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PROBLEMS OF CHEMICAL KINETICS AND CATALYSIS

An Adsorption Calorimetry Study of the Adsorption of Acetone on Raney Nickel under Conditions of Liquid-Phase Hydrogenation

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Abstract—Adsorption calorimetry was used to study the characteristics of the adsorption of acetone on Raney nickel from 2-propanol–water solutions under conditions of liquid-phase hydrogenation. The isotherms of adsorption of acetone on Raney nickel and the dependences of integral and differential heats of adsorption on the adsorption value were obtained. It was established that the adsorption of acetone on Raney nickel occurs by the mechanism of volume filling of micropores in the pore space of the catalyst with adsorbate solution, which consists of partially or completely desolvated acetone molecules irrespective of the concentration of 2-propanol in the solvent.

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The main problems in the theoretical interpretation of the characteristics of adsorption from solution on the surfaces of solids are known to be associated with the displacement or cooperative adsorption interactions of the solutes and solvent in the surface layer [1–3]. According to the Gills classification [2], there are 17 experimentally identified types of isotherms of adsorption from solution, i.e., about four times the number of types of isotherms for the adsorption of vapors and gases in the Brunauer classification [1]. The adsorption of solutes is commonly described within the framework of a thermodynamic approach, which, in turn, may be based on the concept of individual phases of adsorption solutions in the surface layer [1, 4], on two-dimensional equations of state [4], or on integral equations of adsorption isotherms [5]. According to [1–5], the form of the equations for describing partial adsorption isotherms is similar to that of the equations of adsorption isotherms for gases and vapors.

Note that the principal approaches to the theoretical description of the characteristics of adsorption from solutions have been worked out largely for carbon adsorbents [1, 4], active sites of which exhibit no marked catalytic or chemical activity. Little is known about how to describe adsorption on catalytically active surfaces. In particular, the stage of adsorption of the reactants in reactions of liquid-phase hydrogenation is normally described within the framework of the Temkin and Langmuir models of monolayer adsorption [1, 3], models that for the most part not completely reflect the processes in adsorption layers.

Information on the adsorption of reactive organic compounds on metals and catalysts prepared from them under conditions of liquid-phase hydrogenation is very scarce [6–8]. In our opinion, this can be explained by the fact that it is impossible to use the traditional experimental methods for studying adsorption [1, 3], since, in all cases, the adsorption of the compounds to be hydrogenated occurs on surfaces the active sites of which contain adsorbed hydrogen, with the process being accompanied by parallel chemical interactions between the reactants in the surface layer [9]. In a number of studies, for example [6], it was proposed to study the adsorption of organic compounds on spongy blacks without surface hydrogen (removed by thermal treatment), so as to eliminate the effect of side reactions. This approach is, however, methodologically incorrect, since the removal of adsorbed hydrogen [10] is accompanied by a rearrangement of the structure of active sites, a process that may affect the subsequent adsorption of organic compounds.

The aim of the present work was to study the characteristics of the adsorption of acetone from 2-propanol–water solvents on Raney nickel under conditions of liquid-phase hydrogenation.

The choice of the objects of the study was motivated by the following reasons. The kinetics of the liquid-phase hydrogenation of acetone on catalysts of various types has been rather thoroughly studied [9]. It was established that, irrespective of the nature of the catalyst, this reaction involves only one stage and occurs without the formation of noticeable amounts of byproducts. Raney nickel and aqueous solutions of aliphatic alcohols are widely used as a catalyst and solvents, respectively, in various reactions of liquid-phase hydrogenation of organic compounds [8, 9].

EXPERIMENTAL

The Raney nickel catalyst was prepared by treating a Ni : Al : Fe = 49.5 : 50.2 : 0.3 (wt %) dispersed nickel–aluminum alloy (4.8-μm-radius grains) with a 7.5 M aqueous solution of sodium hydroxide at 273–278 K for 1 h and at 370–373 K for 4 h. Every 2 h the worked-out solution was replaced by the fresh one. The active catalyst had a specific surface area of 90 ± 2 m^2/g and a porosity of 0.5 ± 0.05 cm^3/cm^3, with the maximum of the pore radius distribution being situated at 2 nm; i.e., the Raney nickel prepared can be classified as an adsorbent with a developed microporous structure [11, 12]. The hydrogenation of acetone was performed in aqueous solutions of 2-propanol with organic component concentrations of from 0.073 to 1.0 mole fractions both in a liquid-phase-hydrogenation reactor with intense radial stirring [13] and in a special isothermal calorimeter intended for studying heterogeneous catalytic reactions in the liquid phase [8].

The adsorption of acetone under conditions of liquid-phase hydrogenation was investigated using adsorption calorimetry, the fundamentals or which are given in [8, 14]. The method operates as follows. According to [14], the material and heat balance equations for an isothermal calorimeter at an instant of time τ of the measurement period rearranged so as to obtain equations for calculating the integral heat of adsorption of the compound being hydrogenated (R) at its concentration in the solution c_R. For the hydrogenation of acetone in aqueous solutions of 2-propanol, the excess adsorption and integral heat of adsorption are given by [14]

$$\Gamma_R = \frac{1}{m_k}(c_R^0 - c_R - c_{RH_2})V_s, \quad (1)$$

$$Q_a(R) = \frac{1}{m_k} - (Q_\tau - V_s \Delta_h G(R) c_{RH_2}), \quad (2)$$

where c_R^0 is the initial concentration of acetone, c_{RH_2} is the concentration of 2-propanol at an instant of time τ, Q_τ is the heat released by the reaction of hydrogenation by an instant of time τ, $\Delta_h H(R)$ is the heat of hydrogenation of acetone to 2-propanol, m_k is the catalyst mass, and V_s is the solution volume.

The amount of 2-propanol formed by the reaction can be calculated from the volume of absorbed hydrogen, as measured by the volumetric method. Using the excess adsorption Γ_R, the adsorbate equilibrium concentration, and the volume of the micropores in the adsorbent, it is possible to determine the absolute adsorption of acetone a_R [13]. Determining a_R values at various c_R, one can plot adsorption isotherms under the conditions of the reaction. The corresponding integral heats of adsorption can be used to calculate the differential heat of adsorption as a function of the absolute absorption a_R. Thus, to determine the adsorption values and heats of adsorption under conditions of liquid-phase hydrogenation, it is necessary to measure the numbers of moles of acetone subjected to hydrogenation and 2-propanol formed, as well as the heat released by a given instant of time of the calorimetric measurement. The heat of liquid-phase hydrogenation of acetone, which is required to calculate the integral heat of adsorption of the hydrogenated compound by using Eq. (2), can be measured in individual runs or calculated from adsorption-calorimetry data on the total heat release in the experiment [8].

The adsorption of acetone under conditions of liquid-phase hydrogenation was studied as follows. A required amount of the catalyst and an accurately measured volume of the solvent were placed into the calorimeter, the system was tightened and thermostated at 303 K, after which the catalyst was saturated with hydrogen at atmospheric pressure for 15–20 min and the calorimetric experiment was conducted.

After the stationary regime of heat exchange was attained, the reaction of hydrogenation was started by introducing into the system of the known amount of a solution of acetone in the same solvent (thermostatted at the temperature of the experiment). Within a certain period after the beginning of hydrogen absorption, the reaction mixture in the calorimeter was sampled and analyzed for the content of acetone by chromatography. The amount of 2-propanol used was calculated from the volume of the hydrogen absorbed during the reaction, which was measured continuously up to the complete termination of absorption. After the experiment, the energy equivalent of the calorimeter was determined by electric current calibration. The heats of dilution of acetone solutions, quantities required in the calculations, were measured in separate experiments.

A chromatographic analysis of the concentration of acetone in the reaction mixture samples was performed on a LKhM-80 chromatograph equipped with a flame-ionization detector, a 1-m-long stainless steel column packed with a Polychrome containing 10 wt % of polyethyleneglycol sebacate. The carrier gas was helium. The internal reference was toluene. The temperatures of the column and vaporizer were 373 and 393 K, respectively. An analysis of the standard mixture demonstrated that the sensitivity of the analysis to acetone (with allowance made for dilutions) was 6×10^{-5} M, while the error in the measured concentration of the hydrogenated compound in the reaction mixture was within 2.0–2.5%.

Processing the chromatographic analysis data within the framework of Eq. (1) yielded the excess adsorption of acetone, which, when combined with the equilibrium concentration of the adsorbate in the solution and the adsorption volume of the catalyst, made it possible to calculate the absolute adsorption a_R. The adsorption volume of the Raney nickel sample was set equal to the volume of the micropores in it. The calorimetric data in conjunction with the method described in [8] made it possible to calculate the change of the calorimeter temperature at a current instant of time τ and at the end of the reaction with consideration given to corrections for heat exchange, after which the quantity Q_τ and the total heat release in the experiment Q_∞ were determined. Next, the integral heat of adsorption of the

Table 1. Effect of the relative pressure of hydrogen on the values of adsorption a_R (mol/(g Ni)) of acetone on Raney nickel in 2-propanol ($x = 1.0$) under conditions of liquid-phase hydrogenation ($\bar{c}_R$ is the equilibrium concentration of acetone)

p_{rel}	$\bar{c}_R \times 10^2$, M	$a_R \times 10^4$, mol/(g Ni)
0.93 ± 0.01	59.3 ± 0.6	19.6 ± 1.0
0.13 ± 0.01	60.0 ± 0.7	21.5 ± 2.0
$(1.2 \pm 0.1) \times 10^{-4}$	59.0 ± 0.6	18.6 ± 1.5

Table 2. Heats of hydrogenation $\Delta_h H°(R)$, solution $\Delta_{sol} H°(R)$, and hydration $\Delta_r H°(R)$ of acetone in 2-propanol–water binary solutions (kJ/mol) at 303 K

x	$-\Delta_h H°(R)$	$\Delta_{sol} H°(R)$	$-\Delta_r H°(R)$
0.0727	70.25 ± 0.70	−0.08 ± 0.01	70.3 ± 0.7
0.190	72.1 ± 0.8	1.30 ± 0.04	70.8 ± 0.8
0.679	72.4 ± 0.8	3.02 ± 0.03	69.4 ± 0.7
1.0	76.9 ± 0.6	6.68 ± 0.08	70.2 ± 0.7

Note: x is the mole fraction of 2-propanol in the solvent; the experimentally measured values of $\Delta_r H°(R)$ are given; the tabulated value of this quantity is 70.59 kJ/mol [19].

hydrogenated compound was calculated by Eq. (2). The measurement errors in the adsorption values and heats of adsorption were estimated at 3 and 5–7%, respectively; they were largely determined by uncertainties in measuring the acetone concentration.

RESULTS AND DISCUSSION

Preliminary experiments, the aim of which was to substantiate the applicability of Eqs. (1) and (2) to calculating the values and integral heat of adsorption of acetone from adsorption calorimetry measurements, demonstrated that, for all the solvents used, the hydrogenation of 1 mole of acetone consumed 22400 ± 200 cm^3 of hydrogen, a proportion that coincides with the stoichiometry of the reaction with an accuracy of 0.9%. As long as the reaction mixture was sampled at extents of conversion of acetone below 5%, the values and integral heats of adsorption of acetone changed proportionally to the mass of the catalyst, being independent of the moments of sampling and the initial concentration of the reactant.

A specific feature of solutions of ketones is keto-enol equilibrium [9, 15]. According to [15], the concentration of the enol form does not exceed $2.5 \times 10^{-4}\%$. Therefore, keto-enol equilibrium is not expected to influence the results of adsorption calorimetry measurements.

It is known [9, 13] that liquid-phase hydrogenation is accompanied by the displacement of hydrogen adsorbed on active sites of the catalyst's surface. The heat effects of the interaction of hydrogenated compounds with adsorbed hydrogen are expected to affect adsorption-calorimetry measurements [14]. To establish whether this side reaction occurs, we studied how the partial hydrogen pressure changes the value of adsorption of acetone under conditions of liquid-phase hydrogenation. The results obtained are summarized in Table 1. The adsorption values at the atmospheric pressure of hydrogen were measured by adsorption calorimetry, as described above. At hydrogen pressures below atmospheric, these quantities were obtained by processing kinetic curves for the reaction of hydrogenation in a closed system with the use of the method described in [14].

The results obtained show that, over a wide partial hydrogen pressure range, which corresponds to a coverage of the Raney nickel surface with hydrogen of from 0.25–0.30 to 0.95 [16], the adsorption of acetone is independent of the value of preliminary adsorption of hydrogen. The data of Table 1 suggest that the adsorption of hydrogen and acetone are noncompetitive process, as can be seen from the absence of a marked removal of hydrogen adsorbed on active sites at the catalyst surface during acetone hydrogenation. Thus, the contribution from the heat effects of the interaction of acetone with adsorbed hydrogen to the value of Q_τ is expected to be comparable with the measurement error, and, therefore, this side effect can be disregarded in processing the experimental data. Note that the data obtained indirectly support the notion that the adsorption of hydrogen and hydrogenated compounds occur independently, a key concept of the theory of hydrogenation reactions, which underlies many kinetic models [9, 17].

Thus, the preliminary experiments demonstrated that, acetone hydrogenation proceeds in one stage, producing no byproducts, that it takes less than 10 s to attain the state of equilibrium at the stage of adsorption of the hydrogenated compound, that the sorption of 2-propanol produces no effect on the calculated heat of adsorption on Raney nickel during the reaction, and that adsorbed hydrogen is not displaced from the catalyst surface during the reaction. The results of the preliminary experiments are in close agreement with the data reported in [8, 15].

Table 2 lists the experimentally measured heats of liquid-phase hydrogenation of acetone on Raney nickel in aqueous solutions of 2-propanol $\Delta_h H°(R)$ and the heat of solution of acetone $\Delta_{sol} H°(R)$ [18], quantities required to calculate the heat of hydrogenation of liquid acetone to liquid 2-propanol.

Table 2 shows that the measured heat effects of interaction of liquid acetone with hydrogen with the formation of liquid 2-propanol coincide with the thermodynamically calculated values within 0.6%, a result

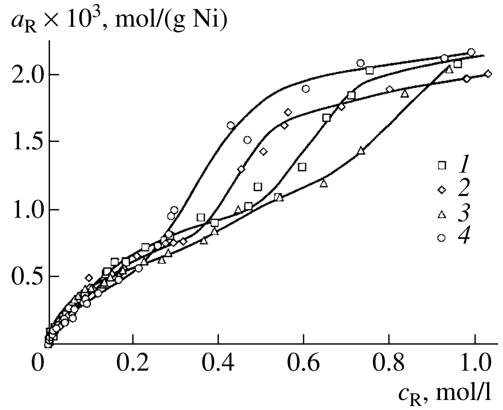

Fig. 1. Isotherms of adsorption of acetone on Raney nickel from 2-propanol–water binary solvents of various compositions: x = (*1*) 0.073, (*2*) 0.190, (*3*) 0.679, and (*4*) 1.0 mole fractions of alcohol; T = 303 K.

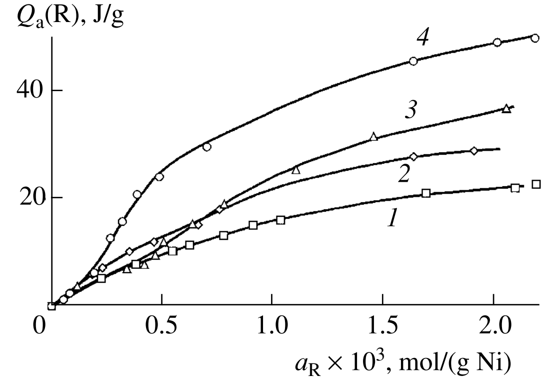

Fig. 2. Dependence of the integral heats of adsorption of acetone Q_a(R) on Raney nickel from 2-propanol–water binary solutions on the adsorption value a_R at 303 K; for *1–4*, see Fig. 1.

indicative of a high reliability of determination of heat effects of liquid phase hydrogenation in the calorimeter used. At the same time, the heat of liquid-phase hydrogenation of acetone depends on the solvent composition due to a change in the heat of solvation of the hydrogenated compound [18].

Figure 1 shows the experimentally measured isotherms of adsorption of acetone on Raney nickel from aqueous solutions of 2-propanol. As can be seen, the shape of the isotherm does not depend on the composition of the solvent. According to the Gills classification, all the isotherms belong to types 3L and 4L, which are characteristic of adsorption with parallel orientation of adsorbate molecules and weak interactions in the surface layer. According to [2], inflections and second plateaus in adsorption isotherms are associated with the reorientation of the molecules on the surface and with the polymolecular character of adsorption. That the shapes of the isotherms of adsorption of acetone in all the solvents are identical to each other can be explained by the unlimited solubility of the adsorbate in aqueous solutions of 2-propanol.

Figure 2 displays the integral heats of adsorption Q_a(R) of acetone on Raney nickel in 2-propanol aqueous solutions at various absolute adsorptions a_R. As can be seen, all the curves monotonically ascend, a behavior characteristic of exothermic adsorption from solutions. Performing numerical differentiation of the spline functions obtained by approximating the data presented in Fig. 2 by a smoothing-interpolating spline, we calculated the differential heats of adsorption of acetone $\Delta_a H$(R); the results are displayed in Fig. 3.

Figure 3 shows that, irrespective of the solvent composition, the differential heats of adsorption of acetone pass through a maximum at adsorption values of (0.3–1.0) × 10^{-3} mol/(g Ni). The maximum values of the heat of adsorption of acetone increase with the concentration of 2-propanol in the solution. As the concentration of the adsorbate increases still further, the heat of adsorption decreases to values close to the heat of solution of acetone in the solvent but with opposite sign. According to [7, 15], the extremal character of the dependence of the heat of adsorptions of organic compounds on the adsorbate concentration can be explained by rearrangement of the surface layer with the formation of saturated adsorption solutions, the composition of which is determined by the chemical nature of the adsorbate and its affinity to the solvent.

The experimental results obtained were processed in the linear coordinates of the equations of the classical adsorption isotherms. We found that none of the known adsorption isotherm equations described the adsorption equilibrium characteristics over the entire range of acetone concentrations. What is more, the limiting adsorption values, even those calculated from the initial segments of the isotherms plotted in the linear coordinates

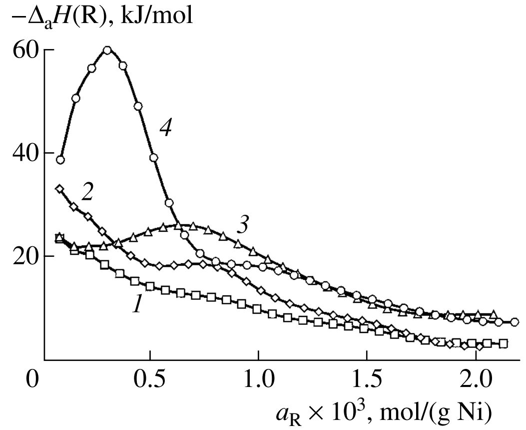

Fig. 3. Dependence of the differential heats of adsorption of acetone $\Delta_a H$(R) on Raney nickel from 2-propanol–water binary solutions on the adsorption value a_R at 303 K; for *1–4*, see Fig. 1.

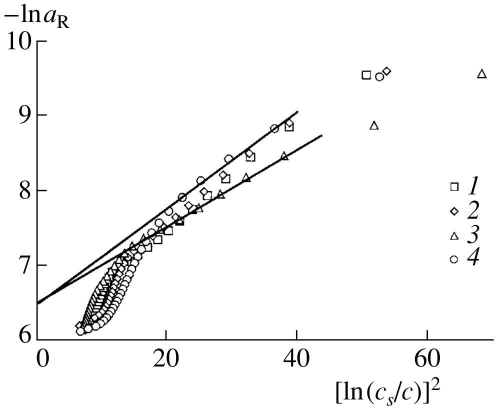

Fig. 4. Isotherms of adsorption of acetone on Raney nickel from 2-propanol–water binary solvents plotted in the linear coordinates of the main TVFM equation at 303 K; for *1–4*, see Fig. 1.

of the Langmuir and Aranovich equations proved to be three to five times higher than the monolayer sorption capacity of Raney nickel. The results obtained show that the adsorption of acetone on hydrogenation catalysts can be described only formally within the framework of the existing models of monomolecular and polymolecular adsorption. In our opinion, the data obtained can be interpreted only by invoking models capable of describing the specific nature of adsorption on adsorbents with branched porous structure.

Figure 4 show the adsorption isotherms of acetone in the linear coordinates of the equation of the theory of volume filling of micropores (TVFM). As can be seen, this equation closely describes the experimental results at low concentrations of acetone (up to 0.2–0.3 M, concentrations that correspond to the maxima in the dependence of the differential heat of adsorption on the adsorbate concentration) in the solution over the entire solvent composition range covered. The applicability of the TVFM to describing adsorption from solutions was substantiated in [4, 20]. When the adsorbate concentration was increased beyond the position of the maximum, a region where the differential heat of adsorption decreased, the TVFM did not describe the adsorption equilibrium for all the solvents tested.

The results of adsorption calorimetry studies provide information on the possible mechanism of acetone adsorption. At low concentrations, the adsorption of acetone on Raney nickel proceeds according to the mechanism of volume filling of micropores in the pore space of the catalyst with complex adsorption solutions composed of partially desolvated acetone molecules; therefore, the adsorption equilibrium is described by the TVFM for microporous adsorbents. This conclusion is qualitatively supported by the observation that the dispersity of the catalyst produces no effect on the shape of the isotherms and on the values and heats of adsorption [8]. At adsorption values above (0.5–0.8) × 10^{-3} mol/(g Ni), the effect of the adsorption potential of the pore walls causes changes in the composition of the adsorption solution, probably due to an increase in the intensity of adsorbate–adsorbate and adsorbate–metal interactions, a factor that manifests itself through the growth of the heat of adsorption to a maximum value, individual for each solvent. At high concentrations, the character of the adsorption process is governed by the condensation of acetone solutions in transport pores and on the external surface of catalyst grains, a process responsible for the decrease of the heat of adsorption to a value close to the heat of solution of the adsorbate in the solvent but with opposite sign.

In our opinion, this explanation holds for all systems involving the adsorption of organic compounds from solutions on solid adsorbents with branched porous structures. A general discussion of the adsorption mechanism can be conducted based on the thermodynamic characteristics of adsorption equilibria, mainly the entropy of adsorption, and on an analysis of the state of the organic compounds in the adsorption solutions filling the pore space of the Raney nickel catalyst.

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