HOKKAIDO UNIVERSITY

Title	ON THE EFFECT OF POROSITY OF SOLIDS UPON THEIR ADSORPTIVE AND CATALYTIC PROPERTIES
Author(s)	BLIZNAKOV, G.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 16(1), 195-216
Issue Date	1968
Doc URL	https://hdl.handle.net/2115/24856
Type	departmental bulletin paper
File Information	16(1)_P195-216.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 16, No. 1, pp. 195 to 216 (1968)

ON THE EFFECT OF POROSITY OF SOLIDS UPON THEIR ADSORPTIVE AND CATALYTIC PROPERTIES

By

G. BLIZNAKOV

Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences,
Sofia, Bulgaria

(Received December 18, 1967)

Abstract

The efiect of surface curvature upon the adsorptive and catalytic properties of solids has been shown on the basis of experimental data and theoretical considerations. The heterogeneity of the surface of silica gel, alumina and silica-alumina with respect to their adsorptive and catalytic properties depends directly on the pore curvature. This has been shown in studying adsorption of ammonia on alumina, interaction between the hydroxyl groups on the silica gel surface, adsorption heats of ammonia on silica gel, decomposition of formic acid on silica gel, dehydration of *i*-pentanol on silica-alumina and so on.

The effect of curvature has been discussed theoretically in the case of semiconductors. It appears when the radius of a pore or particle becomes smaller than the Debye length. In such cases, changes in the adsorptive and catalytic properties of the semiconductor may occur. It has been pointed out that a compensation effect due to the effect of dispersion may be expected.

Introduction

The activity of a catalyst is determined mainly by its chemical nature, including admixtures and deviations from the stoichiometric composition.[1-6] There is a widespread view that specific catalytic activity depends not very much on the state of surface and is determined by the chemical composition of the catalyst and its chemical structure. Whilst this may be true in general, it is necessary to pay attention to numerous catalytic investigation which show the importance of the physical state of the surface. Physical properties such as crystal structure, crystal habit, magnetic state, state of subdivision, porosity and so on very often produce a change in the catalytic activity of solid catalysts.

This is confirmed by investigations of the catalytic activity of different crystal faces which have shown the presence of anisotropy in catalytic action.[7-19]

There are also many examples which show that the surface of a solid differs very much in its chemical nature and physical properties from the bulk. This difference influences the adsorptive and catalytic properties of the solid. The best formulation of the problem is perhaps the one given by S. Z. ROGINSKI:[3] "The chemical composition and structure of a solid determine its initial catalytic activity".

The extent of dispersion of a catalyst affects its activity and depends on its method of formation. This problem has not been elucidated, although already in the thirties P. D. DANKOV[20,21] showed that with the increase in dispersion, the catalytic activity passed through a maximum.

When discussing the influence of dispersion and porosity upon the catalytic activity of solids, attention has mainly been paid to diffusion.[22~25] It has been assumed by WHEELER[26] that "chemical behaviour and catalytic action are independent of pore dimensions". This assumption introduces an essential simplification and gives the possibility of concentrating the attention on the diffusion effects only, which is very conventient with porous catalysts and reactions proceeding in the region of diffusion control. Studies of the active surface of solids with respect to their adsorptive and catalytic properties show that there is a biographical heterogeneity.[27] It is of interest to determine the extent to which this heterogeneity depends on and is caused by dispersion and porosity.

The existence of such a relationship may be expected on the basis of general considerations. The thermodynamic functions of systems which include small phases and those which include large phases differ from each other. This is valid for phases with both convex and concave surfaces. According to the Kelvin-type equation (GIBBS-THOMSON's equation)

$$\Delta\mu = \pm \frac{\text{const}}{R} \qquad (1)$$

Here R is the characteristic of surface curvature; the constant is calcuated on the basis of the free specific interphase energy and the molecular volume and contains a shape factor. As is well known, perceptible differences in the chemcal potentials appear when $R < 10^{-4}$ cm. With porous bodies, this occurs when the average pore diameter corresponds to the specific surface 1 m^2/g *i.e.* with most porous catalysts, adsorbents and small crystals dispersed on carriers. Since the properties of the surface particles of solids depend on curvature and play an important part in catalytic and adsorption processes, a dependence (in the differential and integral forms) of the catalytic and adsorption parameters upon the radius of curvature may be expected.

A similar dependence may exist with semiconductors. With these, the effects of the boundary layer (which is characterized by the Debye length, L, *i.e.* the distance from the surface at which the Fermi level acquires its normal position corresponding to a large crystal) determine the surface properties of semiconductors. The Debye length is usually of the order of 10^{-4}–10^{-6} cm., *i.e.* it is in the same GIBBS-THOMSON's region. With a semiconductor crystal having dimensions $R<L$, the position of the Fermi level will from that for a large crystal. It is evident that the Fermi level position will depend on the crystal dimensions; remember also that it is determined by the chemical potential of the electron system of the solid.

A dependence of the activity of catalysts on their dimensions has been observed by G. M. SCHWAB and E. SCHWAB-AGALLIDIS with the decomposition of ethanol and formic acid on metal oxides and salts. In the papers of V. F. KISSELEV *et al.*[29~35] there are data concerning the dependence of the adsorptivity of silica gel upon the degree of dispersion.

The problem may be eapproached phenomenologically or an attempt can be made to discuss the effect on the basis of more general theoretical considerations.

By varying the extent of dispesity (porosity) we have prepared adsorbents and catalysts with different properties. We have been able to study such classical porous bodies as silica gel, alumina and silica-alumina in detail.

1. Experimental results on the activity of silica gel, alumina and silica-alumina

a) In the literature, the adsorptive and catalytic properties of silica gel, alumina and silica-alumina have generally been associated with the number of hydroxyl groups on their surface which play the part of adsorption and catalytic centers.[36~39] The removal of hydroxyl groups leads to a decrease in activity[40~50] and their substitution by inactive groups has a similar effect.[51~57] There are, however, data which show that with the first amounts of water chemisorbed on silica gel, the silicon tetrahedra can be considered as the primary adsorption centers, the hydroxyl gorups having in this case an indirect action.[62]

The homogeneity or heterogeneity of the surface due to the hydroxyl groups and its effect on adsorption capacity has often been discussed in the literature.[26,58~61] Many investigations (above all the works of V. F. KISSELEV *et al.*) have confirmed that the surface hydroxyl groups differ in their properties. A publication of V. I. KVILIDZE[62] is very interesting in this respect. Using the method of nuclear magnetic resonance, KVILIDZE has shown that at least three types of configuration of hydroxyl groups exist on the silica gel surface: single and double hydroxyl groups as well as more complicated formations. The hydroxyl groups having two, three or more neighbours produce stronger adsor-

ptive properties towards water vapour and amount to about 45 per cent of the total number of hydroxyl groups on the surface of the samples investigated.

Information about the differences in the properties of the hydroxyl groups has also been obtained by IR spectroscopy. Using apparatuses with various resolution abilities, some authors[63~66] have established the existence of 3–5 types of hydroxyl groups on γ-Al_2O_3 and η-Al_2O_3. The number of neighbours of a hydroxyl group may vary from four oxygen ions to four aluminium ions (acidic centers according to LEWIS).

b) Another important problem is the distribution of active centers responsible for a given kind of interction on the surface of a porous solid and the dependenc of this distribution on some principal physical property of the solid. Now the pore curvature can be chosen as a characteristic which can serve as argument of the distribution function.

The method of investigation is given in the papers of I. BAKARDJIEW,[67,68] The surface of a porous solid is divided into numerous elements with a given curvature, the latter being determined within the region of capillary condensation on the basis of the Kelvin equation using $\log p/p_0$.

When changing the volume of condensed liquid by dv, the corresponding part of surface, dS, changes too. dS is related to the curvature by the following dependence:

$$dS = \kappa \log p/p_0 \left(\frac{\partial v}{\partial \log p/p_0} \right)_T d \log p/p_0. \qquad (2)$$

Here, κ depends very little on pressure and may be considered constant.

It follows from this equation that on the basis of the data obtained from the adsorption isotherms concerning the capillary condensation it can be written: $\log p/p_0 \left(\frac{\partial v}{\partial \log p/p_0} \right)_\tau = \varphi(\log p/p_0)$, *i.e.*, the differential distribution curves of surface with respect to its curvature are obtained. Fig. 1 shows these curves (obtained from the adsorption isotherms of butane at 0°C) for several samples of aluminium oxide.

The validity of Eq. (2) has been established by comparing the integral values obtained graphically from the total adsorption isotherms with the corresponding specific surfaces determined by the BET method. Both a series of different samples and a sample modified by the gradual filling of the pores with butane was used. As is evident from Fig. 2, there exists a linear dependence between S and $\int \log p/p_0 \left(\frac{\partial v}{\partial \log p/p_0} \right)_\tau d \log p/p_0$.

The distribution functions of the surface with respect to its curvature may be compared with various properties of the same surface presented in

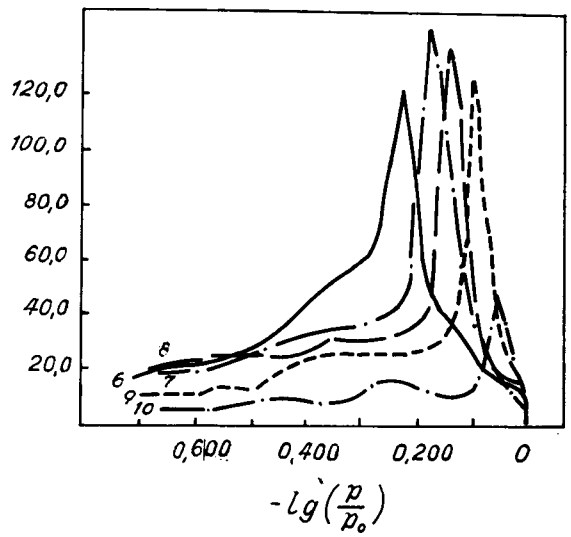

Fig. 1.

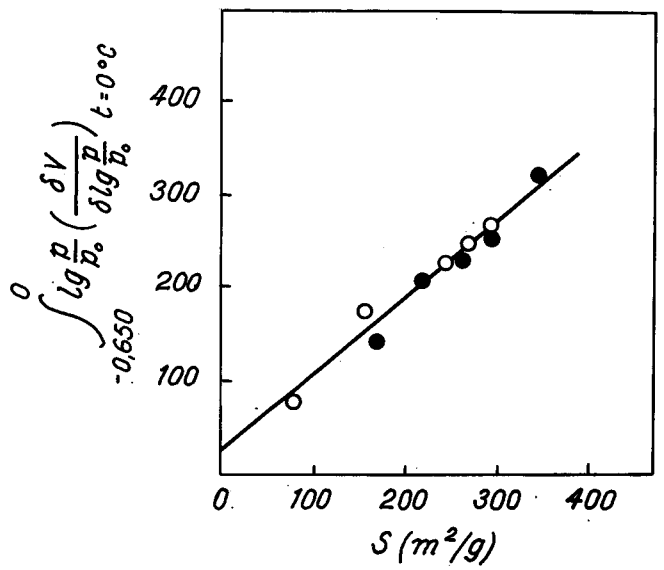

Fig. 2.

differential form, which confirms the existence of corresponding correlations.

c) By investigating the adsorption of ammonia on alumina and silica gel, we have obtained results[69-2)] concerning the interaction between the surface hydroxyl groups.

Samples with various number of hydroxyl groups on the surface (obtained by thermal dehydration or by partial substitution of the hydroxyl groups by methoxy ones) have been investigated. Specimens containing 4.78×10^{-5} mole/m^2 and 1.08×10^{-5} mole/m^2 structural water have been obtained. Their specific surface and pore distribution remained unchanged. A sample containing 9.8×10^{-5} mole/m^2 structural water, *i.e.*, the maximum number of OH groups, has also been investigated. This specimen was obtained by autoclaving the initial γ-Al_2O_3 with steam. As is evident from Fig. 3, the distribution of the surface elements of the sample with respect to curvature is shifted to areas with greater radii (larger pores).

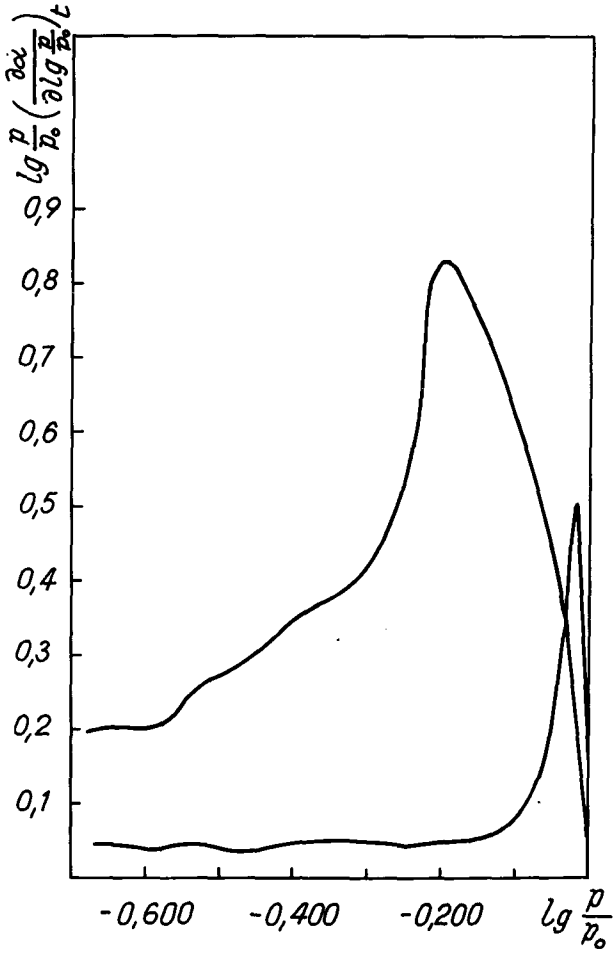

Fig. 3.

The adsorption of ammonia on these samples was studied within the temperature range from −45 to +50°C (Fig. 4). It can be seen that with lower concentration of the hydroxyl groups and higher coverage (considerable amounts of adsorbed ammonia), the adsorption isosteres have a normal course. On the other hand, with samples having a higher concentration of hydroxyl groups and lower coverage, the isosteres are S-shaped and some parts of them have positive slopes. Analogous results were obtained with silica gel thermally dehydrated or modified by methylation.[69-71] The results may be explained by assuming that an interaction between the hydroxyl groups is possible. It should be most pronounced with considerable concentrations and lower temperatures. Rupture of bonds between the hydroxyl groups occurs due to adsorption. This may express itself in a negative thermal effect and a corresponding change of entropy. It may also be concluded that the hydroxyl groups are irregularly distributed on the surface and the dehydration of the latter after heat-tratment proceeds irregularly. The interaction between the hydroxyl groups may also be assumed to be stronger in narrower pores (on areas with greater curvature) and these are perhaps the areas where the process of thermal dehydration begins.

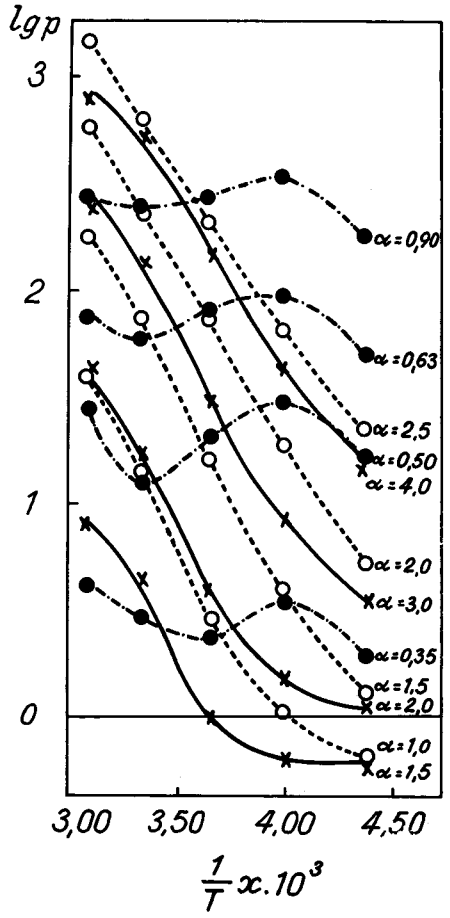

Fig. 4.

Using the data obtained by EGOROV, KRASIL'NIKOV and KISSELEV[74] concerning the process of thermal dehydration of four samples of silica gel with specific surface ranging between 200 and 700 m^2/g, I. BAKARDJIEW[73] has investigated the distribution of OH groups with respect to the surface curvature and the change of this distribution as a result of thermal treatment (within the range of 300–600°C). Fig. 5 shows the differential functions of surface distribution with respect to curvature for the samples investigated. The results

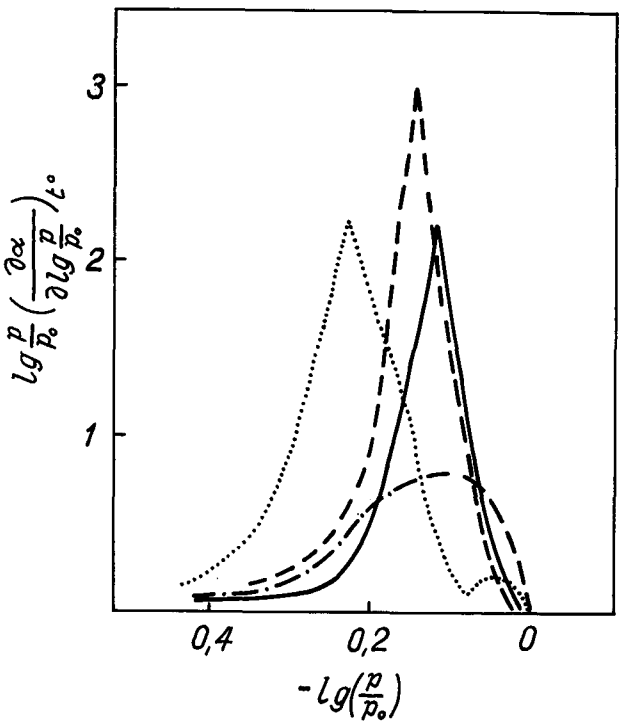

Fig. 5.

of analysis are given in Fig. 6. They show that at lower temperatures the hydroxyl groups in the narrow pores (maximum curvature $\log p/p_0 = -0.3$) are removed. In the range between 200° and 400°C their number decreases quickly. On areas with small curvture, the dehydration proceeds slowly, and with flat areas the OH groups on the surface cannot be removed even at 400°C. The shapes of the curves speak for irregular distribution of the hydroxyl groups on areas with different radii. The narrow pores are dehydrated more easily thus becoming "drier". This happens at 250°–300°C, the temperature at which the samples are usually heat-treated.

d) The results obtained are in good agreement with the data concerning the heat of adsorption of ammonia on silica gel which has been premethylated or dehydrated to a certain extent.[75] Fig. 7 shows the relationship between the differential heat of adsorption and the amounts of adsorbed ammonia for a series of samples with increasing extent of dehydration. The heat of adsorption decrases lineases linearly with coverage. The dehydration leads also to a decrease of the initial values of the heat of adsorption and to a change

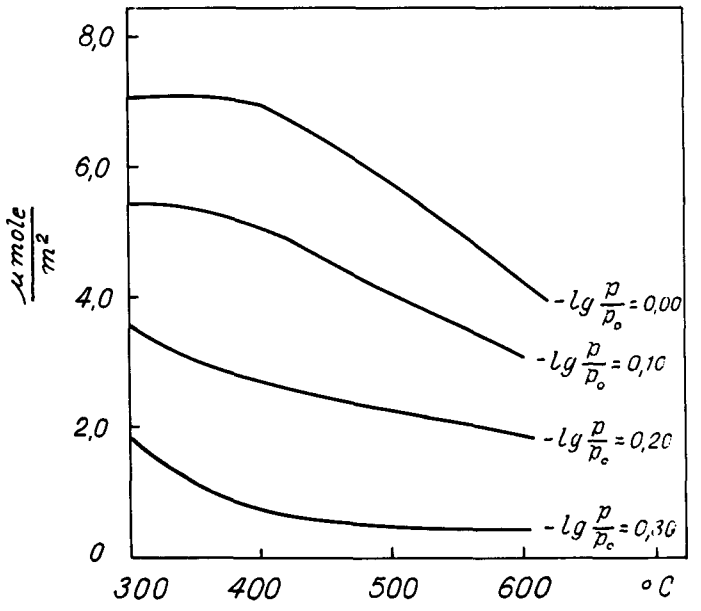
8,0
6,0
4,0
2,0
0
μmole/m²
$-lg\frac{p}{p_o}=0{,}00$
$-lg\frac{p}{p_o}=0{,}10$
$-lg\frac{p}{p_o}=0{,}20$
$-lg\frac{p}{p_o}=0{,}30$
300
400
500
600
°C

Fig. 6.

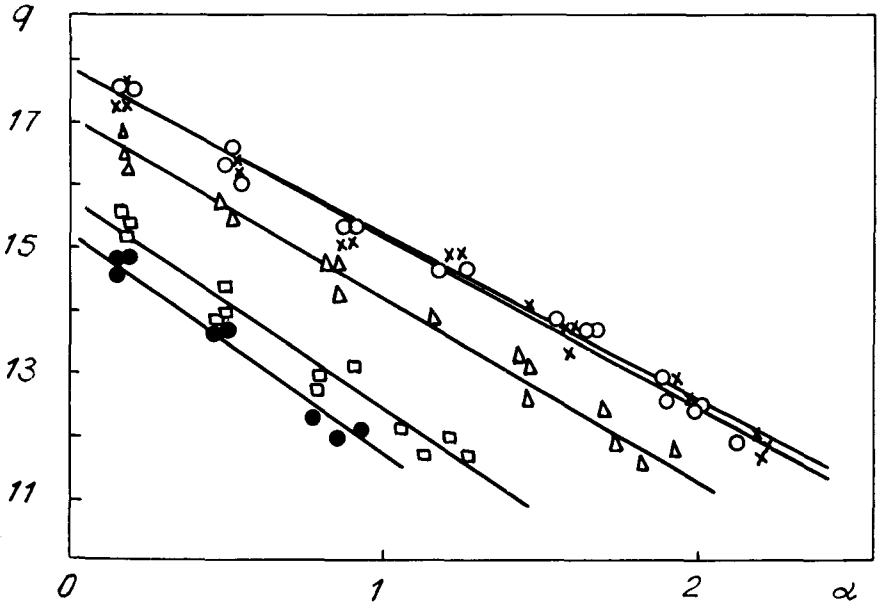
q
17
15
13
11
0
1
2
α

Fig. 7.

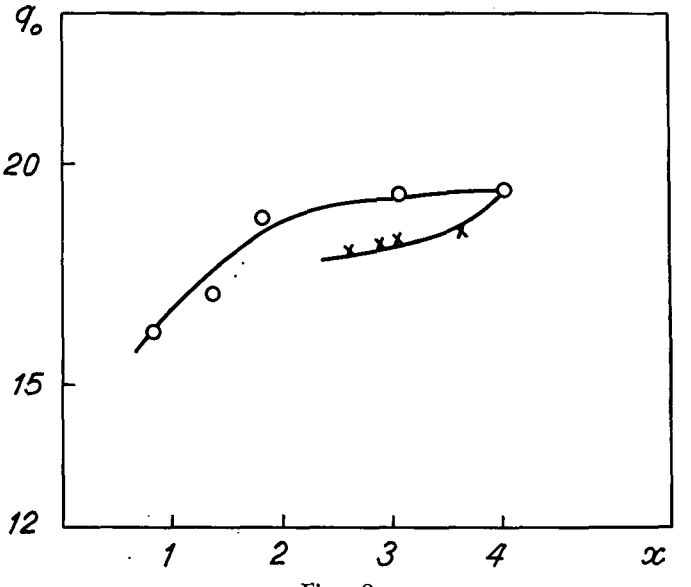

Fig. 8.

of slope in the straight lines. Generally speaking, these results are in agreement with those obtained by J. BASTIK.[76] Analogous data are obtained for samples whose hydroxyl groups are partially replaced by methoxy groups.[75] Fig. 8 illustrates the dependence of the initial differential heat of adsorption upon the concentration of hydroxyl groups on the surface. Ammonia is adsorbed mainly on areas dehydrated to a smaller extent, *i.e.*, on areas with smaller curvature. This follows from the negligible initial change of q_0 with the decrease in number of the hydroxyl groups (○). Since q_0 of methoxylated specimens decreases more quickly, when the hydroxyl groups are replaced by methoxy ones, this means that the areas mentioned are methoxylated most easily (×). The results of these investigations confirm the existence of initial differences in the properties of the surface hydroxyl groups, *i.e.*, of a biographical heterogeneity of the surface (with respect to its chemical structure) expessed by the surlace hydroxyl groups.

e) The most interesting results (from the viewpoint of the main problem being discussed) should be data from catalytic studies. Experiments should be carried out in such a way as to ensure that the reaction proceeds in the region of kinetic control. The kinetics of decomposition of formic acid have been investigated on a series of silica gel samples treated in a special way.[77]

It is known that on silica gel this reaction takes place as a dehydration process, the latter being (according to many authors) directly associated with

the hydroxyl groups on the surface.[78~80] This was confirmed by our experiments as well.

To obtain the necessary samples, the initial silica gel was treated with steam in an autoclave at a pressure of 50 atm with varying duration of treatment (0.1–38 hr) which caused changes in the specific surface (from 330 m^2/g to 85 m^2/g) as well as in its distribution with respect to curvature. Fig. 9

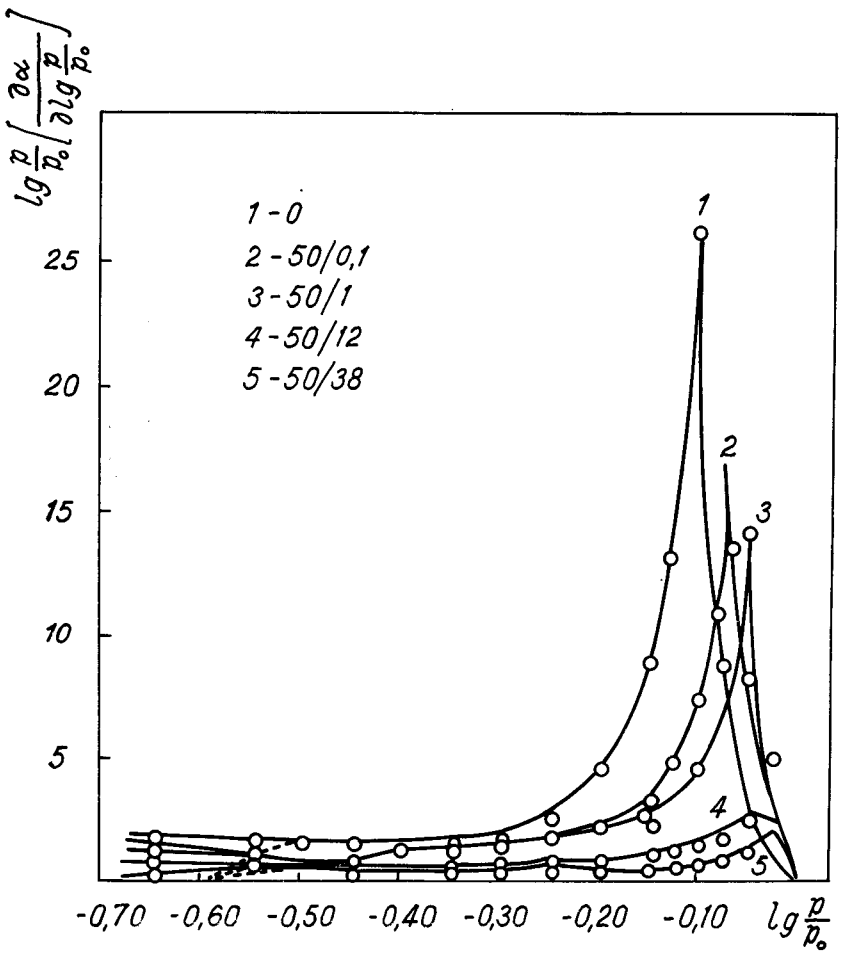

Fig. 9.

shows the differential distribution curves with respect to curvature. It is evident that the specimens are (more or less) monoporous which simplifies the discussion of the results. The integral values of the distribution functions plotted against the corresponding specific surfaces (determined by the BET method)

give a straight line. The decomposition of formic acid was carried out in a static apparatus at an initial pressure of 3 mm Hg and temperature of 180–250°C.

The kinetic curves of decomposition of formic acid at various temperatures were differentiated graphically and the Arrhenius plots were obtained from the extrapolated initial values of the reaction rate.

Fig. 10 shows the activation energy and the frequency factor as function of the curvature corresponding to the maximum of the distribution curves.

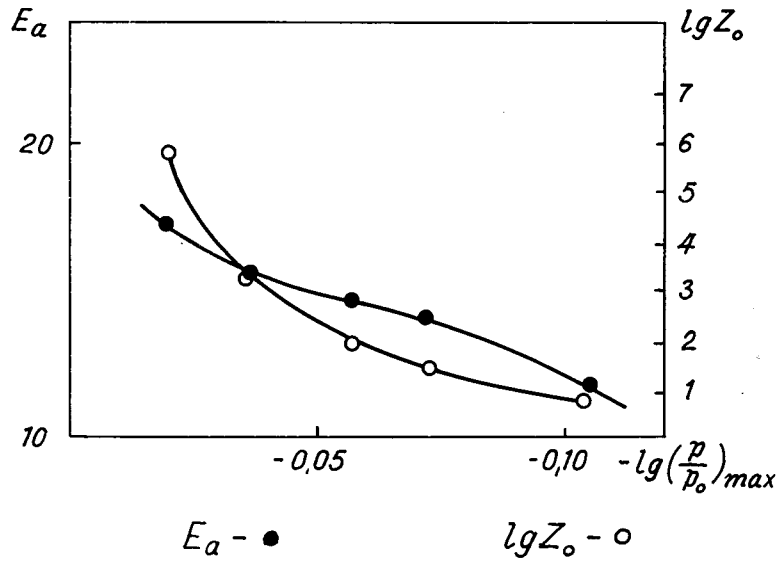

Fig. 10.

The observed phenomenon is similar to a compensation effect. The activation energy is lower in the narrower pores where the number of "active centers" is smaller. The reaction is inhibited on surfaces with less curvature but the number of places where the elementary act of reaction may be realized, increases.

It follows from the differences between the values of E_a and $\ln z_0$, however, that the specific activity is a function of the curvature. In Fig. 11, the de-endence of the specific activity (at 473°C) upon the curvature is presented. With the decrease in curvature, the specific activity decreases too. On this basis, an optimum curvature (depending on the working temperature of the catalyst) with respect to the catalytic activity should exist. It is evident that our investigations carried out at the given temperatures do not include the region of this optimum curvature.

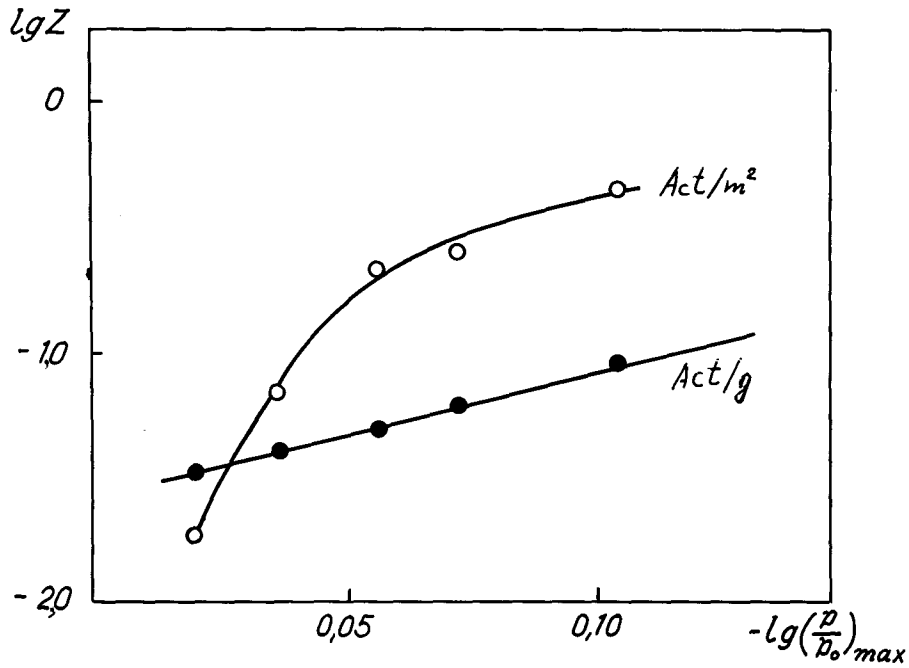
lgZ
0
-1,0
-2,0
Act/m²
Act/g
0,05
0,10
$-lg(\frac{p}{p_o})_{max}$

Fig. 11.

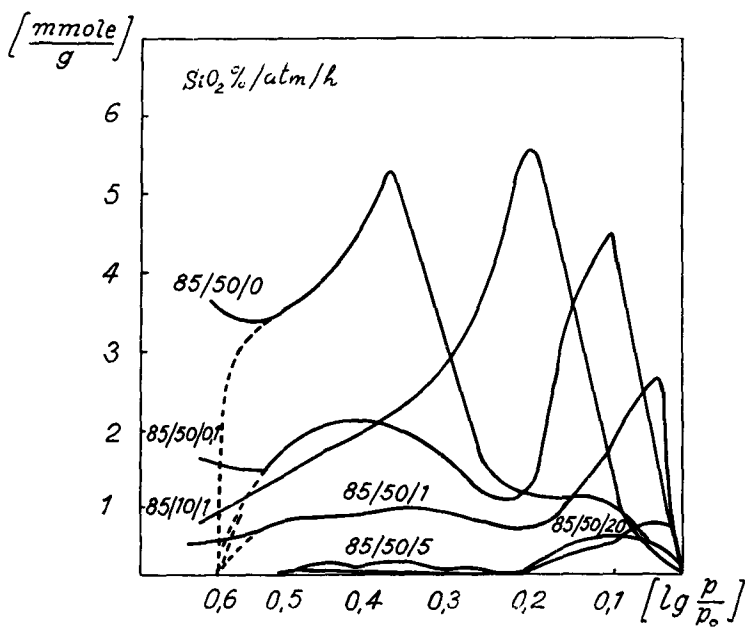
$[\frac{mmole}{g}]$
SiO_2 %/atm/h
6
5
4
3
2
1
85/50/0
85/50/0,1
85/10/1
85/50/1
85/50/20
85/50/5
0,6
0,5
0,4
0,3
0,2
0,1
$[lg\frac{p}{p_o}]$

Fig. 12.

f) I. BAKARDJIEW, K.-H. SCHNABEL and K. WENCKE[81,82] have investigated the relationship between the catalytic and porous properties of silica-alumina towards the dehydration of n-pentanol and i-propanol. This reaction is known to take place on acidic centers.[83~86] We shall say a few words about the isopropanol study. This was carried out on industrial silica-alumina catalyst modified byhydrothermal treatment. The specific surface was varied between 358 and 31 m^2/g. The acidity of the samples was determined by titrating in dimethylformamid medium.[86] The distribution functions are given in Fig. 12.

The dehydration of propanol (degree of conversion up to 15 per cent, temperature range 230–300°C) was investigated in a circulation apparatus. Varying the conditions, the interval can be established within which a reaction of zero order takes place.

The dependence of activation energy, frequency factor and specific acidity upon the surface curvature can be determined using a system of integral equations of the following type:

$$\overline{X}_i = \int_{x_1}^{x_2} X(t)\phi_i(t)dt\,. \qquad (3)$$

Here $\overline{X}_i$ is the mean specific value of any one of the investigated properties, $\phi_i(t)$ denotes the distribution of surface with respect to its curvature innormalized form and $X(t)$ is the studied dependence.

Calculations have shown that the investigated properties may be presented as linear dependent upon curvature with an accuracy of 3.5–7.4%. Fig. 13 shows the dependence of the specific catalytic activity upon the surface curvature.

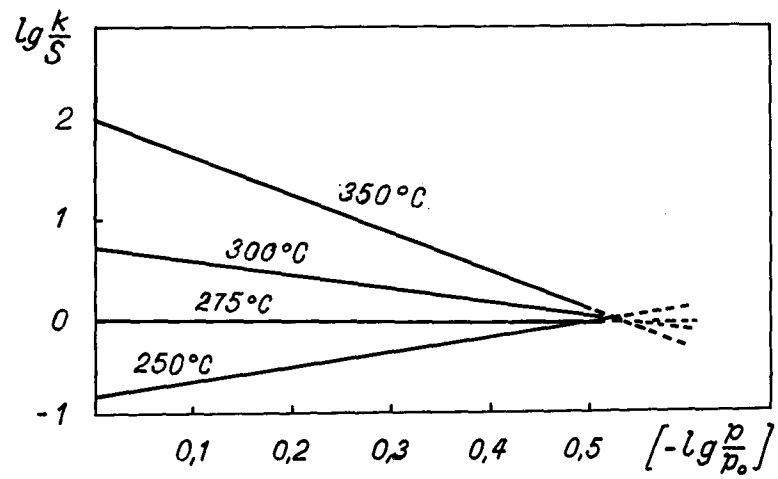

Fig. 13.

The curves show that the effect of curvature with resepct to the specific catalytic activity depends on the working temperature of the catalyst and influences both the frequency factor in the Arrhenius Equation and the energy of activation. It is also evident from Fig. 13 that a temperature exists at which complete compensation is reached and the curvature does not affect the specific catalytic activity. In this case, the surface behaves as pseudohomogeneous. At other temperatures, however, the curvature may cause a change in the specific activity in a positive or negative direction by almost two orders of magnitude.

The investigation enables us to determine the dependence of the specific catalytic activity on the specific acidity of the samples (Fig. 14). It is evident

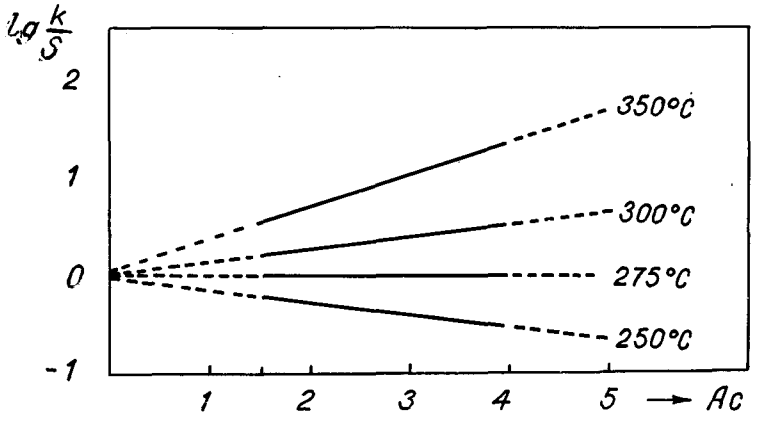

Fig. 14.

that (depending on the working temperature) the increase in the specific acidity may entail an increase or decrease in the specific activity of the catalyst.

2. Theoretical study of the effect of curvature upon the adsorptive and catalytic properties of semiconductors

a) The effect of curvature may also be explained theoretically. In this respect, an attempt has been made by O. PESHEV and G. BLIZNAKOV on the basis of the electron theory of adsorption on semiconductor.[88]

The effect of dispersion upon the adsorptive capacity has been studied in general by KOGAN[89] who has shown that with a thickness of the semiconducting plate of the order of the Debye length, L, or smaller than it, the specific adsorptive capacity depends on the thickness of plate. In all cases, the specific adsorptive capacity decreases with the increase in dispersion (*i.e.*, the ratio S/V increases). The physical nature of this phenomenon is quite clear. With thick plates, the effect of surface charge does not reach the depth

of the crystal (the latter being in this case electrically neutral) and causes no change in the Fermi level position. With a thin plate ($l<L$), the effect of surface charge "penetrates" the whole crystal. Surface and bulk charges are opposite in sign, which means that the Fermi level is shifted with respect to its position in the thick plate, *i. e.*, with acceptor surface levels-downwards, and with donor levels-upwards. As a result, the adsorptive capacity decreases.

In his study, KOGAN assumes two conditions which, however may be not fulfilled. 1) The number of adsorption centers per unit surface and their nature are independent of the thickness of the plate, and 2) The surface charge is made solely of chemisorbed particles. When the free electrons or holes of the semiconductor play the part of adsorption centers, and the first condition is not fulfilled, the effect of KOGAN will increase. The second condition is very essential and its non-fulfilment may play a very important part. Our conclusions are based on the inequality deduced by KOGAN:

$$\frac{d|\sigma|}{dl} > 0 . \qquad (4)$$

Here σ denotes the surface charge density. The inequality is valid regardless of whether the charge is of adsorption origin or not. If there is a great number of charges of non-adsorptive origin on the surface of the specimen, adsorption does not influence essentially the surface charge density. Assuming that these charges have an acceptor character, the Fermi level in a thin plate will be lowered (according to the above inequality) with respect to its position in a large crystal. Therefore, chemisorption of acceptor particles will proceed with difficulty, and that of donor particles will be realized easily. It is clear that in this case the sign of the effect will depend upon the kind of chemisorbed particles.

For the heat of adsorption of acceptor, donor and neutral particles, respectively, one can write the following equations:

$$q = q^- - \varepsilon_S^- ; \quad q = q^+ - \xi^+ \quad \text{and} \quad q = q_0 . \qquad (5)$$

Accordin to the terminology of WOLKENSTEIN,[90,91] q_0 denotes the energy of "weak" bond. In all these cases the specific adsorptive capacity and the heat of adsorption change as functions of dispersion, in the same sense. Since ε_S is function of N, the change of q is determined by the dependence of the Fermi level position on the degree of coverage. The dependence of the adsorption capacity of the semiconductor pores upon curvature (pore radius) has also been investigated. The energy diagram is given in Fig. 15. Using the method of WOLKENSTEIN[90,91] for a wide pore ($R>L$) we obtain the expression

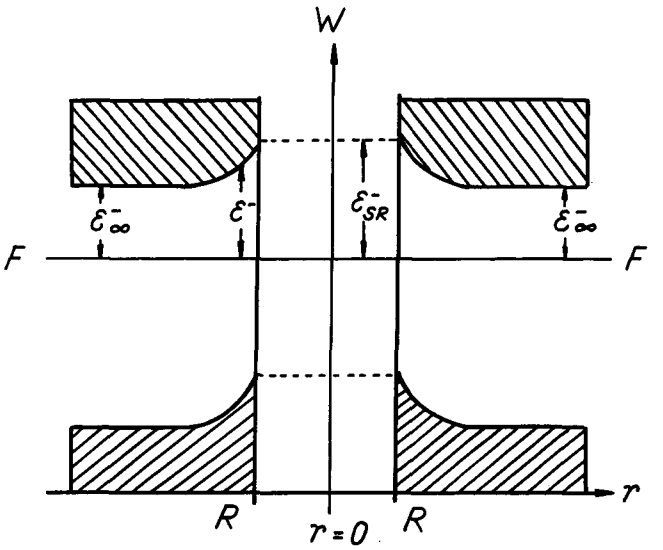

Fig. 15.

$$\psi = \psi_{S,\infty}\sqrt{\frac{R/L}{\xi}}\exp-\left(\xi-\frac{R}{L}\right)\Big] \qquad (6)$$

which gives (in κT units) the bending of energy bands $\psi = \frac{\bar{\varepsilon} - \bar{\varepsilon}_\infty}{\kappa T}$. $\psi_{S,\infty}$ is the bending of energy bands on a plane surface caused by a surface charge of the same density σ; ξ is a dimensionsionless length (radial coordinate in L units).

It is evident that

$$\psi_{S,R} \equiv \psi\left(\xi = \frac{R}{L}\right) = \psi_{S,\infty}, \qquad (7)$$

i.e., the surface of a wide pore behaves practically as a plane surface.

For narrow pore ($R<L$) one obtains

$$\psi = \psi_{S,\infty}\frac{R}{L}\kappa_0(\xi). \qquad (8)$$

Here $\kappa_0(\xi) = \frac{i\pi}{2}H_0^1(i\xi)$, where $H_0^1(i\xi)$ is the first Hankel function of zero order.

For the bending of energy bands in a narrow pore we can write:

$$\psi_{S,R} \equiv \psi\left(\xi = \frac{R}{L}\right) = -\psi_{S,\infty}\frac{R}{L}\ln\frac{R/L}{2}. \qquad (9)$$

When R/L increases from 0 to $2/e$, the factor $-\frac{R}{L}\ln\frac{R/L}{2}$ increases monotonically from 0 to $2/e$. This means that with one and the same value of the surface charge, the bending $\psi_{S,R}$ will be considerably smaller than with a plane surface. It follows that the specific adsorptive capacity and the heat of adsorption in a narrow pore is increased with respect to that on a plane surface. This effect is opposite to the one described by KOGAN.

The obtained results show that the adsorptive properties of disperse semiconductors with convex and concave surfaces differ from those of adsorbents with plane surfaces. These properties depend on surface curvature. As far as adsorption may play an important part in the kinetics of catalytic reactions, the dispersion of a catalyst may influence the kinetic parameters of reaction. With real porous adsorbents, both KOGAN's effeet and the one studied by us may appear simultaneously. The above result holds good for isolated pores, *i.e.*, when the wall thickness exceeds the screening length. If narrow pores appear in a caystal and their number increases, the total and specific adsorptive capacity will also increase. When the number of narrow pores becomes so great that the wall thickness is smaller than the screening length, there appears KOGAN's effect and the specific adsorptive capacity begins to decrease. Hence, with respect to adsorptive capacity, an optimum porosity of semiconducting adsorbents may exist.

b) The extent of semiconductor dispersion may cause the appearance of the so-called compensation effect.[92] With greater extent of dispersion, the density of bulk charge of the semiconductor does not reach zero. This means that the energy bands in the center of a sphere with radius $R<L$ are shifted with respect to their position in the bulk of a great ($R>L$) crystal. This shifting ($\psi_C-\psi_0$, in κT units) is one of the terms in the value of the Fermi level on the surface. With a dispersion degree corresponding to $R\lesssim L$, the shifting of the energy bands is given by the expression

$$\psi_C-\psi_0=\pm\kappa T\ln\frac{3(\mp\sigma)/R}{C_0}$$

while the bending of the energy bands, $\psi_S-\psi_C$, (in κT units) is given by the formula

$$\psi_S-\psi_C=-\frac{1}{2}\frac{R}{l}\cdot\frac{\sigma/l}{C_0}.$$

Here C denotes the absolute density of the positive and negative charges in the bulk of the large crytal.

Thus, both the bending and shifting of the bands depend on the dimensions

of the particles, *i.e.*, on dispersion. With the change in dispersion, the bending and shifting of bands change in opposite directions. In the cases when the rate constant of the catalytic reaction, $\mathscr{K}$, depends on the Fermi level position on the surface, ε_S, this dependence has the following form: $\mathscr{K} \sim \exp(\pm \varepsilon_S / \kappa T)$. For that reason, the bending of energy bands will be a term in the activation energy of the reaction whereas the shifting of bands Will influence the frequency factor. The effect of change in the activation energy with the transition from particles with given dimensions to particles with other dimensions is neutralized to a certain extent by the effect of change in the frequency factor. In this case we may speak about a compensation effect which depends on the degree of dispersion of semiconducting catalysts.

Conclusion

As is evident from what has been said above, the effect of surface curvature of adsorbents and catalysts should not be neglected both in theory and practice (in preparing catalysts). It is also of importance for the investigation of the mechanism and kinetics of catalytic processes. It will be impossible, perhaps, to make a general theory concerning this effect. For each group of catalysts, a special approach is necessary depending, above all, on the nature of the active surface of catalysts as well as on the reagents. The explanation of all separate cases, however, is based on general thermodynamic considerations concerning the change of principal physical properties of solid phases with small dimensions. The tendency towards increasing the dispersion when preparing catalysts is inhibited by the diffusion effect appearing in catalytic reactions and by the changes in the specific activity caused by curvature. The increase in dispersion (porosity) should be evaluated in every case separately. The increase in the specific surface of the catalyst is undesirable when it is accompanied by a simultaneous (or even quicker) decrease in the specific activity. Therefore, an optimum dispersion (curvature) associated with a maximum surface is to be reached with a view of eliminating the diffusion effects and obtaining maximum specific activity.

References

1) С. З. Рогинский, Ж. Ф. Х, **15**, 1 (1941).
2) Г. К. Боресков, Гетерогенный катализ в химической промышленности, 5, Госхимиздат, Москва, (1955).
3) С. З. Рогинский, Проблемы кин. и катал., **9**, 5 (1957).
4) Г. К. Боресков, Научные основы подбора и производства катализаторов, 7, СО АНСССР, Новосибирск, (1964).

5) Г. К. Боресков, Научные основы подбора катализаторов, сер. Проблемы кинетики и катализа XI, 45, Москва, (1966).
6) А. А. Баландин, Научные основы подбора и производства катализаторов, сер. Пробл. кин. и катад. XI, 5, Москва, (1966).
7) A. T. GWATHMEY and A. F. BENTON, J. Phys. Chem., **44**, 35 (1940).
8) A. T. GWATHMEY and R. E. CUNNINGHAM, Advances in Catalysis, **10**, 57 (1958).
9) H. J. LEIDHEISER, and A. T. GWATHMEY, J. Am. Chem. Soc., **70**, 1200, 1206 (1948).
10) O. BEEK, A. E. SMITH, A. WHEELER, Proc. Roy. Soc., **A 177**, 62 (1940).
11) O. BEEK, A. W. RITCHIL, Disc. Faraday Soc., **8**, 159 (1950).
12) О. Бик. Катализ, Вопросы теории и методы исследования, Издатинлит, М., 98, (1955).
13) I. BENARD, I. TALBTO, Rev. Metallurgie, **45**, 78 (1948).
14) T. N. RHODIN, J. Am. Chem. Soc., **73**, 3143 (1950).
15) I. T. KUMMER, J. Phys. Chem., **60**, 666 (1956).
16) С. З. Рогинский, И. И. Третяков, и Б. Шехтер, ДАН СССР, **100**, 487 (1955).
17) K. N AKADA, S. SOTO, S. SHIDA, Proc. Japan Acad. **31**, 449 (1955).
18) G. RIENÄCKER, Wiss. Z. der Humboldt Universität zu Berlin, Nat. R., **9**, 51 (1959/60).
19) G. RIENÄCKER, J. VÖLTER, Z. Anorg. Allgem. Chemie, **302**, 5-6, 292 (1959); **302**, 5-6, 299 (1959).
20) П. Д. Данков, Ж Ф Х, **4**, 326 (1932).
21) П. Д. Данков и А. А. Кочетков, ДАН СССР, **2**, 359 (1934).
22) Я. Б. Зельдович, Ж Ф Х, **13**, 163 (1959).
23) С. Я. Пшежецкий и Р. Н. Рубинщейн, Ж Ф Х, **20**, 1127, 1421 (1946).
24) С. Я. Пшежецкий, Ж Ф Х, **21**, 1019 (1947).
25) С. Я. Пшежецкий и Р. Н. Рубинщейн, Проблемы кинетики и катализа, **6**, 426 (1949).
26) A. WHEELER, Adv. Cat., **3**, 249 (1951).
27) С. З. Рогинский, Адсорбция и катализ на неоднородных поверхностях, цзд. АН СССР, Москва, 1948.
28) G. M. SCHWAB and E. SCHWAB-AGALLIDIS, J. Am. Chem. Soc., **71**, 1806 (1949).
29) В. Ф. Киселев, Ж Ф Х, **34**, 698 (1960).
30) М. М. Егоров, В. Ф. Киселев, и К. Г. Красильников, Ж Ф Х, **35**, 2031 (1961).
31) М. М. Егоров, В. Ф. Киселев и К. Г. Красильников, Ж Ф Х, **35**, 2234 (1961).
32) М. М. Егоров и В. Ф. Киселев, Ж Ф Х, **36**, 318 (1962).
33) E. E. RIDEAL, Trans. Faraday Soc., **32**, 4 (1936).
34) А. В. Киседев, Коллоидн. Ж., **2**, 17 (1936).
35) А. В. Киселев, Поверхностные химические соединения и их роль в явлениях адсорбции, 90, Москва, (1957).
36) А. Н. Теренин, Поверхностные химические соединения и их роль в явлениях адсорбции, 206, Москва, 1957.
37) С. П. Жданов, Ж Ф Х, **32**, 699 (1958).
38) I. E. MAPES and R. R. EISCHENS, J. Phys. Chem., **58**, 1059 (1954).
39) R. P. EISCHENS and W.A. PLISKIN, Advances in Catalysis, **10**, 1 (1958).

40) H. M. BARRET, A. W. BIRINC and M. J. COHEN, J. Am. Chem. Soc., **62**, 2839 (1940).
41) I. SHAPIRO, and J. M. KOLTHOFF, J. Am. Chem. Soc., **72**, 776 (1950).
42) В. А. Дзиско, А. А. Вишневская, и В. С. Чезалова, Ж Ф Х, **24**, 1416 (1950).
43) С. П. Жданов, Д А Н, **68**, 99 (1949); **100**, 1115 (1955); Ж Ф Х, **32**, 699 (1958).
44) А. В. Киселев, К. Г. Красильников, и Л. Н. Соболева, Д А Н, **94**, 85 (1954).
45) А. В. Киселев, Д А Н, **106**, 1046 (1956).
46) М. М. Егоров, К. Г. Красильников, и В. Ф. Киселев, Ж Ф Х, **32**, 2624 (1958).
47) М. М. Егоров, Т. С. Егорова, К. Г. Красильников, и В. В. Мурина, Ж Ф Х, **33**, 65 (1959).
48) J. C. BASTIK, R. Acad. Sci., **234**, 1279 (1952); **247**, 203 (1958).
49) И. Тодек и Я. Юлиш, Изв. АН СССР, **8**, 1336 (1962).
50) J. A. HOCKEY, and B. A. PETHICA, Trans. Faraday Soc., **57**, 12 (1961).
51) О. М. Джигин, Н. Н. Микус-Авгуль, А. В. Киселев, и К. Д. щербакова, Д А Н, **70**, 441 (1950).
52) К. Д. Щербакова, и К. И. Словецкая, ДАН **101**, 855 (1956).
53) К. Д. Щербакова, Сборник Поверхностные химические соединения и их роль в явлениях адсорбции Изд. МТУ, 175 (1957).
54) И. Е. Неймарк, Р. Ю. Шейнфтайн, и Л. Т. Свинцова, Сборник Методы исследования структуры высокодисперсных и пористых тел, АН СССР, 129 (1958).
55) Г. М. Близнаков, И. В. Бакырджиев и Р. А. Поликарова, ДАН СССР, **153**, 1097 (1963).
56) Г. М. Близнаков, И. В. Бакшрджиев и Р. А. Поликарова, Изв. Инст. обща и неорг. химия **8**, 165 (1961).
57) Л. Г. Ганченко, М. М. Дубинин, Е. Д. Заверина, В. Ф. Киселев, и К. Г. Красильников, Изв. АН СССР, ОХН, 1535 (1960).
58) А. В. Киселев и Г. Г. Мутти, Коллоид. Ж. **19**, 562 (1957).
59) Н. М. Каманин и А. В. Киселев, ДАН СССР, **80**, 393 (1951).
60) В. Ф. Киселев, и К. Г. Красильников, Ж Ф Х, **33**, 2621 (1959).
61) М. М. Егоров, Ю. А. Зарифьянц, В. Ф. Киселев, и К. Г. Красильников, ДАН СССР, **120**, 336 (1958).
62) В. И. Квливидзе, ДАН СССР, **157**, 158 (1964).
63) J. B. PERI, and R. B. HANNAN, J. Phys. Chem., **64**, 1526 (1960).
64) J. L. CARTER, P. J. LUCCHESI, P. CORNEIL, D. J. C. YATES and J. H. SINFELD, J. Phys. Chem., **69**, 3070 (1965).
65) J. I. F. SCHOLTEN, P. MARS, P. G. MENON and R. van HARDEFELD, *Proc. 3rd. Intern. Congr. Catalysis* (Amsterdam) **2**, 881 (1965).
66) H. DUNKEN und P. FINK, Z. Chem., **6**, 194 (1966).
67) L. BAKARDJIEW, Z. Phys. Chem., **225**, 273 (1964).
68) И. Бакырджиев, Изв. Инст. Обща и неорг. химия БАН, **4**, 103 (1966).
69) Г. Близнаков, И. Бакърджиев и Д. Механджиев, Изв. Инст. Обша и неорг. химия БАН, **2**, 5 (1964).
70) И. Бакырджиев и Д. Менанджиев, Докл. БАН, **17**, 741 (1964).
71) Г. Близнаков, Д. Механджиев и И. Бакырджиев, Докд. БАН, **17**, 745, (1964).

72) Г. Близнаков, И. Бакырджиев и Д. Дечева, Докл. БАН, **17**, 1103 (1964).
73) И. Бакырджиев, Докл. АН СССР, **168** 618 (1966).
74) М. М. Егоров, К. Г. Красильников и В. Ф. Киселев, Ж Ф Х, **32**, 2448 (1958).
75) Г. Близнаков, И. Марков и И.Бакырджиев, Изв отд. хим. наук БАН/в печати/.
76) J. BASTIK, Compt. Rend., **234**, 1047 (1963).
77) Г. Близнаков, И. Бакырджиев и М. Маждраганова, Докл. БАН, в печати.
78) G. DALMAI, B. IMELIK and M. SÉGUIN, Proc. II. Intern. Congr. Cat. (1960).
79) G. DALMAI, F. DE FRADEL and B. IMELIK, Proc. II. Int. Congr. Cat. **1**, 865 (1960).
80) F. DE FRADEL and B. IMELIK, J. Chem. Phys., **56**, 1 (1959).
81) I. BAKARDJIEW, K.-H. SCHNABEL und K. WENCKE, Z. Phys. Chem., **231**, 391 (1966).
82) I. BAKARDJIEW, K.-H. SCHNABEL und K. WENCKE, Z. Phys. Chem., (im Druck).
83) A. EUCKEN und E. WICKE, Z. Naturforsch., **2 a**, 163 (1947).
84) F. WITHMORE, J. Am. Chem. Soc., **54**, 3274 (1932).
85) H. Pines and W. O. Haag, J. Am. Chem. Soc., **82**, 2471 (1960).
86) К. В. Топчиева, К. Юн-пин, и И. В. Смирнова, Катализ, Труды Первого международного конгресса, 905, Инлит, Москва, (1960).
87) E. R. STRICH, K. BEKER, H. BLUME und I. HILLE, Chem. Techn., **17**, 489 (1965).
88) O. PESHEV and G. BLIZNAKOV, J. Cat., **7**, 18 (1967).
89) С. М. Коган, Пробл. кин. и катал., АН СССР, **10**, 52 (1960).
90) T. WOLKENSTEIN, Adv. Cat., **12**, 247 (1960).
91) T. WOLKENSTEIN, *The Electron Theory of Catalysis on Semiconductors*, Pergamon Press, Oxford, England, 1963.
92) O. PENSHEV, (to be published).