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COMBINED USE OF CALORIMETRIC AND ADSORPTION KINETIC METHODS FOR THE STUDY OF THE MECHANISMS OF CATALYTIC PROCESSES

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Consideration is given to the main results obtained in studies based on calorimetric methods at high temperatures (above room temperature) of the following aspects of the mechanisms of catalytic and sorption processes on powder catalysts: 1) relation between chemisorption and dissolution of gases in the subsurface layers of solids; 2) influence of surface-adsorbed substance on the adsorption of another substance from the gas phase; 3) nature of intermediate species formed during catalytic processes on the catalyst surface. Results are presented of the application of calorimetric methods to measuring the enthalpy change of polymerization in a "dry" system: gaseous monomer — solid catalyst — solid polymer, and to investigating the mechanisms of such processes. Anomalous solubility of gases in the subsurface layers of solids has been shown to be significant for the mechanism of nucleation during phase transitions in solids.

Important information can be obtained about the mechanisms of catalytic and sorption reactions if one applies calorimetric methods of measurements, especially in combination with kinetic measurements. Calorimetric methods have long been used to study sorption processes in gas-solid systems. As long ago as the first half of this century, Titov, Beebe, Beeck, Garner, Kemball, Kiselev, Trapnell and others were engaged in the measurement of sorption heats. Nevertheless, until the sixties heats of physical adsorption and of chemisorption were studied at temperatures not above room temperature. Therefore, thermal effects of activated processes that proceed slowly at room temperature were not studied. However, such processes are of particular interest from the standpoint of the mechanisms of industrial catalytic reactions. Besides, the nature of a gas-solid interaction for such temperatures at which usual catalytic reactions take place is in many cases different from that of processes at low temperatures: the relations between adsorption and dissolution, between physical and chemical adsorption, etc. are different. Therefore, many processes and phenomena which are important for catalysis cannot be studied by calorimetric methods at room temperature. Below we shall mainly be concerned with calorimetric and adsorption data about the interaction of gases with the surfaces of powder catalysts at temperatures far above room temperature. Differential heat-flow microcalorimeters in which resistance thermometers or thermocouple batteries serve for registering the variations of the heat flux from the reacting system are usually applied in these studies. Modern calorimeters with resistance thermometers, such as those developed at the Karpov Institute of Physical Chemistry, Moscow, can measure the liberation or absorption of a few hundredths of a calory in experiments at temperature up to 250° with a power of the order of 10^{-4} cal/sec and within 1% accuracy [1, 2].

The main features of this equipment are described in [3]. Calorimeters with thermocouple batteries (Calvet calorimeters ("Standart" manufactured by Setaram Co, France) [4, 5] have almost the same characteristics). Modern microcalorimmeters so precise that the accuracy of calorimetric results in the studies of gas interactions with powder catalyst surfaces depends on the accuracy of measuring the amounts of reacted substances and the amounts of reaction products rather than on the accuracy of heat measurement. For this reason the quantitative measurement methods are of paramount importance in adsorption-calorimetric studies.

Calorimetric measurement methods are now successfully applied to solving complex problems about the relationship between chemisorption and dissolution of gases in the subsurface layers of porous bodies, about the effect of one surface adsorbed substance on the adsorption of another substance from the gaseous phase, about the nature of intermediate species formed on the catalyst surfaces in catalytic processes, etc., which are significant for the theory of catalysis. Our consideration will be limited to the above three topics. In our discussion, by the heats of sorption of gases we mean not the whole heat liberated when the adsorbate interacts with the catalyst, but only that portion which corresponds to sorption. If a part of the gas reacts and the product is desorbed in the gas phase, such a reaction is accounted for by a corresponding correction.

Results of calorimetric study of the relation between chemisorption and dissolution of gases in catalysts

Figure 1 presents the results of a calorimetric study of hydrogen sorption on iron ammonia synthesis catalyst at 150–200°. The amount of sorbed gas is plotted on the abscissa and the differential heat of sorption on the ordinate. The data from several sequential series of experiments on sorption and desorption [6] are shown here. In sorption experiments the differential heat varied from 26 to 2–3 kcal/mole; in desorption experiments the heat of desorption was at first considerably higher then in the last sorption experiments. Figure 2 shows the results of measurement of the amount of sorbed hydrogen in the same experiments. As one cas see, when the pressure is diminished, part of the sorbed hydrogen is desorbed, and the other part remains on the catalyst; in other words, the sorption is only partly reversible. Hydrogen is accumulated on the catalyst from one series of experiments to another. In order to analyze the results given in Figs 1 and 2, we shall formulate the question in the following way: is adsorption of hydrogen in the amounts shown in the Figures at 200° with a sorption heat equal to 2.5 kcal/mole possible at all? To answer this question, we have used the experimental data [6, 7] for calculation the standard entropy change in this case and compared it with the standard entropy change which could be expected in chemisorption. We have also calculated the change of the standard entropy for a sorption heat equal to 2.5 kcal/mole pertaining to the dissolution of hydrogen in the body of

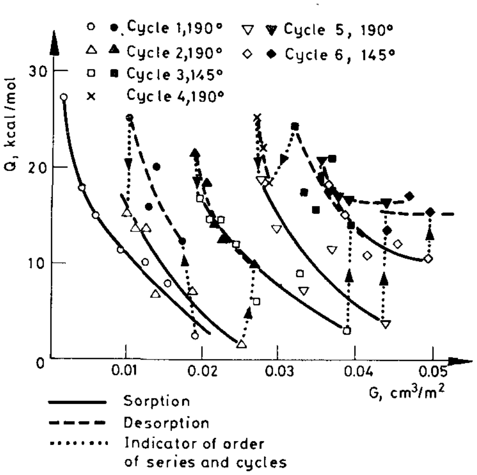

Fig. 1. Heats of H_2 sorption on the ammonia synthesis catalyst. Consecutive sorption-desorption cycles

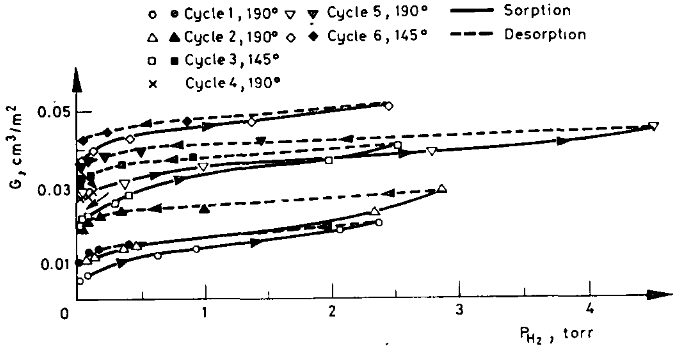

Fig. 2. Hydrogen sorption on the ammonia synthesis catalyst. Consecutive sorption-desorption cycles

sample, and compared it with the change of entropy in the formation of solid hydrogen solutions in iron-like metals.

It follows from this analysis that adsorption of the amounts of hydrogen sorbed at 200° with a sorption heat equal to 2.5 kcal/mole is impossible. A process with such a sorption heat should be regarded as dissolution of hydrogen in the sample body.

When hydrogen interacts with iron, part of the hydrogen is dissolved with a heat of 2.5 kcal/mole or less, and another part is adsorbed with a higher sorption heat. If the pressure is diminished, the adsorbed hydrogen is desorbed, but the

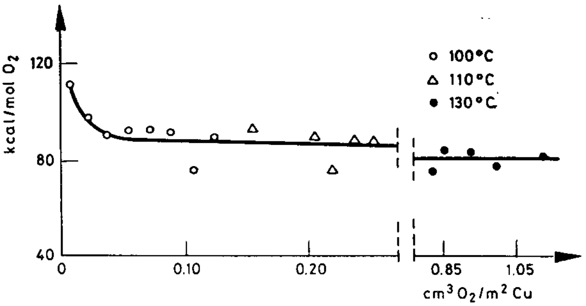

Fig. 3. Oxygen sorption by copper. Rate of sorption as a function of the volume of sorbed O_2

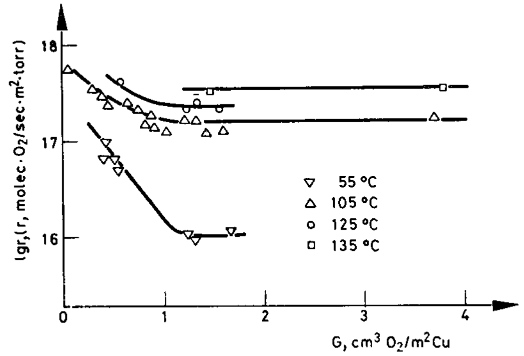

Fig. 4. Differential heats of O_2 sorption by copper

dissolved hydrogen remains in the catalyst on account of kinetic delay. After desorption, a certain amount of hydrogen can be readsorbed, a certain part of that dissolves. Therefore, hydrogen accumulates in the catalyst from one series of experiments to another, and the limiting amount of reversibly adsorbed hydrogen in it is approximately the same after any series of experiments on sorption.

Let us consider now the results of calorimetric [8] and adsorption [9] studies of oxygen interaction with a copper catalyst. Figure 3 presents the differential heat of oxygen sorption by copper as a function of the sorbed amount at 100–130°. The initial heat equals 116 kcal/mole. Then it decreases rapidly, and after the sorption of an amount corresponding to about 20% of the monolayer capacity it reaches 82–90 kcal/mole. The sorption heat remains at this level until sorption of an amount corresponding to four monolayers. The heats of oxidation of copper to CuO and Cu_2O per one mole of oxygen are close to each other, at about 80 kcal/mole. Therefore, one may believe that the sorption of oxygen is accompanied by a phase transition. In order to discuss this topic, let us use the kinetic data [9, 10]. Figure 4 shows the variation of the logarithm of the rate of oxygen sorption by porous copper with the sorbed amount. There are at least four facts which suggest that in these experiments oxygen is sorbed into the sample body, rather than an oxide phase being formed: 1) the specific surface of the sample before the oxygen is sorbed does not differ from that after sorption; 2) there is no extremum of the rate of oxygen sorption as usually observed in phase transitions; 3) the rate of oxygen sorption is proportional to the pressure; 4) in the cycle: oxygen sorption (1) – reduction by hydrogen – oxygen sorption (2), the rate of sorption (1) is equal to the rate of (2) for the same quantity of sorbed oxygen. Thus, there is no phase transition in porous copper catalyst at 50–150° and a pressure below 0.1 torr, until an amount of oxygen is sorbed which corresponds to formation of many monolayers of the oxide. Other data [11, 12] confirm the absence of a phase transition during the sorption of considerable amounts of oxygen by copper. Hence, it follows that only a small part of the total amount of gas sorbed can be on the copper surface (the gas being oxygen) and on the iron surface (the gas being hydrogen).

A similar sorption of substantial amounts of gas into the subsurface layers of solids with a high sorption heat is also observed in sorption by certain oxides. For instance [13, 17], cupric oxide at 100° and above and pressures up to 0.1 torr is capable of sorbing hydrogen in amounts which correspond to more than 10 monolayers without a phase transition in the solid. In this case the hydrogen sorption rate is proportional to its pressure. Similar results were also obtained for chromic oxide and the cupric-chromic spinel $CuCr_2O_4$. A strong influence of oxygen diffusion between the surface and subsurface layers of some oxide catalysts on the degree of reduction of the surface layer, as well as on the strength of the oxygen bond at the surface, have been established by some authors [15]. They measured the energy of surface oxygen on CuO at 327°, making use of the sorption heat of oxidation of carbon monoxide to carbon dioxide with the oxygen being taken from the cupric oxide. The experiments were conducted with intervals. During these the catalyst was heated up to 327°. After each interval the heat of oxidation of carbon monoxide showed an increase. This was explained by the diffusion of oxygen from the sample body to the surface, the increase of its surface concentration and the decrease of the energy of bonding.

According to the above, the rate of diffusion of the adsorbed gas into the sample body may exceed the rate of adsorption over a broad interval of variation of the experimental conditions. In the general case the sample capacity with respect to gas sorption is not determined by the monolayer capacity, and for this reason the rate of sorption cannot be described by an equation of the form

$$r = kP(1 - \Theta)$$

where Θ is the ratio of the sorbed amount to the monolayer capacity, and P is pressure. The sorption of gases by the subsurface layers of catalysts differs essentially from the dissolution of gases into the body of non-porous solids. At 200°

and a pressure of sereral torr the H_2 solubility in bulk iron is of the order of 10^{-4} cm^3/g [16]. The solubility in a porous catalyst which was observed under the same conditions was thousands of times greater. The solubility of oxygen in porous cupper per 1 g is also 3–4 orders of magnitude greater than the corresponding quantity for the bulk metal under the same conditions. In the above cases the sorption of gases by the subsurface layers is an exothermic process, unlike the endothermic dissolution in bulk sample bodies. Thus, sometimes the subsurface layers are characterized by special properties with respect to gas sorption. According to the above results pertaining to sorption of oxygen by copper and hydrogen by cupric oxide, the phase transition occurs after the formation of supersaturated solid solutions in the subsurface layers of the solids. The sorption of oxygen by porous copper (per unit of the mass) may be several orders of magnitude greater than that by the bulk sample. It has been shown in [12], however, that the limiting sorbed amount of oxygen which can be reached before the appearance of the new phase in non-porous samples coincides within the accuracy of the order of magnitude with that for porous samples if it is calculated per unit of surface area. The microscopical crystals of the new phase "precipitate" from the solid solution only after a certain critical degree of supersaturation of the subsurface layer is reached. It is like salt crystal's precipitation from a supersaturated aqueous solution. The nucleation on the contact of the solid with a gas should follow after the state when the diffusion rate of adsorbed particles to the subsurface layers becomes less than the rate of adsorption. Therefore, the smaller the specific surface of a solid, and the higher the pressure of gas, the smaller the amount of gas that can be sorbed per unit mass of the solid before the beginning of nucleation and the more difficult it is to study a given phenomenon. One can understand, in view of the above, the considerable induction period that was observed under the electron microscope between the times of oxygen admission to metal copper and the beginning of surface nucleation [11].

Effect of the presence of one adsorbed substance on the surface on adsorption of another substance from the gas phase

There can be no doubt that study of the mutual influence of gases on each other's sorption is important for the theory of catalysis, since under the conditions of ordinary catalytic reactions there are at least two reacting substances in the gas phase. Frequently the catalyst sorbs more than one substance from the reaction mixture. Their influence on each other's adsorption, however, is usually neglected in derivation of the kinetic equations of the processes. Figure 5 presents plots of the differential heat of hydrogen adsorption on nickel oxide against the adsorbed amount. The series of experiments differed from each other in the amount of oxygen in the catalyst [17]. The variation of the oxygen content in the catalyst was within 0.1–0.2 parts of the surface monolayer capacity. In order to change the oxygen content of the catalyst, experiments on oxygen sorption were done

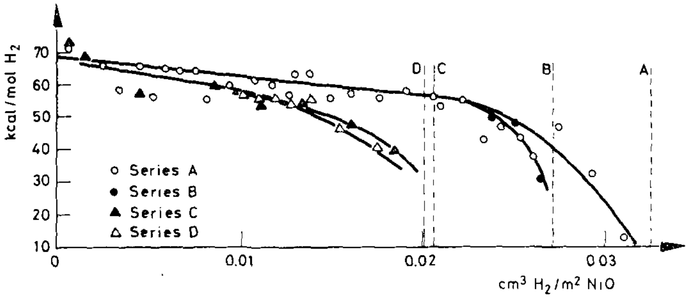

Fig. 5. Differential heats of H_2 sorption by NiO at 190° as a function of the volume of sorbed H_2. In series *A*, *B*, *C* and *D* the catalyst contained different quantities of O_2. Dotted lines indicate maximum sorbed volumes in each series

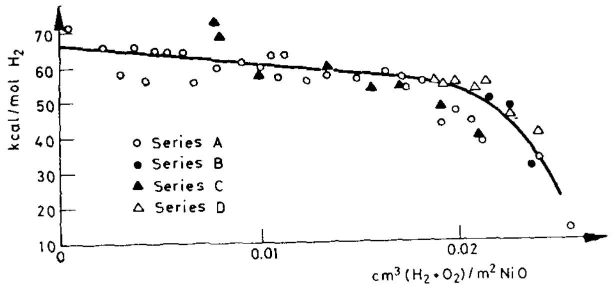

Fig. 6. Differential heats of H_2 sorption by NiO at 190° in series *A*, *B*, *C* and *D* as a function of the sum of the quantities of H_2 and O_2 in the catalyst

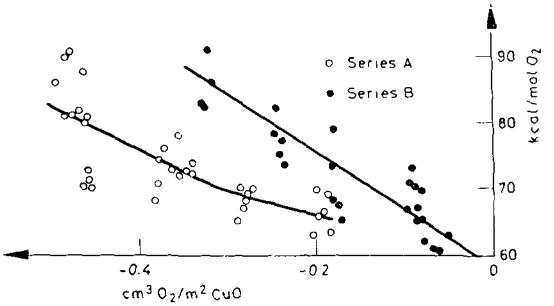

Fig. 7. Differential heats of O_2 sorption by CuO at 200° as a function of the volume of sorbed O_2. In series A and B the catalyst contained different quatities of H_2

between these series. Series are described by different curves, with the limiting sorbed amount (which is shown by dashed vertical straight lines) being different in the series. One is led to think that those differences are random and result from the non-reproducibility of the experimental data. There are no grounds for such

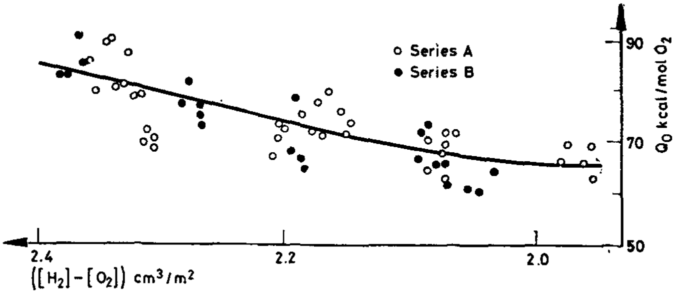

Fig. 8. Differential heats of O_2 sorption by CuO at 200° in series *A* and *B* as a function of the difference between the quantities of H_2 and O_2 in the catalyst

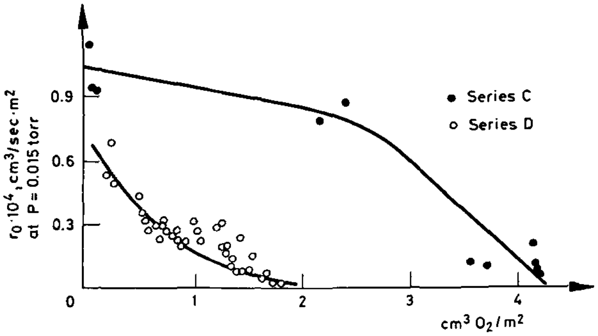

Fig. 9. Rate of O_2 sorption by CuO at 200° in series *C* and *D* as a function of the volume of sorbed O_2. In series *C* and *D* the catalyst contained different quatities of H_2

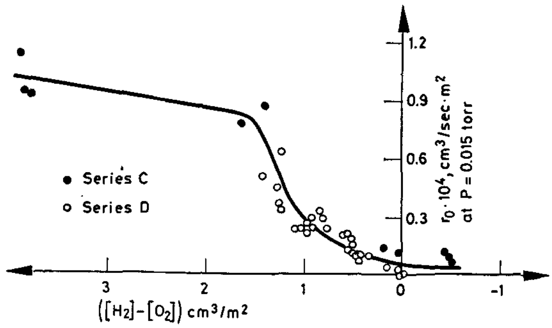

Fig. 10. Rate of O_2 sorption by CuO at 200° in series *C* and *D* as a function of the difference between the quantities of H_2 and O_2 in the catalyst

a conclusion, however, since the experiments were done with the same sample under the same conditions, without contact of the sample with the atmosphere. Figure 6 shows the same data, but as a function of the sum of the oxygen and hydrogen contents of the sample. As one can see, the results of all series fit a single smooth curve. In these co-ordinates the vertical straight lines converge to a single line. This is evidence of the fact that the sorption heat and the limiting amount of sorbed hydrogen on nickel oxide depend on the amount of oxygen in the sample, with the increase of the oxygen concentration causing the decrease of the catalyst's ability to sorb hydrogen. The limiting amount of hydrogen sorbed at 200° is small. When sorption terminates, the area per 2 H atoms on the surface averages about 115 Å^2. The rate of hydrogen sorption is proportional to the pressure and to the proportion of the free surface. Thus, there is no reason to believe that hydrogen on nickel oxide is sorbed into the sample body. The rate of sorption of oxygen on nickel oxide and the heat of its sorption both depend on the amount of hydrogen in the sample [18]. As follows from further studies of other oxides, when there are several gases in the catalyst, their influence on the rate and the heat of sorption of each other is observed in various systems. Oxidized samples of cupric oxide, the surface of which is already incapable of sorbing oxygen, acquire this capability after sorption of hydrogen [13, 14]. Figure 7 shows plots of the dependence of the differential heats of oxygen sorption at 200° on the amount of sorbed oxygen in two series of experiments with the same sample of cupric oxide. The only difference between the catalyst states during the series is that the catalyst contained different amounts of hydrogen. The series are described by two curves. If the abscissa shows the difference between the hydrogen amount and the oxygen amount in the sample as is done in Fig. 8, the results of both series are described by a single smooth curve. The situation is similar in the case of the rate of sorption. Figure 9 presents the rate of oxygen sorption as a function of the sorbed amount for two series of experiments with the same sample of cupric oxide. The difference between the series is in the hydrogen quantity in the sample only. One can see that the rates of sorption can be not the same for the same oxygen content of the catalyst. In Fig. 10 the same results are shown but as functions of the difference between the hydrogen and the oxygen concentrations of the sample; the rate of sorption in both series is described by the same smooth curve. To explain the results about the sorption and the heats of sorption of oxygen on cupric oxide, one has to consider that not only oxygen defects can represent the centers for oxygen sorption, but sorbed hydrogen as well [14]. The amount of sorbed hydrogen could reach 4 cm^3 H_2/m^2, in other words, more than 10 monolayers (with the ratio of the number of copper atoms in the body to the

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* By the term "standard state" we mean the state of the catalyst before the experiments, after its having been treated in vacuum by means of heating in order to purify it from water and carbon dioxide and after subsequent oxidation by oxygen until saturation. The catalyst in the standard state before sorption of hydrogen could not sorb oxygen. If the latter was removed in the form of water from the catalyst by means of its interaction with H_2, it would account for the fact that its content in the catalyst appeared to be smaller than zero.

number of copper atoms on the surface being about 1000). The volume of oxygen sorbed by the samples of cupric oxide over the amount of oxygen in the standard state* also reached 4 cm^3 H^2/m^2. Both the cupric oxide – chromic oxide catalyst ($CuCr_2O_4$) and cupric oxide acquire the ability to sorb additional amounts of oxygen after the sorption of hydrogen.

The above facts demonstrate the effect of the mutual influence of the sorbed substances on the heats and rates of sorption. Further, the data obtained with cupric oxide and $CuCr_2O_4$ illustrate the sorption of gases by the subsurface layers of solids, which was discussed earlier.

The reactions considered represent steps of catalytic processes of oxidation and hydrogenization. Therefore, it follows from the above results that when catalytic reactions occur, variations in the gas composition may result in complex variations of the composition of the catalyst, which involve many subsurface layers. These variations of the catalyst may substantially change the specific adsorption activity, and therefore the specific catalytic activity. Many of publications [19–21] emphasize the importance of such effects. There are only a few systematic quantitative works on this kind of effect, however. The above considerations demonstrate certain possibilities of study by combining calorimetric and adsorption-kinetic methods.

Application of calorimetric methods to establish the nature of intermediate substances formed on catalyst surfaces during catalytic processes

The authors of [5, 22] have described the results of a calorimetric study of carbon monoxide oxidation by oxygen on cerium oxide at 300°. The steps of adsorption of carbon monoxide and oxygen in a system with a cooled trap were investigated. It was established that the preliminary adsorption of carbon monoxide increases the adsorption capability of the catalyst with respect to oxygen. Several consecutive cycles were conducted which consisted of CO adsorption and subsequent adsorption of O_2, every time this being carried out until saturation. After the catalyst had been in contact with CO, it could adsorb an amount of oxygen that was approximately equal to half the amount of carbon monoxide consumed from the gas phase, although until the first cycle CO – O_2 the fresh catalyst could adsorb a considerably smaller amount of O_2. The authors assumed on the basis of this that the interaction of CO and O_2 with the surface results in formation of adsorbed carbon dioxide, CO_2 (ads). The sum of the heat of adsorption of carbon monoxide and half the heat of adsorption of oxygen, $Q_{(CO+1/2\,O_2)}$ was gradually lowered in consecutive experiments from 86 to 69 kcal/mole CO_2. The difference between the enthalpies of carbon dioxide and carbon monoxide is about 68 kcal/mole. According to the results of [22], if during interaction of CO and O_2, carbon dioxide is not given off in the gas phase and $CO_{2(ads)}$ only is formed, then $Q_{(CO+1/2O_2)} = 110$ kcal/mole. It is the authors' opinion that the observed values $68 < Q_{(CO+1/2O_2)} < 86$ kcal/mole proves a partial formation of $CO_{2(ads)}$, and that the gradual lowering of $Q_{(CO-1/2O_2)}$ from one cycle to the next is a result of the

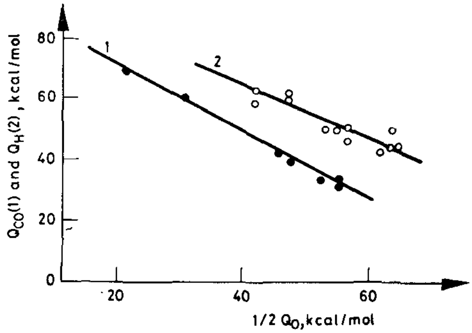

Fig. 11. Differential heats of CO sorption and H_2 sorption by $CuCr_2O_4$ as a function of differential heats of O_2 sorption. Curve 1 : CO; curve 2 : H_2

gradual increase of the proportion of CO_2, the latter being given off in the gas phase and frozen in the trap. In these experiments, however, the carbon dioxide formed was not analyzed quantitatively. Therefore their consideration is only qualitative. The paper contains no precise proof of the fact that the species formed on the surface during adsorption of CO_2 is identical with respect to enthalpy to the species formed as a result of the subsequent adsorption of carbon monoxide and oxygen.

Let us consider some other applications of calorimetric data for clarifying the nature of surface intermediate species that are formed during catalytical processes. Figure 11 (curve 1) presents the results of a study of the adsorption heat of CO (Q_{CO}) as a function of the adsorption heat of oxygen (Q_O), which were obtained at 175° with the cupric-chromic spinel, $CuCr_2O_4$, by the author and A. A. Dyatlov. Carbon monoxide was partially adsorbed and partially oxidized to carbon dioxide, which was frozen in the trap and than subjected to quantitative analysis. The heat of adsorption (or desorption) of CO_2 was determined in special experiments. On an oxidized surface $Q^{I}_{CO_2} = 25.6$ kcal/mole, and on a partially reduced one $Q^{II}_{CO_2} = 16$ kcal/mole. The heat of adsorption of CO in Fig. 11 is given with a correction for the reaction of CO_2 formation. The oxygen adsorption heat was determined once before or once after each experiment on CO adsorption. In order to do this, one measured the heat of adsorption of small amounts of oxygen or the heat of CO interaction with the catalyst when the carbon monoxide is oxidized completely to gaseous carbon dioxide. The linear dependence between Q_{CO} and Q_O proves that adsorbed carbon monoxide is bound to oxygen of the catalyst. The sum of the coordinates of any point on straight line 1in Fig. 11 added to the heat of desorption of CO_2 equals Q_{CO-CO_2} within the accuracy of experiments (Q_{CO-CO_2}) being the difference between the enthalpies of CO and CO_2. The meaning of this is that the process of CO to CO_2 oxidation has the route, at which oxidation consists of the steps of CO adsorption, O_2 adsorption and desorption of CO_2. At this route no other steps of interaction of species in the surface layer with considerable heat effects exist. Then the following should be expected: 1) extrapolation of the straight line 1 of Fig. 11 to the value $Q_O = 0$ should result in $(Q^{II}_{CO_2} + Q_{CO-CO_2}) = 93.2$ kcal/mole; 2) extrapolation of this straight line to the value $Q_{CO} = 0$ should result in $(Q^{I}_{CO_2} + Q_{CO-CO_2}) = 83.6$ kcal/mole. This is confirmed in practical experience. On the abscissa a section is cut off which corresponds to 94.7 kcal/mole, and on the ordinate one corresponding to 84.4 kcal/mole. Apparently, this represents a simple proof of the adsorption at 100 – 200° of CO and CO_2 leads to formation of identical species on the $CuCr_2O_4$ surface. Straight line 2 in Fig. 11 shows the dependence of the heat of hydrogen adsorption (Q_H) on Q_O on the same catalyst. The hydrogen was partially adsorbed and partially oxidized to water which was frozen and analyzed. The heat of water adsorption was determined in special experiments: $Q_{H_2O} = 51.6 \pm 4$ kcal/mole. The linear dependence between Q_H and Q_O means that the hydrogen being adsorbed is bound to the oxygen of the catalyst surface. In the case when a species is formed the enthalpy of which is identical to that of the species formed on adsorption of water, extrapolation of straight line 2 to the value $Q_O = 0$ as well as to the value $Q_H = 0$ should result in $(Q_{H_2O} + Q_{H_2-H_2O}) = 110.2$ kcal/mole, $Q_{H_2-H_2O}$ being the difference between the enthalpies of H_2O and H_2. We observed agreement between the experimental straight line and the theoretical one within the accuracy of experiments: for $Q_O = 0$ it gives $(Q_{H_2O} + Q_{H_2-H_2O}) = 100.2$ kcal/mole, and for $Q_H = 0$ it gives $(Q_{H_2O} + Q_{H_2-H_2O}) = 113.9$ kcal/mole. For any point on straight line 2 in Fig. 11 the sum of its co-ordinates added to the heat of desorption of H_2O equals $Q_{H_2-H_2O}$. Thus, there are no slow steps of surface interaction of species produced on adsorption of O_2 and H_2 which have a considerable enthalpy change. As also follows from the above, adsorption at 100 – 200° of H_2 and H_2O leads to formation of identical species.

Let us consider another example of the application of calorimetric data to clarifying the nature of the intermediates on the surface during catalytic processes.

Temkin' and Pyzhev's equation for the kinetics of ammonia synthesis [23], describing the kinetics at 400 – 550°, is based on the assumption that nitrogen is the most abundant intermediate on the surface of the catalyst, and that one can neglect the surface covering by the products of its hydrogenation. The question has long been discussed in the literature as to whether hydrogen along with nitrogen is included in the most abundant intermediate on the surface of the ammonia synthesis catalyst. In his review Budar says [24] that this question still represents one of the problems of the kinetics of ammonia synthesis. In order to be able to answer this question, we have measured the enthalpy change on dissociation of adsorbed nitrogen-hydrogen radicals into adsorbed nitrogen and gaseous hydrogen [7]. The nitrogen-hydrogen radicals were adsorbed before hand on surface of the industrial catalyst by means of interacting the catalyst with ammonia, part of the hydrogen being desorbed in the gas phase. The change of enthalpy is $\Delta H = 13.300$ kcal/mole of H_2. This value was used for a thermodynamic estimation, which showed that for a partial pressure of hydrogen of 200 atm and the usual temperature of synthesis of NH_3(500°) the most abundant intermediate on the catalyst surface is adsorbed nitrogen; as the temperature decreases the proportion of nitrogen-hydrogen radicals increases, the latter prevailing below 350°. When ammonia synthesis is conducted at atmospheric pressure, adsorbed nitrogen-hydrogen radicals prevail at still lower temperatures.

The combining of the calorimetric method with the method of electron paramagnetic resonance (EPR) leads to interesting possibilities for study of the mechanisms of catalytic reactions. It was observed [25] that when oxygen is adsorbed on the MoO_3/Al_2O_3 catalyst the heat of adsorption at 25° decreases as the adsorbed amount increases. As long as the heat of adsorption is higher than $35-30$ kcal/mole, the adsorbed layer causes no EPR signal. The adsorption of oxygen with a thermal effect of $35-30$ kcal/mole and below resulted in the appearance of a signal which increases as the adsorption proceeds. This demonstrates the emergence of free valences in the catalyst and was interpreted by the authors as oxygen adsorption in the form of O_2^-. It should be noted that the observed concentration of free valences was small compared to the catalyst monolayer capacity and in all experiments was less than 1.10^{13} particles cm^{-2}. In other work [26] concerned with the study of propylene oxidation on MoO_3/MgO the authors came to the following conclusion. If the amount of oxygen in the catalyst was such that the heat of oxygen sorption exceeded 35 kcal/mole, then when small portion of an oxygen-propylene mixture were admitted to the catalyst the oxygen was adsorbed and the propylene remained in the gas phase. When, on the other hand, the heat of oxygen adsorption decreased below 35 kcal/mole, propylene began to react with oxygen, with the intensity of reaction being the greater, the larger, the amounts of weakly bound oxygen in the catalyst. The authors thus arrive at a conclusion that the presence of oxygen particles on the catalyst which represent a carrier of free valence (presumably O_2^-) leads to the catalytic activity of molybdenum trioxide with respect to oxidation of propylene. The authors believe that the only question which remains unclear is whether the appearance of an EPR signal indicates the restructuring of the surface layer from a non-active state into an active one, or the oxygen particle (the carrier of free valence) is itself the necessary intermediate agent for the reaction of propylene oxidation.

We have noted above that the present consideration is concerned with the works devoted to the study of processes occurring on powder catalysts only. The studies conducted at higher temperatures, approaching those at which the processes considered take place in industry, are preferred. This is dependent on the fact that under such conditions the mechanisms of the processes at the gas-solid interface are much more complex than at room temperature. Therefore, the experiments conducted at low temperatures frequently do not yield sufficient information for making judgements on the mechanisms of catalytic processes in industry. In connection with the above we have not taken into account the calorimetric studies of adsorption on deposited films etc., which provided a considerable amount of data on the mechanism of the low-temperature processes (for instance, the works of Brennan, Wedler, Černý and their collaborators) or the articles of other authors devoted to this subject. Only recently the corresponding calorimeters have been described and work has started on the study of high-temperature adsorption processes on deposited films [27]. As followed from the first results of the investigation of the $Ni-H_2$ system, at high temperatures the processes of interaction between a gas and the surface of a solid both on films and on powders are quite complex, and one has to take into account not just the adsorption in the surface layer, but the diffusion of the adsorbate particles deep into the sample body as well, while the presence of impurities in the adsorbate is capable of producing an essential change in the properties of the system [28].

Application of the method of heat measuring in the system gas-solid for determination of enthalpy changes during polymerization and for obtaining certain data on the mechanisms of such processes

The studies we are going to discuss were published several years ago, though the possibilities of the methods applied are far from having been exhausted. These methods make it possible to obtain the changes of enthalpy of polymerization for processes in a "dry" medium, without the liquid phase. Polymerization conducted in a "dry" medium allows one to exclude the processes of dissolution of monomer and polymer in the catalyzate and interaction of the solvent with the catalyst. From the point of view of the methods applied, the measurements of the heat of polymerization resemble in this case the measurements of the heats of adsorption. The change of enthalpy, ΔH°_{298}, was determined for the processes:

$$n(C_2H_4)_{(s)} = (C_2H_4)_{n(s)}$$

and

$$n(C_2H_4O)_{(g)} = (C_2H_4O)_{n(s)}.$$

Ethylene was polymerized [29] on a catalyst which was obtained by treating $TiCl_3$ powder in a calorimetric vessel with vapors of aluminum alkyls, with the subsequent pumping-off of the gaseous products of reactions. After evacuation, ethylene was admitted to the catalyst obtained, and the energy liberation on polymerization and the decrease of the monomer pressure were measured. Ethylene oxide was also [30] polymerized from the vapor phase on previously-pumped, melted potassium hydroxide.

Figure 12 provides an example of recording the thermokinetic curve during a polymerization experiment. The monomer was admitted at point *A*. Point *B* shows the start of freezing of the monomer which has not reacted. The polymerization heat was calculated on the basis of measuring the area under curve *ABC*. A value $\Delta H^\circ_{298} = -25.71$ kcal/mole was obtained for the heat of polymerization of ethylene, and $\Delta H^\circ_{298} = -33.52$ kcal/mole for the heat of polymerization of ethylene oxide. We can point out for the sake of comparison that when the heat of combustion was used as the basis for calculation, a value $\Delta H^\circ_{298} = -25.88$ kcal/mole was obtained for the heat of polymerization of ethylene [31], and a value of

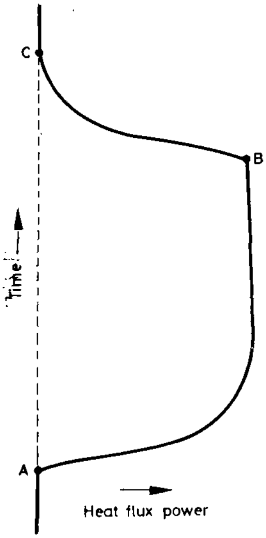

Fig. 12. Thermokinetic curve of polymerization

$\Delta H^{\circ}_{298} = -32.2$ kcal/mole for the heat of polymerization of ethylene oxide [32]. Certain data concerning the mechanism of polymerization under the studied conditions were also obtained. It has been established, for instance [30], that the amount of polyethylene oxide chains is $3.1 \cdot 10^{19}$ per 1 m^2 of the catalyst surface, which is close to the amount of hydroxyl groups per 1 m^2 of the regular crystalline lattice of potassium hydroxide. The calorimetric methods described above were also applied to study of the polymerization of butadiene and the copolymerization of ethylene and butadiene [33].

Conclusion

We have presented results obtained during studies of various aspects of the mechanisms of heterogeneous catalytic reactions by the calorimetric method combined with the adsorption-kinetic one and with some other techniques. Many of the data described are of general significance for understanding the processes occurring in the solid body near the solid-gas interface. During the 15 years that have elapsed from the time of the first publication on the calorimetric study of sorption processes at high temperatures, this method has demonstrated its fruitfulness and has become widely spread. One can expect that the possibilities arising from its application, especially when it is combined with other techniques, as well as the expansion of production of microcalorimeters, will cause further development of the calorimetric method as applied for the study of catalytic and sorption processes at high temperatures.

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Résumé — On examine les principaux résultats obtenus lors des études effectuées à l'aide de méthodes calorimétriques à hautes températures (au-dessus de la température ambiante), sous les aspects suivants du mécanisme des réactions catalytiques et de sorption sur des catalyseurs en poudre: 1) relation entre la chimisorption et la dissolution des gaz dans les sous-couches superficielles des solides, 2) influence d'une substance adsorbée en surface sur l'adsorption d'une autre substance de la phase gazeuse, 3) nature des particules intermédiaires formées lors de la réaction catalytique à la surface du catalyseur. Les résultats de l'application de la méthode calorimétrique à la mesure des variations d'enthalpie au cours de la polymérisation en système «sec» sont présentés: monomère gazeux — catalyseur solide — polymère solide, ainsi que ceux relatifs à l'étude du mécanisme de ces réactions. On montre que la solubilité anormale des gaz dans les sous-couches superficielles des solides joue un rôle important sur le mécanisme de la nucléation lors des transitions de phases dans les solides.

Zusamenfassung — Die wichtigsten Ergebnisse der auf kalorimetrischen Methoden bei hohen Temperaturen (über Raumtemperatur) beruhenden Untersuchungen der Mechanismen von katalytischen und Sorptionsprozessen an pulverförmigen Katalysatoren werden behandelt: 1) Zusammenhang zwischen Chemisorption und Lösung von Gasen in den Schichten von Festkörpern unterhalb der Oberfläche; 2) Einfluß der an der Oberfläche adsorbierten Substanz auf die Adsorption einer anderen Substanz aus der Gasphase; 3) Beschaffenheit der während des katalytischen Vorgangs an der Katalysator-Oberfläche entstandenen Intermediärteilchen.

Ergebnisse der Anwendung der kalorimetrischen Methode zur Messung der Enthalpie-Änderungen der Polymerisation im "trockenen" System: gasförmiges Monomer — fester Katalysator — festes Polymer und zur Untersuchung der Mechanismen solcher Vorgänge werden mitgeteilt. Es wurde gezeigt, daß die anomale Löslichkeit von Gasen in den Schichten unterhalb der Oberfläche von Festkörpern für den Mechanismus der Keimbildung während des Phasenüberganges in Festkörpern von Bedeutung ist.

Резюме — Рассмотрены основные результаты, полученные в исследованиях с помощью калориметрических методов при повышенных температурах (выше комнатной) следующих аспектов механизма каталитических и сорбционных процессов на порошкообразных катализаторах: 1) соотношение между хемосорбцией и растворением газов в подповерхностных слоях твердых тел: 2) влияние присутствия одного адсорбированного вещества на поверхности на адсорбцию другого вещества из газовой фазы; 3) природа промежуточных частиц, образующихся на поверхности катализаторов в ходе протекания каталитических процессов.

Приведены результаты использования калориметрических методов для определения изменения энтальпии при полимеризации в »сухих« системах газообразный мономер — твердый катализатор — твердый полимер и для получения данных о механизме процессов.

Обсужден вопрос о значении явления аномальной растворимости газов в подповерхностных слоях твердых тел для механизма появления зародышей новой фазы при фазовых переходах в твердых телах.