not formed), to a gradual decrease in porosity, and to the formation of a continuous layer. Further condensation of the metal leads to an increase in the thickness of the layer and to a change in its relief.

Table 1

Adsorption of H_2 at −195° on Ni layers condensed at −78°

No.	q	h, Å	$N_a \cdot 10^{16}$	$N_m \cdot 10^{16}$	$N_\Sigma \cdot 10^{16}$	N_m, % of N_Σ
1	0.595	32	23.4	0.87	24.3	3.5
2	2.62	141	56.8	2.33	59.1	3.9

Fig. 1. Dependence of the surface area of a nickel layer, condensed at −78°, on the amount of metal in the layer

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No.	q	h, Å	$N_a \cdot 10^{16}$	$N_m \cdot 10^{16}$	$N_\Sigma \cdot 10^{16}$	N_m, % of N_Σ
3	3.70	198	71.8	2.7	74.5	3.6
4	4.41	236	94.1	4.56	98.7	4.6
5	7.2	386	115.8	4.62	120.4	3.8
6	8.28	440	124.1	4.62	128.7	3.5

Note. q —layer weight in mg; h —mean thickness; N_a —number of H_2 molecules irreversibly chemisorbed on Ni; and N_m —reversibly chemisorbed at $P = 2 \cdot 10^{-2}$ mm; N_Σ —total adsorption of hydrogen ($N_\Sigma = N_a + N_m$).

The results of measuring hydrogen adsorption on nickel layers at various stages of their development, given in Table 1 and in Fig. 1, show that with the described changes in structure and with an increase in the amount of metal in the layer, its chemisorption capacity increases and, at the same time, there is a proportional increase in the strongly bound part of the adsorption, i.e., atomic chemisorption, and in the weak, reversible part of the adsorption, i.e., molecular chemisorption. It is seen from Table 1 that the ratio between molecular and atomic chemisorption remains practically constant, i.e., the change in structure does not affect the qualitative aspect of the phenomenon.

Table 2 gives data characterizing the influence of heating a nickel layer, i.e., recrystallization, on hydrogen adsorption. As we see, in this case as well, the change in the structure of the layer has practically no effect on the qualitative aspect of the phenomenon.

Fig. 1. Dependence of the surface area of a nickel layer, condensed at −78°, on the amount of metal in the layer.

It remains to determine what accounts for the increase in the chemisorption capacity of the layers with respect to hydrogen as they grow and as their structure changes. An answer to this question is provided by data from measurements of the surface area of nickel layers by krypton adsorption at −195° and by the results of comparing the values obtained with the amount of hydrogen adsorbed on the same layers at the same temperature. The data of Table 3 make it possible

Table 2

Influence of heating a nickel layer for 30 min on the magnitude of adsorption and on the ratio between irreversible (N_a molecules) and reversible (N_m molecules) adsorption of hydrogen, as a percentage of the total adsorption N_{Σ}

No.	T_k, °C	T_p, °C	h, Å	$N_a \cdot 10^{16}$	$N_m \cdot 10^{16}$	N_m, % of N_{Σ}
1	−78	−78	440	124	4.62	3.6
2	−78	−78	386	116	4.65	3.8
3	0	200	1350	14.8	0.3–0.4	2–3
4	0	0	1457	37.2	0.6–0.7	2

Note. T_k is the condensation temperature; T_p is the temperature of heating for 30 min.

to assert that hydrogen chemisorbed at −195° practically completely (97-98%) fills the surface with an atomic layer, i.e., that the amount of chemisorbed hydrogen determines the surface area of the nickel layer. It follows from this that the increase in the chemisorption capacity of the metal layer as it grows and as its structure changes is connected with the accompanying increase in total surface area. This conclusion is also confirmed by the data of Porter and Tompkins (^{7}), obtained in the study of iron layers. The magnitude of H_2 chemisorption per unit surface area, i.e., the specific chemisorption capacity, remains constant.

The data presented and their discussion lead to the conclusion that a change in the structure of nickel layers and similar metals during condensation or during re-

Table 3

Adsorption of H_2 and Kr on one and the same layer of nickel at −195°

No.	τ	h, Å	$N_{H2} \cdot 10^{-16}$	$N_{Kr} \cdot 10^{-16}$	S_{Kr}	$\sigma_{H2} \cdot 10^{16}$, cm^2	$\sigma_H \cdot 10^{16}$, cm^2
1	30	1500	11.6	9.71	180	15.5	7.7
2	15	1838	14.2	11.6	215	15.4	7.5
3	30	2535	14.5	11.8	219	15.0	7.5

Note. τ—time of heating of the layer, in minutes; h—mean thickness of the layer; N_{H2}—number of molecules of adsorbed hydrogen; N_{Kr}—number of krypton atoms filling the surface of nickel (calculated according to BET and the Langmuir equation); S_{Kr}—area of the layer in cm^2, calculated from the adsorption of krypton (σ_{Kr} taken equal to 18.5 Å^2); σ_{H2} and σ_H—elementary areas falling to a molecule or to a hydrogen atom, according to the calculated area.

As a result, heating (recrystallization) has practically no qualitative or quantitative effect on their specific chemisorption capacity. The constancy of the specific chemisorption capacity in a number of metals and, possibly, other substances, when their chemical composition is constant, is the reason for the approximate constancy of the specific catalytic activity ([8]).

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Note: Figure translations are in progress. See original paper for figures.